# ENVIRONMENTAL IMPACT ASSESSMENT OF DUMPSITES IN ZARIA METROPOLIS, KADUNA STATE, NIGERIA

**By**

**SANI UBA**

**DEPARTMENT OF CHEMISTRY**
**FACULTY OF SCIENCE**
**AHMADU BELLO UNIVERSITY, ZARIA**
**NIGERIA.**

**FEBRUARY, 2015**

## ABSTRACT

The study assessed the impact of dumpsites on their immediate environments. The particulate dust, hand-dug waters, dumpsite–leachates and refuse waste soils were collected in both the dry and wet seasons while gaseous pollutants and other field data were determined *in situ* using gas mobile gas sensors. Also, young chickens were fed with the solid wastes and leachates for a period of three months in each site across the seasons and then sacrificed. Blood, hair, urine and nail samples were also collected from people residing close to the dumpsites in both the dry and wet seasons. The percentage recoveries of metals were determined on the samples by spiking experiment in order to validate the analytical method and technique used for the analysis. The characterization of the refuse wastes across the sites revealed the ranges of 4.24 to 44.23, 0.85 to 26.74, 13.10 (SH) to 42.11(JK), 16.33(SH) to 58.83(DA) and 3.79 (NTC) to 30.34% (PR) for plastic, papers, textiles, polythene bags and wood, respectively across the sites. The concentration ranges of CO, $H_2S$, FL, $SO_2$, $NO_2$, $NH_3$ across the seasons were 1.50 (CTR) to 11.40(SA), 0.001(CTR) to 0.0039(RA), 0.001(CTR) to 0.0085(SA), 0.001(CTR) to 0.039(SH), BDL(CTR) to 0.0039(JK) and 0.001(CTR) to 8.65(SH)ppm, respectively. The concentrations ranges of these gases were higher than the standard limits of 9(CO), 0.03($H_2S$, $SO_2$), 0.08(FL) and 0.05ppm ($NO_2$, $NH_3$) with few exceptions. Also the ranges of particulates, relative humidity and temperature of the air at vicinity of the dumpsites across the seasons were 0.105 (KU) to 19.305 (RA)ppm, 6.35(AJ) to 77.35(CTR)% and 27.25(CTR) to 38.100$^0$C(RA), respectively. These levels across the sites and seasons were generally above the standard limits of 0.03ppm and 25$^0$C for particulate gases and temperature. The concentration ranges of Zn, Cd, Cu, Pb and Hg in the particulate dust across the seasons were 1.40(JK) to 210.60(SA), BDL (CTR) to 3.74 (RA), 0.241 (KU) to 390.0 (JK), 2.26 (CTR) to 78.260(SH) and BDL (CTR) to 25.69(AJ),

respectively. The ranges of the bioavailable fractions of Zn, Pb, Cu, Cd and Hg in the soils across the seasons were 4.00 (NTC) to 79.08 (BG), 5.37 (SA) to 39.65 (CTR), 0.35 (RA) to 68.57(NTC), 28.14 (SH) to 65.74(DD) and 24.068 (SH) to 80.52% (BG). Also the ranges of the bioavailable fractions of Zn, Pb, Cd, Cu and Hg in leachates samples across the sites were 53.387(NTC) to 95.625(AJ), BDL(CTR) to 97.584(BG), 96.452(BG) to 1100(KU, CTR, AJ, SA, SH, RA, PR, NTC), BDL(CTR) to 100(RA, JK, DD) and 53.848(KU) to 100%(SH, SA, DD). Also the ranges of 31.499(NTC) to 99.513(AJ), BDL(CTR) to 100(BG, DD, SA), BDL(CTR) to 100(RA, DD, JK), 67.884(PR) to 100(NTC, RA, SA, KU, JK, DD & BG) AND 85.729(NTC) to 100%(BG, CTR, DD, JK, KU, SA and PR) for Zn, Pb, Cd, Cu and Hg. Also, the water quality indices (WQI) of 123799.1 and 110501.6 were recorded in wet and dry seasons and were >300, indicating that they were unfit for drinking. Also, the concentration ranges of BDL (CTR) to 8.844(JK), BDL(CTR) to 2.850(BG), BDL(CTR) to 0.099(BG), BDL(CTR) to 128.017(NTC) and BDL(CTR) to 83.122mg/kg(DD) were recorded for Zn, Pb, Cd, Cu and Hg in the chicken samples across the sites and seasons. Similarly, the concentration ranges of Zn: 0.414 to 1.102mg/L(RA), 0.738(RA) to 4.047mg/L(DD), 0.485(JK) to 8.568mg/kg(DD) and 0.719(BG) to 13.641mg/kg(NTC); Pb: 0.060(RA) 0.180mg/L(JK), 0.011(CTR) to 0.244mg/L(JK), 0.090(PR) to 0.900mg/kg(DD), BDL(CTR) to 0.413mg/kg(AJ); Cu: BDL(AJ) to 0.088mg/L(PR), BDL(CTR) to 0.171mg/L(PR), BDL(CTR) to 0.905mg/kg(DD), BDL(CTR) to 0.312mg/kg(AJ); Cd: BDL(DD) to 0.029mg/L(KU), BDL(DD) to 1.648mg/L(RA), BDL(DD) to 1.144mg/kg(KU), BDL(DD) to 1.119mg/kg(NTC) and Hg: BDL(CTR) to 3.187mg/L(NTC), BDL(CTR) to 3.460mg/L(SA), BDL(CTR) to 3.871mg/kg(RA), BDL(BG, CTR) to 2.935mg/kg((DD) were recorded in the urine, blood nail and hair samples of human residents of the dumpsites. The results indicate that the levels of Pb, Cd and Hg were generally above the

toxic limits of 0.001, 0.05 and 0.30mg/kg in the human residents. The non-toxic bismuth electrode was designed and tested which shows the detection limits of 0.005, 0.029, 0.033, 0.027 and 0.570μM for Cu, Pb, Zn, Cd and Hg, respectively. High levels of these gases and toxic metals reduce the oxygen carrying capacity of the blood, block oxygen transfer, poison cell enzymes, etc. The concentrations of the metals in chicken samples were generally below the tolerable limits with few exceptions which clearly show that the residents at the vicinity of these dumpsites are directly affected. Further work on bismuth working electrode should be carried out to improve the detection limits of these metals for environmental studies.

# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 Background to the Study

The term "solid waste" means garbage, refuse, or sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility and other discarded material including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining and agricultural operations (US Law –Solid Waste Act 2, 1999). The term disposal means the discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste, hazardous waste on any land or water so that such solid wastes, hazardous wastes, or any constituent thereof may enter the environment or be emitted into the air or discharged into waters including ground water from community activities (US Law-Solid Waste Act 2, 1999, Salam, 2010).

The disposal of waste in the world is a problem that continues to grow with the development of industrialized nations and the growth of population. All over the world the talk is about various ways of handling garbage. It was estimated that 1.375billion tons of solid waste are generated annually and this number is expected to increase by 20 % (WHO, 1999). Solid wastes were classified into three different categorie: non-hazardous, hazardous and special wastes. Non-hazardous wastes are those that pose no immediate threat to human health and the environment while hazardous wastes have common hazardous properties such as ignitibility, reactivity etc. The last type, special waste, is very specific in nature, some are radioactive and they are regulated with specific guidelines (Luke, 2008).

Currently, world cities generate about 1.3 billion tonnes of solid waste per year (What a waste, 2013). This volume is expected to increase to 2.2 billion tonnes by 2025

(What a Waste, 2013). Waste generation rates will more than double over the next twenty years in lower income countries. Globally, solid waste management cost will increase from today's annual $205.4billion to about $375.5billion by 2025. Cost increases will be most severe in low - income countries (more than five - fold increases) and lower - middle income countries (more than five - fold increases) (What a Waste, 2013).

Poorly managed waste has an enormous impact on health, local and global environments, and economy. Improperly managed waste generally results in down-stream costs higher than what it would have costed to manage the waste properly (What a waste, 2013).

In 1999, the World Bank published What a Waste: Solid Waste Management in Asia (Hoornweg and Thomas, 1999) with an estimate of waste quantities and composition for Asia (What a Waste, 2013). In the intervening decade more accurate and comprehensive data became available for most regions of the world (What a Waste, 2013). OECD estimates are typically reliable and consistent added to these were comprehensive studies for China, and India and the Pan American Health Organisation's study for Latin America. Therefore, a global update of 1999 report is possible and timely (What a Waste, 2013).

Solid waste collection and disposal have become a global business, the European school is rather dominated by policies initially espoused in Germany and later modified by the 15 - member European Union (EU). The underlying principle is "polluter pays". The companies that manufacture and sell products are the "polluters" not the consumers who purchase the products. Therefore, the EU has decreed that polluters should pay to collect and recycle all the packaging materials (Vasuki, 2001).

Most of the countries within the West African sub-region are emergent nations which, for along time, have been grouped among the less developed countries of the world.

Due to the low level of development, these countries have generally considered economic growth, social and educational development and industrialization as key development priorities, while protection of the environment has not been given the same importance.

The cities of the third world countries are growing at very rapid rates compared to those in the developed nations. For instance, a United Nations Habitat report observed that Africa is the fastest urbanizing continent having cities like Nairobi, Cairo, Lagos and Kinshasa, among others, growing at fast rates that would make them triple their current sizes by the year 2050 (UN-habitat, 2009). The increasing growth of cities therefore has implication for municipal waste management among other social services required in the urban communities. Data from many of the cities show inadequacy in the social services like shelter, provision of safe drinking water and efficient management of solid waste. The cities are, therefore, littered with mountains of rubbish in the landfills and open waste dumps which are covered with flies and thus serve as breeding grounds for rodents and mosquitoes which are carriers of diseases (UN-habitat, 2009).

Industrialization and population increment result in changes in the composition and quantity of waste generated. This is one of the main causes of environmental pollution and degradation in many cities of the developing world (UNIDO, 2003). Poor waste management poses several challenges for the well-being of the city residents, particularly those living adjascent to the dumpsites due to the potential of the waste to pollute the water, food sources, land, air and vegetation (Njoroge *et al.*, 2007). Dumping of solid wastes without proper separation increases the concentration of heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg) and zinc (Zn). These heavy metals when present in solid wastes have been known to produce major environmental impacts (Suman *et al*., 2011; Ebong *et al*., 2007).

Studies have shown that soil and groundwater system can be polluted due to poorly designed waste disposal facilities, leakage from underground storage tanks and agricultural wastes. Soil and groundwater acidification and nitrification have been linked to waste dumps (Bacud *et al*., 1994) as well as microbial contamination of soil and groundwater system (Awomeso *et al*., 2010; Amadi *et al*., 2011). The contamination of soil, water and air with heavy metals even at low concentrations are known to have potential impact on the environmental quality and human health. These metals also pose a long term risk to ground water and ecosystem (Ebong *et al*., 2007). Reports further indicate that these metals are toxic or poisonous even at low concentrations and create definite health hazards when they enter the ecosystem (Lenntech *et al*., 2004; Duruibe *et al*., 2007; Okoronkwo *et al*., 2006). Cancer, heart diseases and teratogenic abnormalities are attributed to groundwater pollution via leachate from the waste dumps. Increase in population and rapid expansion of cities have resulted to generation of huge amount of waste (Sia Su *et al*., 2008).

Pollution of soil by leachate from surrounding municipal waste dumps has been recognized for a long time (Alloway *et al*., 1990; Amadi *et al*., 2010). In Nigeria, like in other developing countries, open dump is the only available option for solid waste disposal in its cities. The depressions into which solid wastes are often dumped include valleys and excavations (Amadi *et al*., 2011). Solid waste management has remained an intractable environmental sanitation problem in Nigeria. This problem has manifested in the form of piles of indiscriminately disposed heaps of uncovered waste and illegal dumpsites along major roads and at street corners in cities and urban areas. This problem is compounded by rapid urbanization and population growth which have led to generation of enormous quantities of solid waste which are often

discarded by open dumping (Uwakwe, 2012). Open dumping of municipal solid waste disposal practiced by three fourth of countries and territories around the world. It is the major cause of environmental degradation and public health concerns in many developing countries including Nigeria. These waste dumps may contain a mixture of generated waste and toxic infectious or radioactive wastes and are susceptible to burning and exposure to scavengers (Uwakwe, 2012). There are a number of major risks and impacts of the dumpsites on the environment. Air pollution from open burning due to emission of greenhouse gases, rats and fly infestation and nuisance effects are among the health and environmental impacts of poor solid waste management. In addition, scattering of wastes by wind and scavenging by birds, animals and waste pickers create aesthetic nuisance. Malodour emanating due to degradation of the waste in the dumpsite has nuisance effect and decreases the economic and social values in the locality (Uwakwe, 2012). In many dumpsites, the waste is directly increasing global concern over the public health impact attributed to environmental pollution particularly the environmental quality and human health risks associated with the waste dumps.

The World Health Organization estimated that about a quarter of diseases facing mankind today occur due to prolongeg exposure to environmental pollution and it seems to be the highest (Uwakwe, 2012). To determine whether to rehabilitate and close or remediate, upgrade and operate a dumpsite may require an environmental impact assessment studies. In countries like Nigeria where the number of existing dumpsites (both legal and illegal) are many, economic considerations of evaluation process must be taken into consideration in recommending a suitable approach or methodology. Assessing the relative health and environmental hazards posed by the dumpsites existing throughout the

developing countries help prioritize, plan and initiate dumpsite rehabilitation (Uwakwe, 2012).

Solid waste handling and disposal is a major environmental problem in many urban centers of Nigeria (Amusan *et al.,* 2005). City dwellers have long contended that any form of waste with proper composting and processing can be made into fertilizer. Municipal refuse may contain paper, food wastes, metals, glass, ceramics and hairs (Carlson, 1976). Dumpsite soils are known to contain different kinds and levels of heavy metals depending on the peculiarities of the neigbourhood (Harrison and Chirgawi, 1989; Udosen *et al.,* 1990; Odukoya *et al.,* 2000). According to Carlson (1976) and Alloway (1996), heavy metals in dumpsites soils can be accumulated to environmentally hazardous levels.

Heavy metals are environmental pollutants (Onyeri *et al.,* 1991; and Gratani *et al.,* 1992) and could be increasingly introduced anthoropogenically as co-products and finished products into dumpsite soils (Shuaibu and Ayodele, 2002). Heavy metals in soil could be greatly influenced by man mediated activities such as industrial and agricultural activities, waste disposal, etc. (Udosen *et al*., 1990; Eja *et al*., 2003; Benson 2004; Zauyah *et al.,* 2004). Pollution is the introduction into the environment of a substance or effect that is potentially harmful or interferes with species habitats (Porteus *et al.,* 1985). The substance that causes pollution is known as pollutant. Heavy metals are of significant environmental concern owing to their relative toxicity and accumulation potentials (Yusuf *et al.,* 2003).

Most abandoned waste dumpsites in many towns and villages in Nigeria are considered as fertile grounds for cultivating varieties of crops. The cultivated plants take up the metals either as mobile ions present in the soil solution through the roots (Davies, 1983)

or through foliar absorption (Chapel, 1986; and Amusan *et al.*, 2005). The uptake of metals by crops results in bioaccumulation of these elements in plant tissues. This is known to be influenced by the metal species, plant species and the part of the plant (Juste and Mench, 1992). Alloway *et al., (*1971) reported that plants grown on soils possessing enhanced metal concentration due to pollution have increased heavy metal ion content which, if not carefully regulated, may lead to accumulation in man.

Monitoring and systematic gathering of information on heavy metal levels in the environment are essential components of any pollution control system. The establishment of such control system often presupposes the existence of minimum pollution standard and regulations. Most countries within the African sub-region do not have such control standards and environmental impact studies become very imperative.

The United State Environmental Protection Agency (USEPA) is a government agency established to enforce the proper disposal of wastes and conduct research in related areas. It reported that 208 millions tons of municipal solid wastes were generated in the United States annually (Luke, 2008). There are many different methods of disposing wastes, these are; land filling, incineration and pumping of wastes into deep wells but there is strong opposition to this method because of the apparent explosions, earthquakes and underground water pollution that may results due to heavy metal pollution (Luke, 2008).

Municipal solid waste disposal is an enormous concern in developing countries across the world, as poverty, population growth and high urbanization rates combine with ineffectual and under-funded government to prevent efficient management of wastes (Doan, 1998; Cointreau, 1982). From American perspective, the sheer magnitude of solid waste problem in Nigeria is hard to comprehend as the garbage “dumps” are located on the road sides of highways in cities and town. Since there are no means for containment, wastes

often spread into roads, blocking traffic in many towns and cities in the country (Stephen, 2004).

Nigeria is a nation that exemplifies chronic waste management problems in conjunction with population growth. It is the most populous country in Africa with over 140million residents (World Bank, 2002). Over the past 50 years, Nigeria's annual growth rate was 5.51% which is the third largest urban growth rate in the world. The Federal government has very little control over environmental regulation as a whole. The Federal Environmental Protection Agency (FEPA) was established in 1988 to control the growing problems of waste management and pollution in Nigeria (Onibokun, 2003). Vision 2010 was FEPA's attempt to address environmental problems in the nation. The FEPA report proposed the goals to be accomplished by the year 2010 that would lead toward sustainable development. With regards to solid waste management, the report says the goal is to achieve not less than 80% effective management of the volume of municipal solid wastes generated at all levels and ensure environmentally sound management (Vision 2010, 2003). Strategies to achieve these goals include education and awareness programs, developing collaborative approaches to integrative management of municipal solid waste strengthening existing laws and ensuring compliance and encouraging local and private sector participation. However, poverty and corruption had prevented the implementation of these plans.

Water is the most important substance for human existence (Melese *et al*.,1998). It is the cradle of life, without which no living thing can survive in this world. Freshwater from rivers, lakes and ground is used to irrigate crops, to provide drinking water, and to act as a sanitation system (Economopoulos, 1993). Frequently, rivers act as conduits for

pollutants by collecting and carrying wastewater from catchments and ultimately discharging it into the ocean and storm water which can also be rich in nutrients, organic matter and pollutants, finds its way into rivers, lakes and other water bodies.

Zaria, in Northern Nigeria, with population of over one million four hundred and ninety thousand (1,490,000) that came from different parts of the world faces problems of environmental sanitation such as improper refuse disposal near residential areas, poor refuse collection and handling etc. The environmental pollution posed by solid waste ranged from health hazard to soil and water pollution (Eddy *et al.,* 2006).

Some metals are essential components of living systems such as iron in haemoglobin, zinc as an essential component of many enzymes and coenzymes (Nayak, 2000). Respiratory pigments of many mollusks and higher crustaceans contain copper. However, when these metals are present in higher concentrations they accumulate and become toxic to organisms (Nayak, 2000).

## 1.2 The Research Problem

Zaria metropolis is located at latitude $11^{0}3^{'}$ N and longitude $7\ ^{o}40^{'}$E and is presently one of the most important cities in Northern Nigeria. It has a population of 1, 490,000 people (population census, 2006). Like many cities in Nigeria, Zaria faces problems of environmental sanitation such as improper disposal of refuse near residential areas; poor refuse collection and handling etc. For example, it is common to find huge refuse dumpsites within residential areas and along some minor and major roads (Plate I). City dwellers have long contended that any form of waste with proper composting and processing can be made into fertilizers that farmers will gladly pay for (Amusan *et al*., 200)

## 1.3 Justification

The presence of toxic heavy metals in the environment continues to generate a lot of concern to environmental scientists, government agencies and health practitioners because of health implications of their presence (Awofolu, 2005).

Heavy metals have been referred to as common pollutants are widely distributed in the environment with sources mainly from soils and weathering of rocks (Merian, 1991; and O' Neil, 1993). However, levels of these metals in the environment have increased tremendously as a result of human inputs and activities (Awofolu, 2005). According to Oskarson *et al*. (1992), there exist transfer of heavy metals from contaminated soil to plants and from plants to animals with the subsequent transfer through the food chain up to man. It is not uncommon to find ruminants feeding on grasses and birds feed on insects and earthworms on the dumpsite soils. High concentrations of metals in the environment may lead to accumulation, becoming toxic to plants and animals with possible danger to human health.

**Plate I: Kusfa (KU) Dumpsite Zaria Metropolis**

Solid waste disposal tends to pollute under ground water at the vicinity of dumpsites which has been a serious problem for the entire world. It threatens the health and well-being of the residents, plants, and animals. All water pollution is dangerous to the health of living organisms; it has been reported that the quality of the underground water close to dumpsites is compromised resulting in serious health problems to residents. In some areas, the population has only one source of water and if this water is polluted, the population has no choice but to use it (Ince and Howard, 1999).

The effect of toxic substances and a wide range of other adverse effects can occur when waste products are introduced into the water body leading to changes in physical, chemical and biological parameters such as infectious agents, temperature, turbidity, color, pH, salinity and oxygen concentrations. Changes in any of these parameters have direct environmental effects and can also produce impact by modifying other parameters (Chapman, 1992).

The role of some heavy metals (Cd and Pb) is very critical in determining the quality of our atmosphere because air, soil and water are directly interacting with each other. Growing heavy metals pollution especially in air has led to increased respiratory diseases, infant mortality and also affects the functioning of the blood, liver, kidney and brain. The measurement of Pb, Cd, Cu, Zn and Ni accumulation in soil and plant appears to be a useful tool for evaluating the potential heavy metal hazards of the environment (Mudassir *et al*., 2005).

In Nigeria at present, little data is available on the extent of soil-vertebrates-human pollution. Clearly, there is a gap in knowledge related to dumpsite soil-water-animal-human pollution especially in Nigeria and empirical data are needed as the basis for wider modeling assessment.

## 1.4 Research Questions

The research was aimed to answer the following questions:

i. What are the effects of dumpsites on the air quality at the vicinity of dumpsites
ii. What are the effects of dumpsites on the water quality at the vicinity of the dumpsites
iii. What are the effects of the dumpsites on the soil physico-chemical parameters and heavy metal contents (Zn, Cu, Hg, Cd and Pb).
iv. What are the effects of dumpsites on the different organs of the chickens' feeding on the dumpsites
v. What are the effects of the dumpsites with respect to the particulate dust emanating from the dumpsites
vi. What are the effects of the dumpsites on residents with respect to some heavy metal (Zn, Cu, Hg, Cd and Pb) contents.

## 1.5 Aim and Objectives

The aim of this investigation was to assess the dynamics of dust particulates –soil leachates – water – vertebrates - human pollution with special preference to heavy metals (Hg, Cu, Cd, Zn and Pb), and some gaseous pollutants ($SO_2$, $NO_2$, $H_2S$, $NH_3$, flammable gas (Fl) and CO) from dumpsites of Zaria Metropolis, Kaduna State, Nigeria in dry and wet seasons. This aim was designed to be achieved through the following objectives:

i. To Assess quality of the groundwater near the dumpsites in comparison with the standard limits.
ii. To characterize the refuse wastes, determine physicochemical parameters and levels of metals in the soils and leachates using sequential extraction method.

iii. To assess the quality of the air around the dumpsites and compare it/them to standard limits.

iv. To determine the concentrations of the heavy metals in the tissues and organs of chickens fed with the refuse wastes.

v. To determine the concentrations of the afore mentioned heavy metals in blood, nails, hair and urine samples of people living at the vicinity of dumpsites across the seasons.

vi. To develop a bismuth electrode (BiEs) and ascertain its workablity compared to other analytical methods for the determination of heavy metals in water samples.

## 1.6 Research Hypotheses

The study was guided by the following hypotheses:

i. The null hypotheses ($H_0$) states that

   a. the water quality at the dumpsites is not significantly different from that at the control site

   b. the air quality at the dumpsites is not significantly different from that at the control site

   c. there is no significant difference in the physico-chemical parameters and heavy metal contents between soils from dumpsite and those of the control site

   d. there is no significant difference between the heavy metals in chickens' tissues and organs fed with the refuse waste and those at the control site.

   e. there is no significant difference between heavy metals in human blood, nail, hair and urine collected from people living at the vicinity of the dumpsites and those from the control site.

f. there is no significant difference between square wave technique and the atomic absorption spectrometry

ii. the alternative hypotheses ($H_1$), which states that there is significant differences in a, b, c, d and e.

## 1.7 Significance of the Study

In Zaria metropolis, little data is available on the extent of soil – vertebrates - human pollution around the dumpsites. A variety of metal ions and hazardous gaseous pollutants demonstrate a wide range of uptake capacities and interaction mechanisms as reported in literatures from developed countries. Clearly, there is a gap in knowledge related to dumpsite soils – water – animals - human pollution especially in Nigeria, a developing country. Therefore, an empirical data is needed as the basis for wider modeling assessment which forms the basis of this research.

## 1.8 Scope and Limitations

The study was designed to assess the impact of dumpsites in Zaria Metropolis and their environments to include air, soil, water, leachates, animals, birds and human kind across the four seasons of the year in 10 dumpsites and a control site. However, during the sampling, it was obvious that the research could not be sustained for the four seasons due to finance, hence, the research was limited to two seasons (dry and wet ) of the year.

# CHAPTER TWO

## 2.0 LITERATURE REVIEW

### 2.1 Health Implications of Open Waste Disposal

Improper disposal of solid waste disposal is one of the main causes of environmental pollution and degradation in many cities, especially in developing countries (UNEP, 2005). Many of these cities lack solid waste regulations and proper disposal facilities including those for harmful waste which may be infectious, toxic or even radioactive (UNEP, 2005).

Municipal waste dumpsites are designated places set aside for waste disposal. Depending on a city's level of waste management, such waste may be dumped in an uncontrolled manner, segregated for recycling purposes or simply burnt. Poor waste management poses a great challenge to the well-being of city residents particularly those living adjacent to them as they pollute water, food sources, land, air and vegetation (UNEP, 2005). The poor handling and disposal of waste thus leads to environmental degradation, destruction of the ecosystem and poses great risks to public health (UNEP, 2005), Fig. 4.1 summarizes the major threats of dumpsites to public health.

### 2.2 Heavy Metals

The term heavy metals refers to any metallic element that has a relatively high toxicity or poisonous effect even at low concentration (Lenntech, 2004; Duruibe *et al.*, 2007). It is a general collective term which applies to the group of metals and metalloids with atomic density greater than $4g/cm^3$ or five times or greater than water (Nriagu, 1989). However, being a heavy metal has nothing to do with density but concerns with chemical properties. Heavy metals include lead, cadmium, zinc, mercury, arsenic, silver, chromium, copper, iron and platinum group

elements. Environment is defined as the totality of circumstances surrounding organisms especially the combination of external physical conditions that affect and influence the growth, development and survival of organisms (Farlex, 2005). It consists of the flora, fauna and the biotic and includes the aquatic, terrestrial, and atmospheric habitats. The environment is considered in terms of the most tangible aspects like air, water and food and less tangible though not less important, the communities we live in (Gorek, 1997). A pollutant is any substance in the environment which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Such a substance has to be present in the environment beyond a set of tolerance limit, which could itself be either desirable or acceptable within the limit.

Thus, environmental pollution is the presence of a pollutant in the environment which may be poisonous or toxic and will cause harm to living things in the polluted environment (Duruibe *et al*., 2007).

## 2.3 Human Exposure to Heavy Metals through Food, Air, and Water

Heavy metal pollution of surface and underground water sources results in considerable soil pollution and the pollution tends to increase with increase in the dumping activities. Polluting the dumpsites soil leads to the pollution of the plants grown with that soil as farmers are gladly using dumpsite waste soil as source of fertilizer. These metals consequently accumulate in their tissues. Animals that graze on such contaminated plants and drink from polluted waters as well as marine lives that breed in heavy metal polluted waters also accumulate such metals in their tissues, and milk, if lactating (Habashi, 1992,

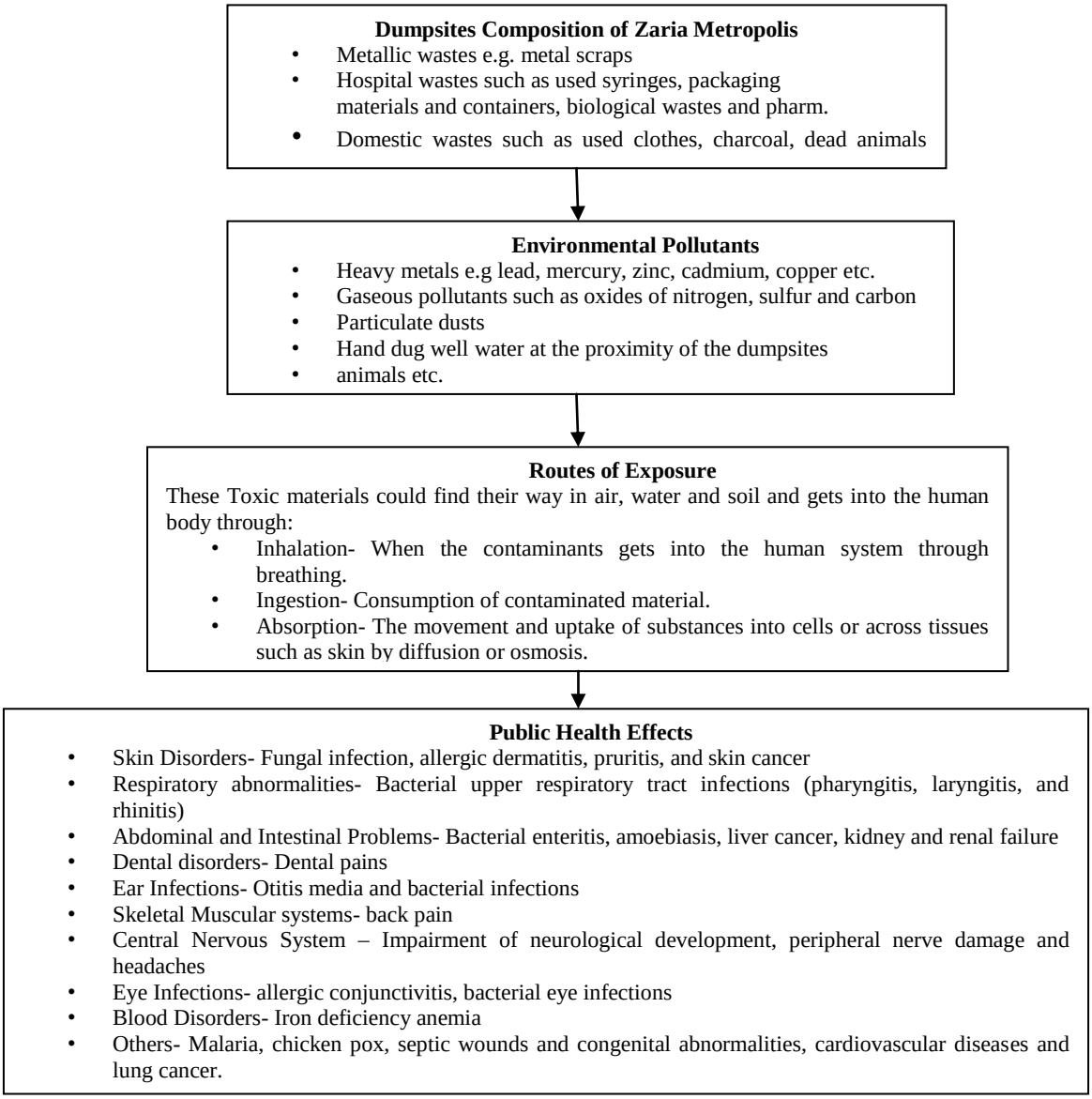


**Fig. 2.1 Summary of major threats of dumpsites to public health**.

Garbarino *etal*., 1995; Horsfall and Spiff, 1999). People are, in turn exposed to heavy metals by consuming contaminated plants and animals, and this has been known to result in various biochemical disorders. In summary, all living organisms within a given ecosystem are contaminated along their cycles of food chain (Duruibe *et al.*,2007).

Heavy metal pollutants can localize and lay dormant, which can have severe effects on the environment through precipitation of their compounds or by ion exchange into soils and mud. Plants, mushrooms, or microorganisms are occasionally successfully used to remove some heavy metals such as mercury. Plants which exhibit hyper accumulation can be used to remove heavy metals from soils by concentrating them in their bio-matter (Duruibe *et al.*,2007).

**2.4 Bio-importance of Heavy Metals** Some heavy metals (such as Fe, Zn) are known to be of bio-importance to man and their daily medicinal and dietary allowances had been recommended. Their tolerance limits in drinking water have been reported. However, some others (like As, Cd, Pb, and methylated forms of Hg) have been reported to have no known bio-importance in human bio-chemistry and physiology and when consumed even at very low concentrations can be toxic (Nolan, 2003; Young, 2005, Duruibe *etal*.,2007).

Zinc is a "masculine" element that balances copper in the body and is essential for male reproductive activity (Nolan, 2003). It serves as a co-factor for dehydrogenating enzymes and in carbonic anhydrase (Holum, 1983). Zinc deficiency causes anaemia and retardation of growth and development (McClugggage, 1991, Duruibe etal., 2007). Lead, cadmium and mercury have not been reported to have any known function in human biochemistry or physiology, and do not occur naturally in living organisms (Lenntech,

2004). Thus, dietary intake of these metals even at low concentrations can be very harmful because they bioaccumulate (Duruibe *et al.*, 2007).

**2.5 Heavy Metals Poisoning and Biotoxicity** The biotoxic effects of heavy metals refer to the harmful effect of the metals when consumed above the bio-recommended limits (Duruibe *et al.*, 2007). Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with cadmium, lead, arsenic, mercury, zinc and aluminum poisoning: gastrointestinal (GI) disorders, diarrhoea, stomatitis, tremor, haemoglobinuria causing a rust-red colour stool, ataxia, paralysis, vomiting and convulsion, depression and pneumonia when volatile vapours and fumes are inhaled (McCluggage, 1991). The nature of effects could be toxic (acute, chronic, or sub-chronic), neurotoxic, carcinogenic, mutagenic, or teratogenic (Duruibe *et al*.,2007).

Cadmium is toxic even at extremely low levels. In humans, long term exposure results in renal dysfunction, characterized by tubular proteinuria. High exposure can lead to obstructive lung disease, cadmium pneumonitis, resulting from inhaled dusts and fumes. It is characterized by chest pain, cough with foamy and bloody sputum, and death of the lining of the lung tissues because of excessive accumulation of watery fluids. Cadmium is also associated with bone defects, namely, osteomalacia, osteoporosis, and spontaneous fractures, increased blood pressure and myodic dysfunctions (Duruibe *et al.*, 2007). Depending on severity of exposure, the symptoms of effects include nausea, and muscular weaknesses. Severe exposure may result in pulmonary oedema and death. Pulmonary effects (emphysema, bronchiolitis, and alveolitis) and renal effects may occur following sub chronic inhalation exposure to cadmium and its compounds (Young, 2005).

Lead is the most significant toxin and its inorganic forms are absorbed by ingestion in food, water and inhalation (Ferner, 2001). A notably serious effect of lead toxicity is its teratogenic effect. Lead poisoning also causes inhibition of the synthesis of haemoglobin, dysfunctions in the kidneys, joints and reproductive systems, cardiovascular system, acute and chronic damage to the central nervous system (CNS) and peripheral nervous system (PNS) (Ogwuegbu and Muhanga, 2005). Other effects include damage to the gastrointestinal tract (GIT) and urinary tract resulting in the bloody urine, neurological disorder and may cause severe and permanent brain damage. While inorganic forms of lead, typically affect the CNS, PNS, GIT in poor biosystems, organic forms predominantly affect the CNS PNS, GIT and other biosystems, organic forms of lead predominantly affect the CNS (Mcluggage, 1991; INECAR, 2000; Ferner, 2001; Lenntech, 2004). Lead affects children by leading to poor development of the grey matter of the brain, thereby resulting in poor intelligent quotient (IQ) (Udedi, 2003). Its absorption in the body is enhanced by Ca and Zn deficiencies. Acute and chronic effects of lead result in psychosis.

Zinc has been reported to have the same signs of illness as does lead and can easily be mistakenly diagnosed as lead poisoning (McCluggage, 1991). Zinc is considered to be relatively non-toxic, especially if taken orally. However, excess amount can cause system dysfunctions that result in impairment of growth and reproduction (INECAR, 2000; Nolan, 2003). The clinical signs of zinc toxicosis have been reported as vomiting, diarrhea, bloody urine, icterus (yellow mucous membrane), liver failure and anaemia (Fosmire, 1990).

Mercury is toxic and has no known function in human biochemistry and physiology (Duruibe *et al.*, 2007). Inorganic forms of mercury cause spontaneous abortion, congenital malformation and GI disorders (such as corrosive esophagitis and hematochezia). Poisoning

by its organic forms, which include monomethyl and dimethylmercury presents with erethism (an abnormal irritation or sensitivity of an organ or body part to stimulation), acrodynia (pink disease, which is characterized by rash and desquamation of the hands and feet), gingivitis, stomatitis, neurological disorders, total damage to the brain and CNS and are also associated with congenital malformation (Ferner, 2001; Lenntech, 2004).

**2.6 Heavy Metals in Nigerian Dumpsite Soils** Dumpsite soils are known to contain different kinds and levels of heavy metals depending on the peculiarities of the neigbourhood (Harrison and Chirgawi, 1989; Udosen *et al.,* 1990; Odukoya *et al.,* 2000). Most abandoned waste dumpsites in many towns and villages in Nigeria are considered as fertile grounds for cultivating varieties of crops (Amusan *et al.,* 2005). According to Carlson (1976) and Alloway (1996), heavy metals in dumpsite soils can accumulate to environmentally hazardous levels. Heavy metals are environmental pollutants (Onyeri *et al.,* 1991; and Gratani *et al.,* 1992) and could increasingly be introduced anthoropogenically as co-products and finished products into dumpsite soils (Shuaibu and Ayodele, 2002).

Heavy metals in soil could be greatly influenced by man mediated-activities such as industrial and agricultural activities, waste disposal etc. (Udosen *et al.,* 1990; Eja *et al.,* 2003; Benson 2004; Zauyah *et al.,* 2004). They are of significant environmental concern owing to their relative toxicity and accumulation potentials (Yusuf *et al.,* 2003).

**2.7 Heavy Metals in Dumpsite Particulate Dust** Man-made pollutants like CO, NOx, SOx, $CO_2$, hydrocarbons, particulates, etc, are released into the atmosphere as a result of burning of refuse wastes, industrial wastes, etc. These have surpassed the pollutants contributed by nature thousand-fold. The magnitude of the problem

of air pollution is alarming due to population explosion, industrialization, urbanization, automobiles and other human activities (Dara, 2008). The pollutants travel through the air, disperse and interact with other substances in the atmosphere before they reach a sink such as an ocean or a human receptor. If the pollutants enter the atmosphere at a faster rate than are absorbed by the natural sinks, then they gradually accumulate in the air. Such a disturbance in the dynamic equilibrium in the atmosphere by the air pollutants released by anthropogenic activities resulting in considerable accumulation in the atmosphere may affect the very life on earth and its environment (Dara, 2008).

Open dumping, which is still the most popular way for municipal solid waste (MSW) disposal in developing countries, takes up lots of land and leads to serious pollution of its surrounding (Mor *et al*., 2006). They cause bad odours and environmental risks due to the emissions of green house gases (GHGS), hazardous organic compounds and landfill gas (LFG) (Tchobanoglous *et al*., 1993; Cooper *et al.*, 1992; Obuli *et al*., 2011). The composition and flow rate of LFG depends on social factors such as waste composition and generation rate, recycling/reuse practices, physico-chemical and microbiological condition such as moisture, temperature, pH, nutrient content, microbial population and site management factors such as type of disposal site, waste processing, leachate recycling and age of refuse (Mcbean *et al*., 1995, Obuli *et al*., 2011).

Typically, landfill gas consists of 50 - 60% methane, 30 - 40% of carbon dioxide, trace amount of numerous chemical compounds, and heavy metals (Obuli *et al*., 2012). Furthermore, it also contains small amount of $N_2$ , $O_2$, $NH_3$, $H_2$, CO, $H_2S$ and traces of toxic substances including saturated and unsaturated hydrocarbons, acidic hydrocarbons and organic alcohols, aromatic hydrocarbons (many of them volatile organic compounds); halogenated compounds, sulphur compounds ( such as carbon disulphide and mercaptans)

and inorganic compounds such as mercury (Allen *et al*; 1997 ATSDR, 2001; Teleghani and Shabani–Kia, 2005).

Epidemiological and toxicological studies indicate a line between air pollution and respiratory conditions like chronic bronchitis, bronchial asthma, pulmonary emphysema and lung cancer. The vulnerability of air pollution depends upon age, sex, general health status, nutrition, pre–existing disease, concurrent exposures, concentration and native of the pollutants involved, extent of explosive, temperature, time of exposure, irritation of nose, eyes, throat and bad odours due to air pollutants, cause annoyance, allergy and health hazards (Dara, 2008). Esakku *et al*. (2003), highlighted that the heavy metals cause blood and bone disorders, kidney damage and decreases mental capacity associated neurolological damage in exposed human beings. Generally, the two possible sources through which the metal ions get into aerosols are emission of particulate matter and open burning/self-ignition due to methane production from waste degradation (Obuli *et al*., 2011).

Air quality standards indicate the levels of pollutants that cannot be exceeded during a specified time period in a specified geographic area with a reference to the method of measurement, units of measurement, concentration and time of exposure. These are derived from air quality citeria which are in turn derived on the basis of effects of ambient air pollution on human health, vegetation, animals, materials, visibility, etc. (Dara, 2008).

**2.8 Heavy Metals in Chickens Feeding on Dumpsites** Contaminations by heavy metals are major concern worldwide, regional and local levels and influence the functional and structural integrity of an ecosystem. Birds' populations are particularly susceptible to the effects of anthropogenic activities on the environment. Several biological

and physiological processes, such as eating habits, growth, age, breeding, moulting may influence metal concentration and distribution in birds (Kim *et al*., 2007). The concentration of heavy metals in internal tissues of chickens have been extensively investigated by several researchers (Mariam *et al*., 2004; Iwagbue *et al*., 2008; Uluozlu *et al*., 2009). However, data on the trace element levels in chickens and other domestic birds in Nigeria are still scarce. Bioaccumulation of heavy metals in tissues of birds has received intense attention because of the lethal and sub-lethal effect of their accumulation, apart from the fact that birds are often located in high levels in the food chain which makes them suitable for use in bioaccumulation studies (Burglar *et al*., 1994). The risk of heavy metal contamination in meat is of great concern for both food safety and human health because of the toxic nature of heavy metals at relatively minute concentrations (Akan *et al*., 2010). According to Duruibe *et al*., (2007), some heavy metal ions that are known to be potentially toxic include arsenic, cadmium and lead and also essential metals such as iron, manganese, copper, zinc, selenium, nickel and cobalt. Toxic elements can be harmful to birds even at low concentrations when ingested over a long period of time (Nolan, 2003; Young, 2005).

However, the concentrations of heavy metals seem to vary among the species. Chicken meat is a major source of protein to human population and is widely consumed in many countries of the world. Meat of chicken is a valuable food source rich in many of the essential nutrients including protein (essential amino acids), minerals (e.g., iron, zinc, selenium), vitamins (e.g., vitamin E) and fat (essential fatty acids such as Omega 3 fatty acids) (Schonfeldt *et al*., 2008). According to Oskarson *et al*. (1992), there exist transfer of heavy metals from contaminated soil to plants and from plants to animals with subsequent transfer through the food chain up to man. It is not uncommon to find ruminants feeding on grasses and birds feed on insects and

earthworms on the dumpsite soils. High concentrations of heavy metals in the environment may lead to accumulation, becoming toxic to plants and animals with possible danger to human health.

## 2.9 Heavy Metals in Dumpsite - leachates and Health Implications

The open dumpsites are well known for releasing large amounts of hazardous and otherwise deleterious chemicals to nearby groundwater, surface water, soil and to the air via leachates and landfill gases. It is known that such releases contain a variety of potential carcinogens and potentially toxic chemicals that represent a threat to public health. Leachates have been implicated as environmental pollutants such as air, soil, plants, surface and ground waters pollution. Sufficient number of individuals near dumpsites would experience an average increased cancer risk at least 1 in 1000 (Fredlee *et al*., 2003). Municipal refuse may increase heavy metal concentrations in soils and underground water (Carlson, 1976; Albores *et al*., 2000; Okoronkwo *et al*., 2005; Okoronkwo *et al*., 2006) which may have effects on the host soils crops and human health (Smith *et al*., 1996; Nyle and Ray 1999).

Thus, the environmental impacts of leachates emanating from dumpsites are greatly influenced by their heavy metal contents. However, while total heavy metal content is a critical measure of assessing risk of a refuse dumpsite, it does not provide a predictive insights on the bioavailability, mobility and fate of the heavy metals contaminants (Albores *et al*., 2000). Thus, it is the chemical form or species of the heavy metals that is an important factor in assessing their impacts on the environment as it controls their bioavailability and mobility (Norvell, 1984).

## 2.10 Heavy Metals in Hand-Dug Well-water Near the Dumpsites

Any human activity that impairs the use of water as a resource may be called water

pollution and the increasing population, industrialization and urbanization, water pollution by agriculture, municipal and industrial sources, has become a major concern for the welfare of mankind (Dara, 2008). Water is essential for survival of any form of life and human being consumes about two litres of water every day. It accounts for about 70% of the weight of human body, however, considerable part of this limited quantity of water is polluted by sewage, leachates from the municipal wastes, industrial wastes and a wide array of synthetic chemicals. The menace of water-borne diseases and epidemics still threatens the well-being of the populace, particularly in underdeveloped and developing countries (Dara, 2008). Thus, the quality and the quantity of clean water supply are of vital significance for the welfare of mankind (Dara, 2008). In Nigeria, it is generally believed that individuals, government and environmental agencies pay little attention to the environmental impact of waste disposal and its impact on public health. Organizations like the Federal Environmental Protection Agency (FEPA), Ministry of Environment, and even local government authorities are responsible for planning a defined line of action for the disposal and management of waste generated on a daily basis in our society. Unfortunately, they have failed in this regard (Umeakuka and Mba, 1999; Awekunmi *et al*., 2010). Poor management of refuse has caused traffic delays in some strategic parts of our urban centres (Awekunmi *et al*., 2010) and caused serious problems to the underground waters and consequently, affects the public health resulting in different kinds of ailments such as typhoid, malaria fever, etc.

## 2.11 Heavy Metals in Human samples Tissues(Blood, Urine, Hair and Nails)

Heavy metals are elements that are present in both natural and contaminated environments and cause serious problems to public health. The elements that are of concern include lead, mercury, cadmium, arsenic, chromium, zinc, nickel and copper. These metals may be released into the environment from metal smelting and refining industries, scrap metal, plastic and rubber industries, various consumer products and from burning of waste containing these products (UNEP, 2008).

On being released to the air, the elements travel over large distances and are deposited onto the soil, vegetation and water depending on their density. Once the metals are deposited they are not degraded and they persist into the environment for many years poisoning humans through inhalation, ingestion and skin absorption. Acute exposure to toxic metals leads to nausea, anorexia, vomiting, gastrointestinal abnormalities and dermatitis (UNEP, 2008). Table 2.1 summarizes the reported cases of the dumpsite pollution to residents in various countries in selected states of the US.

**Table 2.1: Reported cases of cancer and other serious illnesses in communities near closed dumps in selected ountries of the US states**

| State | County | Town/Place | Year | Effect |
|---|---|---|---|---|
| California | Carson Los Angeles | Towne Avenue Elementary School | 1999 | 10 out of 31 have been diagnosed of various types of cancer (breast cancer) |
| | Farifax Marim | Oak Manor Canyon | 1980 | Alarmed rate of cancer was reported |
| | Laytonville, Mendicino | Laytonville disposal site | 1980 | Various types of cancer respiratory problems including asthma |
| | Casanova Oak Knoll, Monterey | Naval Auxilliary Air | 2001 | Residents concerns about the possibility of a cancer cluster in the neighbourhood |
| | Sun Valley, Los Angeles | John H. Francis polytechnic high school | 2007 | High rate of cancer have been reported |
| Connecticut | Hamden New Haven | Newhall street neigbourhood | 2004 | High cancer rate |
| | Port ST. Lucie | St Lucie | 1990 | Possible cancer cluster |
| IDAHO | Moreland | Bingham | 1993 | Brain cancer have been reported |
| Illinios | Chicago | Cook | 2007 | Cancer, lung ailments, heart problems, asthma, birth defects and miscarriage which are associated to chemicals in the soil and groundwater |
| Loisiana | New Orleans | Orlean | 1994 | DDT, arsenic, lead, mercury and barium were |

| | | | | |
|---|---|---|---|---|
| | | | | found in soil and groundwater close to dumpsite. High rate of breast cancer had been reported in the neighbourhood |
| | Shreveport | Caddo | 1997 | Health problems were caused by carcinogenic chemicals within the dump |
| Massachusetts | Ashland, | Middlesex | 2006 | Ashland cancer cluster was linked to Nyanza chemical waste dump |
| New York | Elmira | Chemung | 2000 | Possible cancer cluster were found due to high chromium and polycyclic aromatic hydrocarbons at the spots |
| | Haverstraw | Rockland | 1990 | Residents health problems like headaches, rashes, diarrhea, and breathing problems were associated to dumpsites. |
| | Love canal | Niagra falls | 1980 | Residents relocated after identifying childhood illnesses and high rate of birth defects. |

*Retrieved from www.toxicsites.org, 2013*

## 2.12 Water Quality Assessment

The quality of water is the degree of its potability and is determined by the amount and level of physico-chemical, microbial and heavy metals (which include suspended and dissolved substances in the water, the degree of alkalinity, pH, temperature, appearance in terms of colour, taste, odour and the presence of non-desirable microorganisms). Water for domestic purposes should therefore be free from these substances in order to prevent waterborne diseases. The sources of water used for water supply remains societal, economic and of conservational importance. Water quality index (WQI) is a very useful and efficient method for assessing the water quality. It is also a very useful tool for communicating the information on overall quality of water (Asadi *et al*., 2007) to the concerned citizens and policy makers. It is an important parameter for the assessment and management of water quality (both surface and groundwater).

WQI reflects the composite influence of different water quality parameters and is calculated from the point of view of the suitability of both surface and groundwater for human consumption. In general, water quality indices incorporate data from multiple water quality parameters into a mathematical equation that rates the health of water body with number (Yogendra *et al*., 2008). Water quality depends on the physical, chemical and biological composition of the water. The most important characteristics that determine water quality are as follows:

### 2.12.1 Water Characteristics

i. Physical characteristics - colour, turbidity, taste, odour, temperature, amount of suspended solidcontent.

ii. Chemical characteristics - reaction, amount of dissolved solid, hardness, amount of nitrogenous matter, degree of acidity (pH), presence of toxic substances, and other substances such as copper, iron, magnesium, manganese, zinc and sulphate.

iii. Biological characteristics - bacteriological content, amount of dissolved oxygen and biological oxygen demand

**a. pH**

This is universally used to express the intensity of the acid or alkaline due to presence of a solute. Most of the water samples are slightly alkaline due to presence of carbonates and bicarbonates (Murhekar, 2011). One important water quality parameter, the pH of water affects the biochemical process in water (Chapman, 1996). The WHO guide level for pH in drinking water quality is 6.5 to 8.5 (WHO, 1993). Most drinking water have a pH from 4 to 9 and the majority are slightly alkaline due to carbonates and bicarbonates of calcium and magnesium dissolved in such water (Hutton, 2006). According to WHO(1997), water with a pH > 8.5 indicates that the water is hard. Most metals become more soluble and more toxic with increase in acidity (Mosley *et al.* 2004).

**b. Total Suspended Solids**

The test for the total content of solid matter of various kinds is very useful, but the result cannot represent accurately many mineral impurities contained in the wastewater. Different types of suspended solids are discharged daily into streams and coastal waters. These include inert minerals waste like oil and grease and other insoluble finely divided organic solids. The organic solids are biodegraded rather slowly and this causes a reduction of dissolved oxygen content of water. Small-suspended particles cause turbidity in water and reduce light penetration and hence photosynthesis and plant growth are restricted. Total suspended solids (TSS) could act as a vector of nutrients such as phosphorus (Heathwaite,

1994) and toxic compounds such as pesticides and herbicides from the land surface to the water body (Kronvang *et al*., 2005). TSS could also cause difference in invertebrates' population (Brottta & Brazier, 2008).

**c. Electrical Conductivity**

Electrical Conductivity is the ability of an aqueous solution to carry an electric current and this ability depends on the presence of ions, as waters with high inorganic compounds are relatively good conductors indicating its good quality. Electrical conductivity of the water is related to total concentration of ions in the water, their valence charge and mobility. Changes in conductivity of water sample may signal changes in mineral composition of water seasonal variation in reservoirs and pollution of water from industrial wastes (AWWA, 2000).

**d. Hardness**

Total hardness depends upon the amount of calcium and magnesium salts or both (Olajire & Imeokparia, 2000). According to Sawyer and McCarhty (1967) the level of the river hardness can be classified as moderately hard water. This can be leached from the nearby dumpsites into the underground water area. Hardness is the property of water which prevents leather formation with soap and increases the boiling points of water (Trivedi *et al.*, 1986). Hardness is a measure of concentration of calcium and magnesium salts in water and is an important variable for drinking water quality.

**e. Dissolved Oxygen**

Dissolved oxygen is essential for a healthy and diverse water body. Waters with consistently high dissolved oxygen (between 80 and 100%) are considered healthy and stable, capable of supporting a large variety of aquatic lives.

**f. Colour (Jaiswal, 2004)**

Colour is a qualitative characteristic that can be used to assess the general condition of wastewater. Wastewater that is grey in colour is a characteristic of wastewaters that have undergone some degree of decomposition or that have been in the collection system for some time. Lastly, if the colour is dark grey or black, the wastewater is typically septic, having undergone extensive bacterial decomposition under anaerobic conditions. Colour is measured by comparison with standards.

**g. Nitrate-nitrogen**

Nitrate is an end-product of decay of nitrogenous materials such as nitrate fertilizers or animal and human excreta (Hutton, 2006). Its presence in a water supply usually denotes bacterial activity as a result of recent or on-going pollution, often from sewerage. In developing countries especially there is risk of ground water pollution by onsite sanitation (Lewis, 1982). Nitrate in drinking water is detrimental to infant health, it causes a disease known as methemoglobinaemia (Taiwo, 1998). Nitrogen fertilizers results to high level of nitrates in water supplies (Andreoli, 1993). Health hazards of high nitrate level in drinking water include shortness of breath the blue-baby syndrome and other disorders (Sandra, 2002; WHO, 2006).

**h. Sulphate-sulphur**

Sulphates occur in most natural water in wide range of concentrations. Consumption of high levels of sulphates above 200mg/l can lead to attack of diarrhoea especially in new comers to the high sulphate in water supply. The WHO guide level is 400mg/l on organoleptic grounds. Waters in contact with sulphate rocks such as gypsum often have high sulphate values, acid mine water particularly from sulphate bearing ores

and industrial wastes may also contribute large amount of sulphate to natural water. In developing countries drinking water containing high sulphate can contributes to problem of sewer corrosion and related health hazards (Hutton, 2006).

**i. Phosphate-phosphorous**

Phosphates are used for special glasses, sodium lamps, in steel production, in military applications (incendiary bombs and smoke screening), and in other applications such as pyrotechnics, pesticides, toothpaste and detergents. Phosphates enter waterways from human and animal waste, laundry cleaning, industrial effluents, and fertilizer runoff and leachates from the waste disposal sites. If too much phosphate is present in the water, algae and weeds will grow rapidly, and choke the waterway. The net result of the eutrophication is the depletion of oxygen in the water due to the heavy oxygen demand by microorganisms as they decompose the organic material. Little attention has been given to management strategies to minimise the non-point movement of phosphorus in the landscape because of the easier identification and control of point source inputs of phosphorus to surface waters and lack of direct human health risks associated with eutrophication. Phosphates exist in three forms: orthophosphate, meta-phosphate (polyphosphate) and organically bound phosphate (Baeyens *et al*., 1998). Each compound contains phosphorus in a different chemical formula. Ortho forms are produced by natural processes and found in sewage.

Poly forms are used for treating water boilers and in detergents. In water, they change into the ortho form. Organic phosphates are important in nature; their occurrence may result from the breakdown of organic pesticides which contain phosphates. Phosphates are not toxic to man or animals unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphate (USEPA, 1986). Excessive

amount of phosphate actually constitutes pollution usually by infiltration of waste water from domestic and industrial sources or agricultural run-off phosphate derived from detergent, hardness treatment. Phosphorus is often the limiting nutrient for growth of organisms in water, and too much phosphate can lead to rapid eutrophication especially in lakes reservoirs and ponds where other nutrients such as nitrate may be present. Such rapid growth in hot climate where the dissolved oxygen in water is already low can create problem of taste and odour (WHO, 2006).

**j. Biological Oxygen Demand (BOD)**

The BOD test is used to determine the strength of domestic and industrial effluents and expresses the amount of oxygen required to stabilize them if discharged into natural waters with aerobic condition. The test is important in the control of stream pollution, in the regulatory work and in studies designed to evaluate the purification capacity of receiving waters. BOD is a bioassay procedure which measures the oxygen consumed by bacterial while utilizing the organic matter present in waste under conditions as close as possible to nature. Oxygen has a limited solubility in water (9mg/L) at 20□C, so strong wastewater must be diluted to demand levels in keeping with this value. It is important to note that the environmental condition of the test is suitable for living organisms (bacteria), large percentage of the wastes is oxidized within five days and so the test has been developed on the 5-day standard incubation period.

Many studies in Nigeria have reported that municipal refuse may increase heavy metals concentrations in soil and underground water (Carlson, 1976; Alloway, 1996; Amusan *et al.,* 2005; Okoronkwo *et al.,* 2006), which may have negeative effects on the hosts' soils, crops and human health (Smith *et al*., 1996; Nyle and Ray, 1999). Thus, the

environmental impacts of municipal refuse are greatly influenced by their heavy metal contents. Assessment of the species of metals enables one to evaluate the bioavailability and find the suitability of decomposed waste as compost material (Essaku *et al.,* 2005).

According to Onyeka *et al.*(1987), the major cause of land pollution in Onitsha is solid waste. Ademoroti (1993), correlated total heavy metal contents of vegetables and that of the soils and he concluded that the environment where solid waste is being dumped is polluted by heavy metals. According to Etekpo (1999), health hazards associated with improper disposal of waste included harbouring and favouring rodents and breeding of other harmful reptiles.

Heavy metals have been referred to as common pollutants widely distributed in the environment with sources mainly from soils and weathering of rocks (Merian, 1991; O' Neil, 1993). However, levels of these metals in the environment have increased tremendously as a result of human inputs and activities (Awofolu, 2005). According to Oskarson *et al*. (1992), there exists transfer of heavy metals from contaminated soil to plants and from plants to animals with the subsequent transfer through the food chain up to man. It is not uncommon to find ruminants feeding on grasses and birds feed on insects and earthworms on the dumpsite soils. High concentrations of metals in the environment may lead to accumulation, becoming toxic to plants and animals with possible danger to human health.

The role of some heavy metals (Cd and Pb) is very critical in determining the quality of our atmosphere because air, soil and water are directly interacting with each other. Growing heavy metals pollution especially in air has led to an increase in respiratory diseases, infant mortality and also affects the functioning of the blood, liver, kidney and brain. The measurement of Pb, Cd, Cu, Zn and Ni accumulation in soil and plant appears to

be a useful tool for evaluating the potential heavy metal hazards of the environment (Mudassir *et al*., 2005).

In Nigeria, the Federal Environmental Protection Agency (FEPA) (for example Kaduna State Environmental Agency KASEPA) and even local authorities are responsible for planning a defined line of action for the disposal and management of waste generated on daily basis in our society. According to Umaakuka and Mba (1999), refuse dumps have caused traffic delays in some strategic parts of our urban centres which are a sign of poor management. Determining the potency of the wastes and some pollutants' effect on soil and animals, residents' tissues and fluids, underground, etc, through soil analysis will go along way in providing solution to the problem (Uba *et al*., 2009).

## 2.13 Chemistry of Heavy Metals Pollution

Literature survey shows that heavy metals in dumpsites are leached and carried by acidic water downstream. They can be acted upon by bacteria and methylated to yield organic forms such as monomethyl-mercury and dimethyl-cadmium etc. This conversion is caused by bacteria in water in the presence of organic matter, according to the following equation;

$$M + \text{organic matter} \rightarrow CH_3M \text{ and } (CH_3)_2M, \text{ where M is a metal ion.}$$

The following reactions have been identified for mercury

$$Hg^{2+} \rightarrow HgS \rightarrow Hg_2SO_4 \rightarrow CH_3Hg^{+}$$

These organic forms have been reported to be very toxic and adversely affect water qualities by seepage to pollute underground water sources. Low pH values do not need to be established for metals to be released from the dumpsites at adverse concentrations because near neutral pH (pH 6-7) have been established for some metals such as Zn, Cd,

and As (INECR, 2000). Factors such as downstream distances from the dumpsites, colloids loads, pH perturbations and dilution ultimately control the quality of water sources.

The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes. When ingested, in the acid medium of the stomach, they are converted to their stable oxidation states ($Pb^{2+,}$ $Zn^{2+}$, $Cd^{2+}$, $As^{2+}$, $Hg^{2+}$ and $Ag^{+}$ ) and combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds. The equations below show the reactions during bond formation with the sulphydryl groups (-SH) of cysteine and sulphur atoms of methionine ($-SCH_3$) (Ogwuegbu and Ijioma, 2003).

$P\ OR\ E(SH)_2 + M^{2+} \rightarrow P\ or\ E(S)_2M + 2H^{+}$……..….…A

$Por\ E(SCH_3)_2 + 2M^{+} \rightarrow 2(P\ or\ ES\text{-}M\text{-}S) + 4CH_3^{+}$……..….B

A = intramolecular bonding, B = intermolecular bonding P = protein, E = enzymes M = metal. The hydrogen atoms or the metal groups in the above case replaced by the poisoning metal and enzyme is thus inhibited from functioning, whereas the protein-metal compounds act as a substrate and reacts with a metabolic enzyme. In a scheme shown below, enzymes (E) react with substrates (S) in either lock and key pattern or the induced-fit pattern. In both cases, a substrate fits into an enzyme chirality's, to form an enzyme substrate complex (E-S*) as follows (Holum, 1983; Duruibe, 2007):

$$E + S \rightarrow E\text{-}S \rightarrow E\text{-}S^* \rightarrow E\text{-}P \rightarrow E+P$$

E = Enzyme, S = substrate, P = product, * = activated complex

While at the E-S, E-S* and E-P states, an enzyme cannot accommodate any other substrate until it is freed. Sometimes, the enzymes for an entire sequence coexist together in one multi-enzyme complex consisting of three or four enzymes. The products from one

enzyme react with a second enzyme in a chain process with the last enzyme yielding the final product as follows

A →B →C →D →F, the reaction in the presence of enzyme $E_1$, $E_2$, $E_3$ and $E_4$.

The final product goes back to react with the first enzyme thereby inhibiting further reaction since it is not the starting material for the process. Hence, the enzyme $E_1$ becomes incapable of accommodating any other substrate until F leaves, F can only leave if the body utilizes it. If the body cannot utilize the product formed from the heavy metal-protein substrate, there will be a permanent blockage of the enzyme $E_1$, which then cannot initiate any other bioreaction of its kind. Therefore, the metal remains embedded in the tissue, and will result in biodysfunctions of various gravities (Holum, 1983; Duruibe, 2007).

Furthermore, a metal ion in the body's metallo-enzyme can be conveniently replaced by another metal ion of similar size. Thus, $Cd^{2+}$ can replace $Zn^{2+}$, in some dehydrogenating enzymes, leading to cadmium toxicity. In the process of inhibition, the structure of a protein molecule can be mutilated to bio-inactive form, and in that case the enzyme can be completely destroyed. For example toxic $As^{3+}$ occurs in herbicide, fungicides and insecticides, and can attack –SH groups in enzymes to inhibit their bioactivities as shown below (Duruibe, 2007; Ogwuegbu and Ijioma, 2003).

$$E(SH)_2 + As(O)^{2-} \rightarrow E(S)_2AsO^- + 2OH^-$$

The most toxic forms of these metals in their ionic forms are the most stable oxidation states. For example, $Cd^{2+}$, $Pb2^+$, $Hg2^+$, $Ag^+$, and $As^{3+}$ in their most stable oxidation states, they form very stable biotoxic compounds with the body's biomolecules which become difficult to be dissociated, due to their bio-stabilities, during extraction from their body by medical detoxification therapy (Duruibe, 2007).

**2.14 Heavy Metal Fractionation** Heavy metal fractionation is defined as a process of classifying analytes or a group of analytes from a certain sample according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties (Templeton *et al.,* 2000). The process can be based on properties of the chemical species, such as size, solubility, affinity, charge, and hydrophobicity. Soil fractionation studies of heavy metals can provide insight into their solubility and chemical reactivity in terms of labile and non-labile pools of these metals (Che Fauziah *et al.,* 2007).

Scientific literatures have indicated that heavy metals in soils are often present in many forms (Che Fauziah *et al*., 2007) and assessment of the impact of a metal cannot be made based solely on its total concentration. It is also often not possible to determine the concentrations of the different chemical species that sum up to the total concentration of an element in a given matrix (Buffle and Tercier, 1997). This is because chemical species present in a given sample are not stable enough to be determined as such. In the process of the measurement, the partitioning of the metal among its species may be changed either due to change in pH or due to the analytical procedure, or by intrinsic properties of measurement methods that affect the equilibrium between species. The practice has been to identify various classes of species of an element and to determine the sum of its concentrations in each class (Buffle, *et al*., 1997). This is useful and will continue to be because it will give information on the distribution of the different chemical forms of the metals in soils or sludge and can provide insight into their solubility and chemical reactivity (Stumm and Morgan 1981).

In most soil analysis, the total concentrations are usually evaluated (Kapoor and Viraraghavan, 1998; Dantas *et al.*, 2003; Chen *et al.*, 2010) but these do not provide sufficient information about the bioavailability and toxicity of the metals, since changes in

the environmental conditions such as temperature, pH, redox potential or organic ligand concentration cause selective release of the total metal content from the solid to the liquid phase (Sahuquillo *et al.*, 2003). Identifying the chemical forms in which the metals are retained in soil is helpful to predict their potential mobility to water sources, plant availability and the amount of metal cycling through the food chain.

Partial or sequential extraction methods are among the oldest and most commonly used methods of chemical partitioning of environmental solid samples (Ryan *et al.,* 2005). These techniques are easy to apply, inexpensive and require little data analysis. In the past, many schemes have been presented by many workers (Kuo *et al.,* 1983; Shuman, 1985; Ahnstrom and Parker, 1999). However, the original work on sequential extraction performed by Tessier *et al.,* (1979) is one of the most thoroughly researched and widely used method to evaluate trace metals behaviour. In a sequential extraction procedure, the soil sample is treated with a series of progressively harsher reagents to dissolve increasingly refractory forms. Ideally, the reagents are chosen to selectively attack a specific soil compartment with minimal dissolution of non-targeted fractions (Kabala and Singh, 2006). In practice, however, the integrity of the sequential extractions and meaningfulness of the results are questioned because of poor reagent selectivity, possible redistribution or re-adsorption of elements during extraction, or poor extraction efficiency (Gworek and Moce, 2003; Kim and Fergusson, 1991). Despite these limitations, sequential dissolution techniques furnish more useful information on metal binding and mobility than available with single extractions (Han *et al*., 2003).

Several workers such as Ahnstrom and Parker (1999), Kuo *et al.* (1983), Ma and Rao (1997), McLaren and Crawford (1973) and Shuman (1985) proposed and presented sequential extraction schemes. These proposals are usually

improvements upon the original work of Tessier *et al.,* (1979) which was widely accepted as the most thoroughly researched and widely used procedure in evaluating trace metals behaviour in the environment. The improvements usually involved replacing reagents, introducing new extractants, or modifying conditions of the extraction (Burt *et al*., 2003; Keller and Vedy, 1994). For instance, Shrivastava and Banerjee (2004) substituted $MgCl_2$ with $Mg(NO_3)$ in the extraction of exchangeable fractions because the former was found to complex with metals (Shuman, 1985) and increase the solubility of several heavy metals sludge added to soil (Evans *et al.*, 1992). In addition, the extraction of the oxidizable phase was also undertaken after the extraction of the exchangeable phase. This sequence allows the destruction of the organic matter which entraps the mineral materials and then provides a better extraction of the subsequent phases (Shrivastava and Banerjee, 2004). For the residual fraction (Res.), a combination of aqua-regia/hydrofluoric acid ($HCl$-$HNO_3$/HF was adopted instead of the HF-$HClO_4$ (Sanchez *et al*., 1994; Maiz *et al*., 1997).

The selective extraction scheme described by Ma and Rao (1997) is based on six operationally defined fractions (I - VI): Water soluble (I), Exchangeable (II), Acid soluble (III), Reducible (IV), Oxidizable (V) and Residual fractions (VI). According to Harrison (1981), the mobility and bioavailability of metal decreases approximately in the order of the extracting sequence. In other words, the operationally defined extraction sequence follows the order of decreasing solubility of the geochemical forms of the metals. Ma and Rao (1997) concluded that assuming bioavailability is related to solubility, then metal bioavailability decreases in the order: water soluble > exchangeable > carbonate > Fe-Mn oxide > organic > residual. However, this order is just a generalization and offers only qualitative information about metal bioavailability. This further suggested that metals in the non-residual fractions are more bioavailable than metals associated with the residual

fraction. The nonresidual fraction is the sum of all fractions except the residual fraction. Stover *et al*., (1976) stated that the water soluble and the exchangeable fractions may represent the most available forms for plant uptake.

Previous researches on dumpsite soils have shown that the water soluble fraction could be extracted with deionized water, for instance Ma and Rao (1997) extracted 1g of the contaminated soil with 15mL of de-ionized water for 2 hours while Kabala and Singh (2006) extracted 2g of the contaminated soil using 20mL of de-ionized water for one hour at 20$^{o}$C. Shrivastava and Banerjee (2004) reported low concentrations of the heavy metals in extracted fractions. The metals in the residual fraction (bound to silicates and detrital materials) are tightly bound and would not be expected to be released under natural conditions (Xian, 1989). The fractions are not available to biological diagenetic processes except over a very long time scales (Tessier *et al*., 1979). Researchers conclude that due to the strong association between heavy metals and the residual fraction of contaminated soils and sediments the non-residual fraction has been used as an indicator of anthropogenic enrichment (Arakel and Hongjum, 1992; Sutherland and Verloo, 2000).

Previous investigations had indicated that the chemical partitioning trends of the heavy metals were found to be different for each metal (Shrivastava and Banerji, 2004). Mineral and organic soils can bind metals to different extent. Organic matter, Fe and Mn hydrous oxides, and clay content are significant soil properties influencing sorption reactions (Bolan and Duraisamy, 2003). Shrivastava and Banerjee (2004) also reported Cu and Zn to be mostly concentrated in the ratio 1:1 in the non-residual and residual fractions, respectively. The difference in the distribution patterns might be attributed to possible mobilization of the metals. Additionally, soil pH, cation exchange capacity (CEC) and redox potential can also regulate the mobility of metals in soils (Lombi and Gerzabek,

1998).Studies have shown that organic matter and Fe-Mn oxide have a scavenging affect and may provide a sink for Pb (Fytianos *et al.*, 1995; Yu *et al.*, 2001). It has been reported that Zn is commonly found to exist in contaminated soils and sediments mainly in association with Zn and Mn oxides. This was partly attributed to the ability of Zn to substitute for Fe in the structure of oxide minerals (Stumm and Morgan, 1981). Zinc is mainly bound to non-residual fractions (Caplat *et al.*, 2005). Fe-Mn oxides and organic fraction were reported to be the main carriers of Zn for the aquatic environment in Gulf of Aden sediments. This is in agreement with the reported work of Fernandes, (1997).

Earlier researchers have reported that Cd and Cu have high tendency of binding to organic matter in soils (Gale *et al.*, 2002). The predominance of Cu in organic fraction has also been reported to be due to formation of metal – organic complexes (Egila and Nimyeh, 2002). The organic fraction is generally considered not very mobile or available, since it is thought to be associated with high molecular weight stable humic substances, which could release small amount of the metals in a very slow fashion (Egila and Nimyeh, 2002). Other studies on polluted sediments (Pardo *et al.*, 1993; Marin *et al.*, 1997), also concluded that extractable copper is mainly in association with the oxidizable phase, where it is likely to occur as organically complexed metal species. This behaviour can be explained by the well-known high affinity of Cu to humic substances, which are chemically very active in Cu complexion (Pempkowiak *et al.*, 1999; Fytianos and Lourantou, 2004). Rapin *et al.*, (1983) reported that Cu was mostly bound to the organic matter/sulfide fraction in marine sediment in highly polluted area of Villefranche Bay. Copper can easily complex with organic matters because of the high formation constants of organic-Cu compounds (Stumm and Morgan, 1981). In aquatic systems, the distribution of Cu is mainly affected by natural organic matter such as humic materials and amino acids.

The higher association with the residual fraction indicates its low bioavailability (Kotoky *et al.,* 2003). The percentage of metal in the residual fraction cannot be easily released to the environment since the metal is about to crystal lattice. The tendency of copper to be associated with the oxidizable fraction which implies association with organic matter in the sediments has been reported in previous studies (Pardo *et al*., 1990). This is attributed to the great stability of organo-Cu complexes when compared with Pb and Zn (Stumm and Morgan 1981). The presence of cations can affect metal adsorption in soils (Oviasogie and Ndiokwere, 2008). For instance, Ca competes effectively with cationic heavy metals for adsorption and exchange sites, and this competition seemed to be greater for Zn and Cd than for Cu and Pb (KieKens, 1983; Pierangel *et al*., 2003).

## 2.15 Theory of Flame Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) as shown in Plate II is a spectro-analytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples employed in pharmacology, biophysics and toxicology research as shown in Fig. 2.2. Atomic absorption spectrometry was first used as an analytical technique, and the underlying principles were established in the second half of the 19th century by Robert Wilhelm Bunsen and Gustav Robert Kirchhoff, both professors at the University of Heidelberg, Germany (McCarthy and Walsh, 2012).

The modern form of AAS was largely developed during the 1950s by a team of Australian chemists led by Sir Alan Walsh at the CSIRO (Commonwealth Scientific and Industrial Research Organization), Division of Chemical Physics, Melbourne, Australia.

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on the Beer-Lambert law. In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This measures of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using the Beer-lambert law (McCarthy and Walsh, 2012). In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electrothermal (graphite tube) atomizers. The atoms should then be irradiated by optical radiation, and the radiation source could be an element-specific line radiation source or a continuum radiation source.

**Plate II: The schematic diagram of atomic absorption spectrophotometer as retrieved from Wikipedia, 2011**

**Instrumentation**

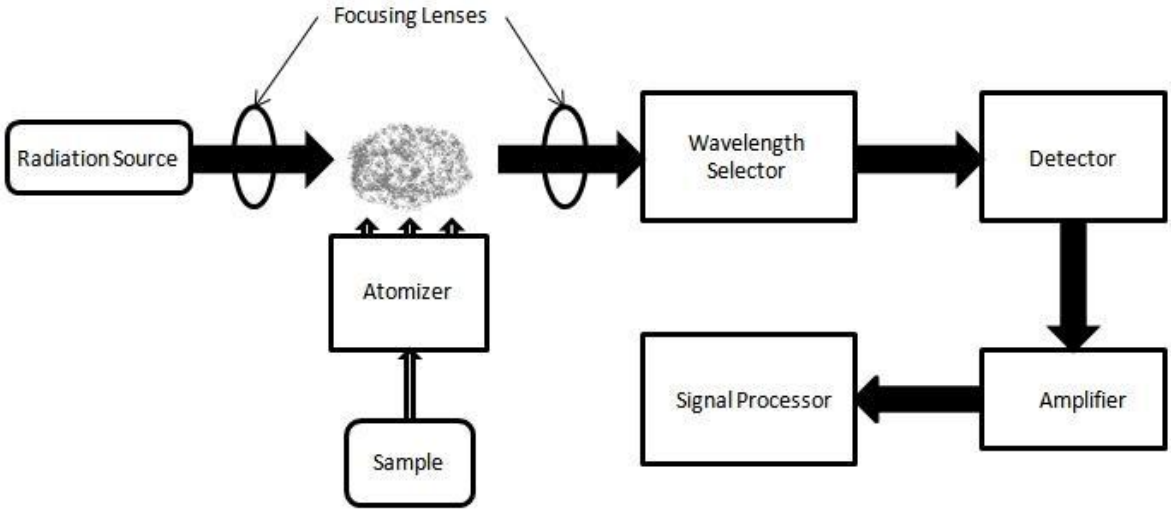


**Figure 2.2: The atomic absorption spectrometer block diagram**

The radiation then passes through a monochromator in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector (McCarthy and Walsh, 2012).

## 2.16 Difficulty in Analysing Mercury with AAS and the Need for Faster and Cheaper Method

The major existing techniques for trace metal analyses are spectroscopic (in particular graphite furnace atomic absorption spectroscopy (GF-AAS), and inductively coupled plasma mass-spectroscopy (ICP-MS) and neutron activation analysis (NAA). Their major drawbacks are their much higher cost and above all the facts that measurements using these techniques are feasible only. Consequently, speciation measurements using these techniques are feasible by coupling them with separation and extraction procedures. However, such steps significantly increase the risk of contaminations or chemical species modifications during sample storage or sample handling and dramatically increase the cost of the analyses (Buffle and Tercier, 2005). This is a major barrier to their applications to routine speciation measurements on large sample sets even though it would be the only means to interpret correctly the environmental impact of metals (Buffle and Tercier, 2005).

Electrochemistry is the study of chemical response of a system to an electrical stimulation. The scientists studying electrochemistry study the loss or gain of electrons that a material undergoes during the electrical stimulation. Voltammetry is the name given to a group of electrochemical techniques where current is studied as a response to potential. These techniques have a broad range and applicability in modern chemistry and provide chemists with information about thermodynamics and kinetics of chemical reactions and they can be used to identify and quantitate different species in solution. In most electrochemical techniques, there are three electrodes –the reference, working and auxiliary

electrodes. One characteristic of voltammetric measurements make them particularly well suited for automatic in situ speciation measurements with no or minimum sample change (Buffle and Tercier, 2005). In a typical electrochemical experiment a potential is applied to the working electrode and the resulting current measured then plotted versus time. In another, the potential is varied and the resulting current plotted versus the applied potential. The different combination of parameters and working electrode types make along list of electrochemical techniques which include; polarography, cyclic voltammetry, linear sweep voltammetry, differential pulse voltammetry, square wave voltammetry, anodic stripping voltammetry etc. Electroanalytical techniques need system like dropping mercury electrode because it has an easily renewable smooth surface and wide potential region of ideal polarizability but interest on it is waning because of high toxicity (Tavo *et al.*, 2008). Bismuth is non-toxic metal and the solid surface has some advantage over liquid interface. It is not sensitive to the mechanical movement and the cleavage of the solid electrode. It is quicker than the mercury drop removal procedure (Tavo *et al.*, 2008). Moreover, the solid bismuth surface can be studied by several modern methods including in-situ STM (Kallip *et al.*, 2005; Kallip *et al.*, 2008) and infrared reflectance spectroscopy (Ramann *et al.*, 2007), more easily than the liquid mercury surface (Romann, 2008). The Bismuth film electrode has attracted increasing attention in anode stripping analysis of Ni, Cu, and Sn (Tavo *et al.*, 2008), adsorptive stripping analysis of Ni, Co, U, and Cr and also of direct cathodic electrochemical detection of organic compounds like 2-nitrophenoland duonomycin (Tavo *et al*., 2008).

The Modern electroanalysis and mainly ESA combined with bismuth electrodes (BiEs) has clocked over a decade since the publication of the first pioneering report (Svancara *et al*., 2010). Since then, the area has experienced a remarkable progress

resulting in a database of nearly two hundreds scientific reports on a wide variety of bismuth–based electrodes (BiBEs), sensors and detectors of various types, configurations or constructions most of them offering a widespread applicability in solving the challenging analytical problems (Svancara *et al*., 2010).

The actual database features practically all typical aspects of present day's electroanalysis: i) Preference of environmentally friendly materials and procedures ii) favourable economic considerations iii) wide adaptability to miniaturized computer controlled instrumentation v) prospective diversity in use and course vi) still attractive electroanalytical performance for the individual measurements. The bismuth electrode has vii) favourable electrochemical characteristics in faradaic and non- faradaic measurements viii) insensitivity to the presence of oxygen ix) excellent mechanical stability in almost all forms in which this metal is being used x) versatility in coupling with an inert electrode substrate and xi) acting as chemical modifier. Bismuth electrodes broaden the scope for electroanalysis in the field as deployable sensors because of their non-toxicity and can be operated in the oxygenated media (Svancara *et al*., 2010). The Wang group in 2000 reported the possible preparation of bismuth-film electrode by external pre-plating with subsequent employment in adsorptive stripping voltammetry (Svancara *et al*., 2010) as shown in Table 2.2.

The application of BiEs to medical samples has included monitoring the release of zinc from pancreatic islets (Meghasi *et al*., 2004) the determination of Co, and Ni in aqueous humour (from human eye) and cerebrospinal fluid (Hutton *et al*., 2006), the analysis of urine (Paulikaite *et al*., 2002), the analysis of blood samples (Cao *et al*., 2008). Great diversity exists in the use of BiEs for the determination of heavy metals in food samples including wine and fruit juice (Vytras *et al*., 2005). Further interesting applications

have been included in the analysis of gunshot residue (Baldo *et al*., 2003), medical formulation (anti-inflammatory drugs) (Rodriguez *et al*., 2004) and Chinese medical products (Svancara *et al*., 2010).

The analysis of various metallurgical samples including iron ore, (Morfobos and Economou, 2004), bronze, phosphate rock samples (Krolicka *et al*., 2006) dolomite (Mandil and Amine, 2009) and the leaching of lead from Moroccan traditional cookware (Svancara *et al*., 2010). The reported limits of detection achieved at the bismuth-based electrodes (Svancara *et al*., 2010) as are summarised in Table 2.3.

**Table 2.2: Electrode configurations of BiEs highlighting the substrate for the bismuth film, its form and additional layers applied with the associated number of example(N) appearing in the literature**

| **Substrate** | | **Form of bismuth** | | **Additional layer** | **N** |
|---|---|---|---|---|---|
| Glassy carbon | 86 | Bismuth film (in situ) | 76 | Nafion | 14 |
| Carbon paste | 19 | Bismuth film (ex situ) | 74 | Other polymer | 5 |
| Screen printed ink | 14 | Bismuth powder | 9 | Nafion composite | 4 |
| Metal (Au,Cu Pt) | 11 | Solid/bulk bismuth | 7 | Nanotube composite | 3 |
| Chip(wafer) | 4 | | | | |
| Boron doped diamond | 3 | | | | |
| Carbon film | 2 | | | | |

***Retrieved fromSvancara et al., 2010, Electroanalysis 2010, 22, N0.13, 1405-1420***

## 2.17 Square Wave Stripping Voltammetry (SWV)

Electrochemical stripping analysis has been widely recognised as a powerful technique for simultaneous measurement of multiple trace metals in various samples. It has some intrinsic advantageous features such as quick analysis speed, high precision and accuracy, relatively portable and inexpensive instrumentations and can be used 'on-site' for biomedical, environmental and industrial applications (Wang *et al*., 2006).

In the striping analysis, the proper choice of the working electrode is crucial for the success of measurement. Traditionally, mercury-based electrodes such as hanging drop mercury electrodes (HDME) are prepared for ESA due to their reproducibility and sensitivity (Wang *et al*., 2006). However, the health implications and safety regulations severely restrict its application due to its toxicity (Wang *et al*., 2006). The 'environmentally friendly' bismuth electrodes display many excellent properties such as low toxicity, ability to form alloys with many metals, wide cathodic potential window, insensitivity to dissolved oxygen, etc (Wang *et al*., 2006).

Essentially, stripping analysis is a two-step technique; the first step involves the electrolytic deposition of a small portion of the metal ions in solution to pre-concentrate the metals (Wang *et al*., 2006). This is followed by dissolution (stripping) of the deposit. Different versions of the stripping analysis can be employed depending on the nature of the deposition measurement steps. The two major forms of the stripping methods are anodic and cathodic (Wang *et al*., 2006).

SWV is a rapid technique in which analysis time can only be few seconds to record a complete voltammogram; this was attributed to fast scan rate. Thus, the SWV is an effective technique to study kinetics parameters of the electrode (Fuge *et al*., 1991). The technique is carried out at a stationary electrode and its waveform consists of many cycles

**Table 2.3: The lowest limit of detection achieved at bismuth-based electrodes as reported by Svancara *et al*., 2010**

| Limit of detection | Analyte Interest | Technique | Reference |
|---|---|---|---|
| $9x10^{-13}M$ | As(III) | SWCSV(30)deposition) | Long *et al*., 2007 |
| $2x10^{-11}M$ | Sb(III) | SWCS (30 deposition) | Zong *et al*., 2009 |
| $2x10^{-11}M$ | Co(II) | DPASV(300s deposition) | Koroliczik *et al*., 2005 |
| $4x10^{-11}M$ | Co(II) | DPASV(180s deposition) | Wang *et al*., 2009 |
| $6x10^{-11}M$ | Co(II) | SWCtSV(120s deposition) | Korolczik *et al.*, 2007 |
| $1x10^{-10}M$ | Pb(II) | SWAdSV(600s deposition) | Torma *et al*., 2009 |
| $1x10^{-10}M$ | Tl(I) | SWASV(600s deposition) | Lee *et al*., 2008 |
| $2x10^{-10}M$ | Cd(II) | DPASV(300s deposition) | Li *et al*., 2009 |
| 3x10-10M | Cr(VI) | SWCtSV(420s deposition) | Lin *et al*., 2005 |
| 3x10-10M | Se(IV) | SWCtSV(30s deposition) | Long *et al*., 2007 |

in which each tread of the stair case scan has superimposed a symmetrical double pulse one of which is in forward direction and another in the reverse direction.

This shows that the background current is supressed because the forward and reverse currents are sampled at the end of each pulse, when the charging current is negligible compared to the faradaic current (Wang *et al*., 2006).

## 2.18 Electrochemical Atomic Force, Scanning and Optical Microscopic Studies of Electrode Surface

The technique was used to study the structural changes that occur at the electrode-electrolyte interface in response to a change in the applied potential or the nature of the surrounding solution. The electrochemical double layer is responsible for controlling processes such as the stability of colloidal particles in electrolyte solutions and in ion partitioning at biological membranes. AFM provides insights into the structural arrangements of the metal substrate, absorbents and interfacial solvents molecules in the electrical double layer. This in turn allows the study of the charge transfer reaction and adsorption processes occurring at the surface of the electrified double layer to be altered. However, this technique is insensitive to chemical identification. For very weakly bound adsorbates, the pressure exerted by the tip as it images the surface has been led in some cases to detachment or surface deformation.

# CHAPTER THREE

## 3.0 MATERIALS AND METHODS

### 3.1 Materials

3.1.1 Study area

Zaria Metropolis is located at latitude $11^0$ 07' N and longitude $07^0$ 42' E and is presently one of the most important cities in Northern Nigeria (Uba *et al*., 2008). It has total area of 300$Km^2$ and constitutes four major settlements, namely, Zaria City, Tudun Wada, Sabon Gari and Samaru covering two local government area: Sabon Gari and Zaria. It has problems of environmental sanitation such as improper disposal of refuse near residential areas resulting in contamination of the underground water via leachates emanating from the dumpsites since most of the wells near the dumpsites were poorly covered or not at all.

It has a tropical continental climate with a pronounced dry season, lasting up to seven months (October - May). During the dry season, a cold period is usually experienced between November and February. This emanates from the influence of the North-easternly winds (the harmattan) which controls the tropical continental air mass coming from the Sahara (Ahmadu Bello University, 2013). This weather prevails over most parts of the country. The North-East (NE) winds are characterized by hazy to dusty conditions and low temperatures, as low as $10^0$C at night. In the afternoon, up to $40^0$C is sometimes recorded. The humidity also drops to less than 15% in December/January (Ahmadu Bello University, 2013).

Zaria experiences a brief period of hot but dry weather in March and April, followed by a progressive incursion of tropical maritime air mass from the Atlantic Ocean which displaces the NE (Harmattan) winds. During this short period, the mean daily maximum temperatures are fairly stable, and range from 38 to $42^0$C (Ahmadu Bello

University, 2013). The rainy season lasts from May to September/October with long-term annual rainfall of 1040mm in about 90 rainy days. The relatively deep tropical ferruginous soils and climate conditions of Zaria are suitable and can sustain a good cover of savanna woodland (Northern Guinea Savanna) with a variety of grasses woody shrubs and short trees (Ahmadu Bello University, 2013).

### 3.1.2 Description of sampling sites

10 huge dumpsites were selected based on their size and volume of wastes deposited in addition to various activities such as tobacco production, residential areas, presence of wells and workshops which constitute the sources of waste deposited. Furthermore, control / uncontaminated site was selected 300m away from Kusfa dumpsite. The selected dumpsites were: Samaru (SA), Alkali Jae (AJ), Babban gwani (BG), Kusfa (KU), Shafi Road (SH), Prince Road (PR), Jeka-da-kwarinka (JK) Dandaji (DD), Nigerian Tobacco Company (NTC), Railway Station (RA), Table 3.1 summarizes the various activities at the dumpsites while Table 3.2 gives the geographical locations of the sampling sites. The map of Zaria metropolis showing the location of the dumpsites investigated in this study is shown in Figure 3.1. The photographs of the dumpsites were also presented in Plates III - XIII.

**Table 3.1: Dumpsites descriptions and their respective abbreviations**

| Dumpsite | Abbreviation | Description |
|---|---|---|
| Railway Station | RA | This dumpsite is located in Sabon Gari L.G. A. Most of the waste deposited at the dumpsites are from household in Sabon Gari and the saw mill giving rise to a big mountain of garbage. |
| Samaru | SA | This dumpsite is located at Samaru, Sabon Gari L.G.A. Dumping at the site is unrestricted |
| Alkali Jae | AJ | This dumpsite is located close to some minor roads. Dumping at the site is restricted to domestic wastes. |
| Prince road | PR | The location of this dumpsite is at Sabon Gari. Tonnes of wastes are deposited on this dumpsite on daily basis., the source is domestic |
| Nigerian Tobacco Company | NTC | This dumpsite is located in Sabon Gari. Tonnes of wastes generated by Nigerian Tobacco Company (NTC) are dumped as well as those from the residential areas. |
| Dandaji | DD | Dandaji dumpsite is located in Tudun Wada, Zaria. Refuse dumps from residential areas are largely the major source of wastes. |
| Shafi | SH | This dumpsite is located in Tudun wada, Zaria. Dumping at this site is unrestricted and domestic and agricultural wastes were the major constituents of the dumpsites |
| Kusfa | KU | The dumpsite was located in Zaria city, Zaria. Wastes generated and collected from various locations are deposited in it on a daily basis. |
| Jeka-da-kwarinka | JK | This dumpsite was located in Sabon Gari, Zaria. Dumping at this site is unrestricted and domestic wastes were the major sources. |
| Babban gwani | BG | This dumpsite is located in zaria city. Dumping at the site is unrestricted and domestic and agricultural wastes were the major sources. |
| Control | CTR | This is located about 100m from Kusfa dumpsite and no dumping activities is taking place. |

**Table 3.2 Coordinates of the sampling points**

| Sampling site Code | Sampling site | GPS Grid Coordinates | |
|---|---|---|---|
| | | Latitude (N) | Longitude (E) |
| DD | Dandaji | $11^0$ 05□ 02.1192 | $07^0$ 44□ 01.2086 |
| KU | Kusfa | $11^0$ 03□ 53.2836 | $07^0$ 43□ 04.8864 |
| AJ | Alkali Jae | $11^0$ 03□ 09.4788 | $07^0$ 42□ 55.4976 |
| BG | Babban Gwani | $11^0$ 04□ 01.6282 | $07^0$ 41□ 42.4896 |
| RA | Railway Station | $11^0$ 07□ 34.3956 | $07^0$ 42□ 56.5416 |
| SA | Samaru | $11^0$ 09□ 46.8540 | $07^0$ 39□ 28.9908 |
| NTC | Nigerian Tobacco Company | $11^0$ 08□ 26.5416 | $07^0$ 44□ 21.0228 |
| PR | Prince Road | $11^0$ 07□ 20.8344 | $07^0$ 44□ 16.8540 |
| JK | Jeka-da-kwarinka | $11^0$ 06□ 59.9760 | $07^0$ 44□ 06.4212 |
| SH | Shafi Road | $11^0$ 05□ 24.0216 | $07^0$ 43□ 21.5724 |
| CTR | Control | $11^0$ 01□ 53.3424 | $07^0$ 39□ 17.5176 |

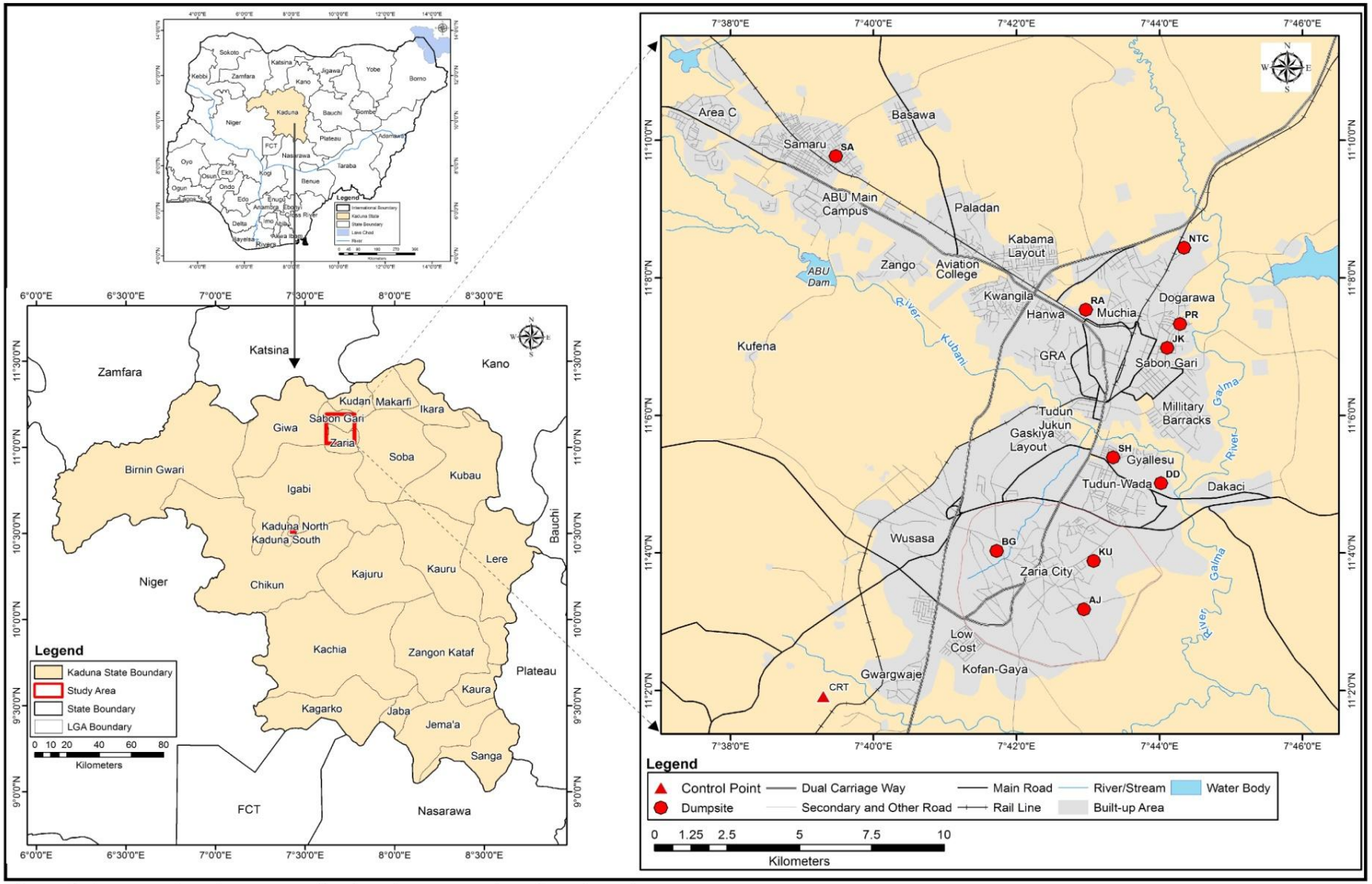


Figure 3.1: Map of Zaria Metropolis showing Dumpsites Sample Points.
Source: Modified from Zaria Topographic map and Field work, 2011.

**Plate III: Railway Station Dumpsite**

**Plate IV**: **Samaru dumpsite**

**Plate V: Alkali Jae Dumpsite**


**Plate VI: Prince Road Dumpsite (PR)**

**Plate VII: NTC Dumpsite**

**Plate VIII: Dandaji Dumpsite (DD)**

**Plate IX: Shafi Road Dumpsite**


**Plate X: Kusfa Dumpsite**

**Plate XI: Babban Gwani Dumpsite**

**Plate XII: Jeka da Kwarinka Dumpsite (JK)**

**Plate XIII: Control site (CTR**

3.1.3 Data and sample collections

The air pollutants, amount of particulate and other field data (temperature and humidity), particulate dust, dumpsite soils, dumpsite leachates, underground water, and samples from human and chicken were collected for the study. With the exception of leachates samples that were collected during wet season, all other samples were collected both in the dry and wet seasons between February and December, 2011.

***a. Gaseous pollutants, particulates and other field data***

The concentrations of the gaseous pollutants (CO, $H_2S$, $SO_2$, $NO_2$, FL, $NH_3$), and particulates were determined on-site using mobile gas sensors manufactured by CROWCON – GASMETER, Model HRD.1000, USA. Humidity and the temperature were determined by TES, 1360 equipment (Temp/Humid/MT), USA.

***b. Particulate dust***

66 samples of dust across the sampling points were collected between February and December, 2011 from the study sites. Dust samples were collected using a plastic brush and tray (Loredo *et al*., 2003; Yeung *et al*., 2003) and were stored in plastic bags (Ayodele and Gaya 1998).

***c. Soil***

The areas used for sampling in each location were divided into four quadrants (Nuonamo *et al.*, 2000). Soil samples were collected from each site with the aid of an auger stainless spoon at 0 – 15cm profile and the samples were placed in polythene bags and labelled.

***d. Blood***

Blood samples (10ml) were collected from the residents in the dry and rainy seasons. The blood samples were dispensed into EDTA–coated tubes to prevent

coagulation and labeled appropriately. Samples were kept frozen prior to digestion (Musa *et al.*, 2011). Plate XIV showed how the blood samples were collected at the sampling points.

***e. Urine***

Urine samples were collected directly into 100ml disposable bottles on first day in the morning. The people sampled were divided into experimental and control groups within the age group of 25-45 years. The experimental group was the residents of dumpsites while the control groups were the residents of the control site. The samples were then taken to the laboratory for analysis (Esimai and Awoleye, 2009)

**f. *Hair and Nails***

Hair and nails samples were collected from subjects within the age group of 25-45 years. Nail samples were collected in polyethylene containers and washed in 1% solution of TritonX-100 in de-ionized water in an ultra-sonic bath. The samples were then air dried and stored in small plastic tubes (Inyengar, 1984). Nails and hair samples were collected using clipper and nail cutter as presented in Plates XVand XVI and described by Kucera *et al*. (1996) and Ayodele *et al.* (2009), respectively.

***g. Leachates***

Leachate samples were collected from the 10 dumpsites and a control site from June to August, 2011 during the wet season from randomly selected leachate drains at the dumpsites. The samples were collected in a well labeled clean polythene bottles that were rinsed with the leachates prior to the sample collection. A total of 33 leachate samples were collected and were used for the physico-chemical parameters, total metal determinations and sequential extraction analyses in polyethylene bottles while those for mercury analysis were collected in glass bottles (APHA, 2005).

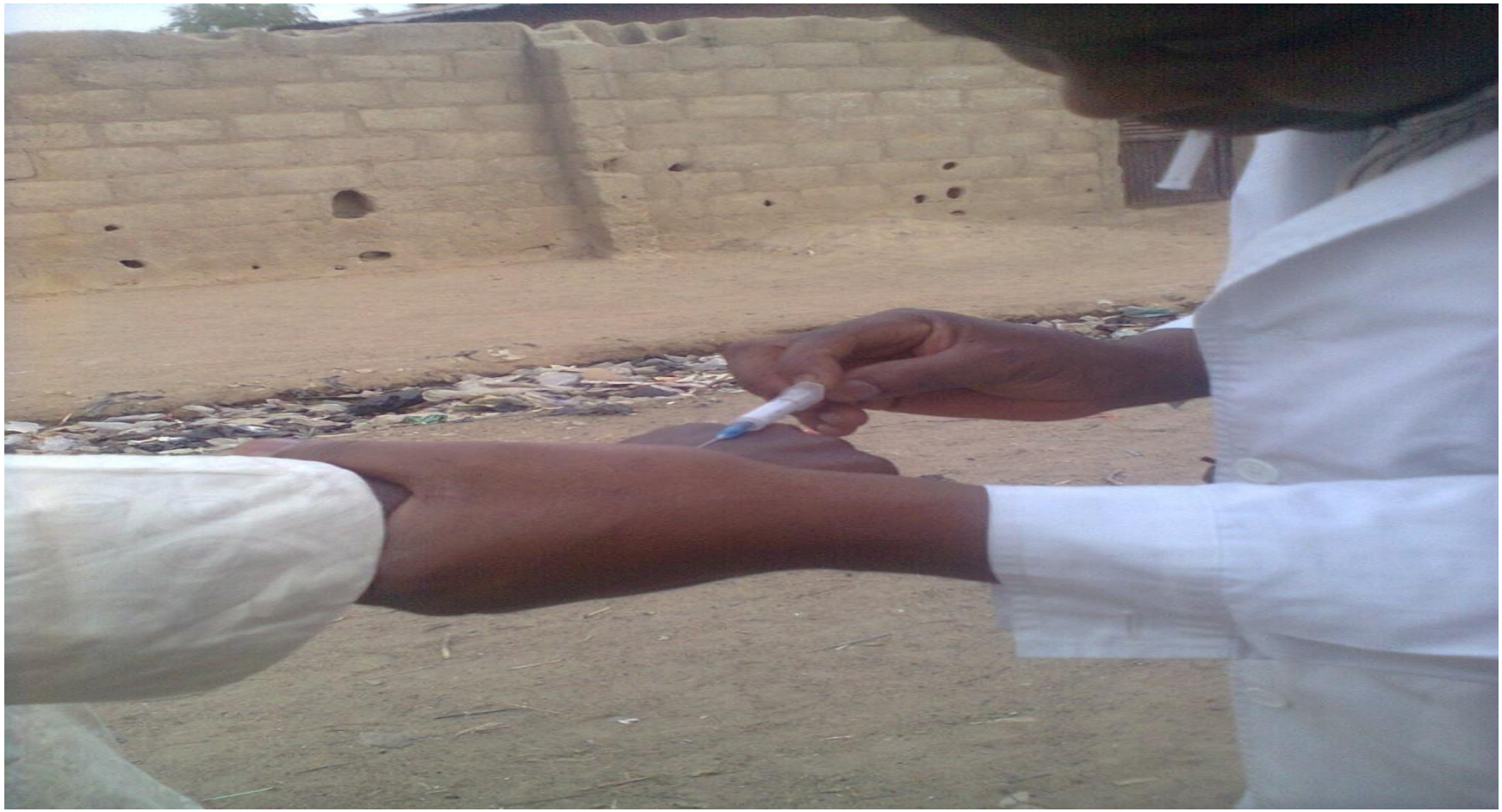

**Plate XIV: Blood Collection from the Resident of One of the Sampling Points**

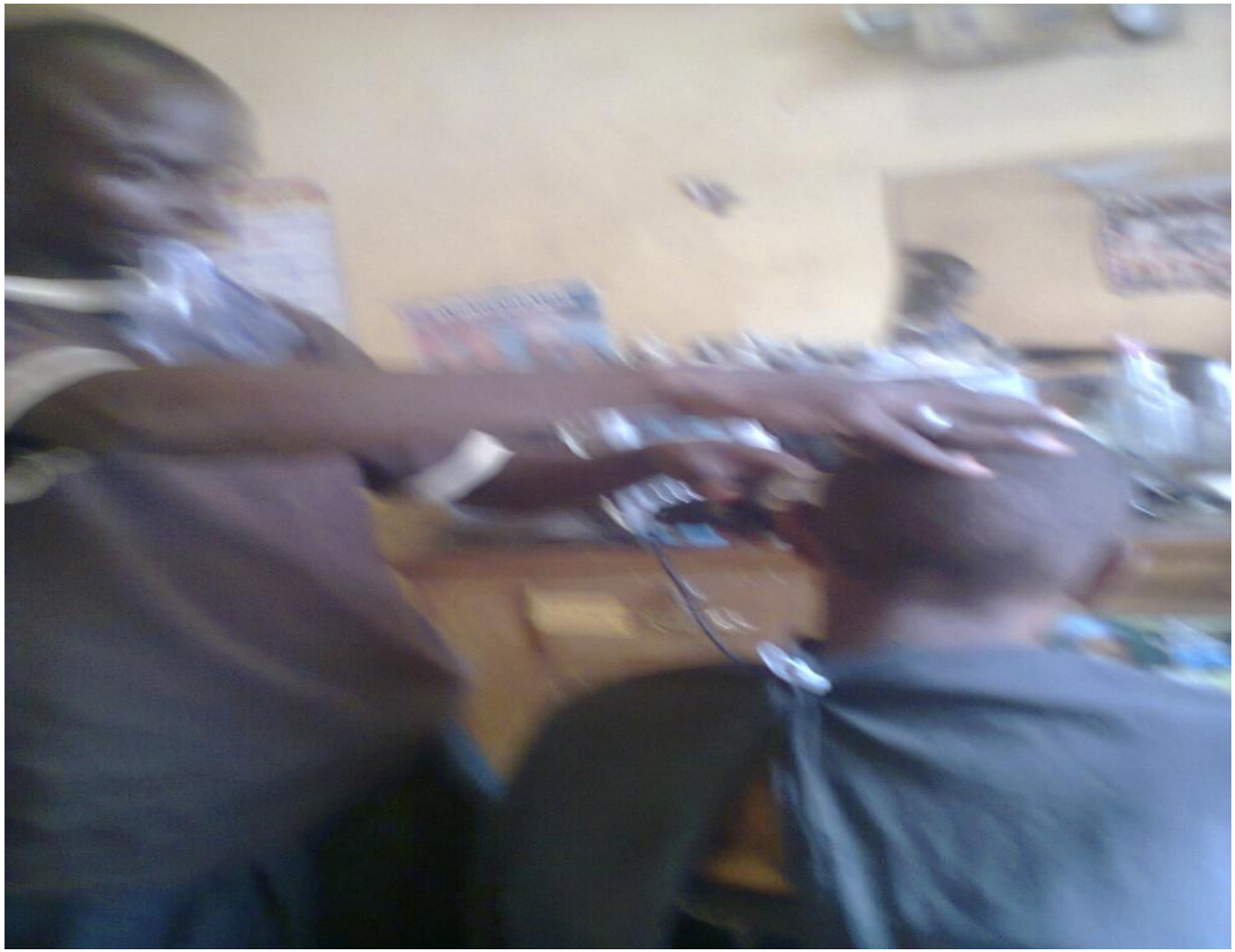

**Plate XV: Hair Samples Collection at from the Resident of One of the Sampling Points**

**Plate XVI: Nail Samples Collection from the Resident of one of the Sampling point**

### *h. Chickens*

Chickens were purchased from the dumpsites residents and fed with the dumpsite wastes and waste water only for a period of three month in each season. They were then slaughtered and their respective oesophagus, lungs, bones, kidney, intestine, head, gizzard, feather, wattles, skin, heart, muscles, legs, liver and brain were removed and analysed for Zn, Pb, Cu, Hg, and Cd contents. Figure 3.2 showed various organs of the chicken sample for toxicity studies.

## 3.2 Methods

### 3.2.1 Sampling method

The sample size is an important feature of any empirical study in which the goal is to make inferences about a sample population. Larger sample size generally leads to increased precision when estimating unknown parameters and Several fundamental facts of mathematical statistics describe this phenomenon (Wikipedia, 2011).

Number of sampling sites was determined statistically from previous reported data (Uba *et al*., 2008). Mean concentration of Pb in soil sample is 48.18mg/kg.

Standard deviation = ± 0.67
Using the formula
$n \geq (ts/d)^2$

Where: t = confidence interval
s = standard deviation
d = Deviation from global mean
n = number of samples
Number of replicates = 3, Degree of freedom= 2;
Hence, t = 2.920 from student t-table.

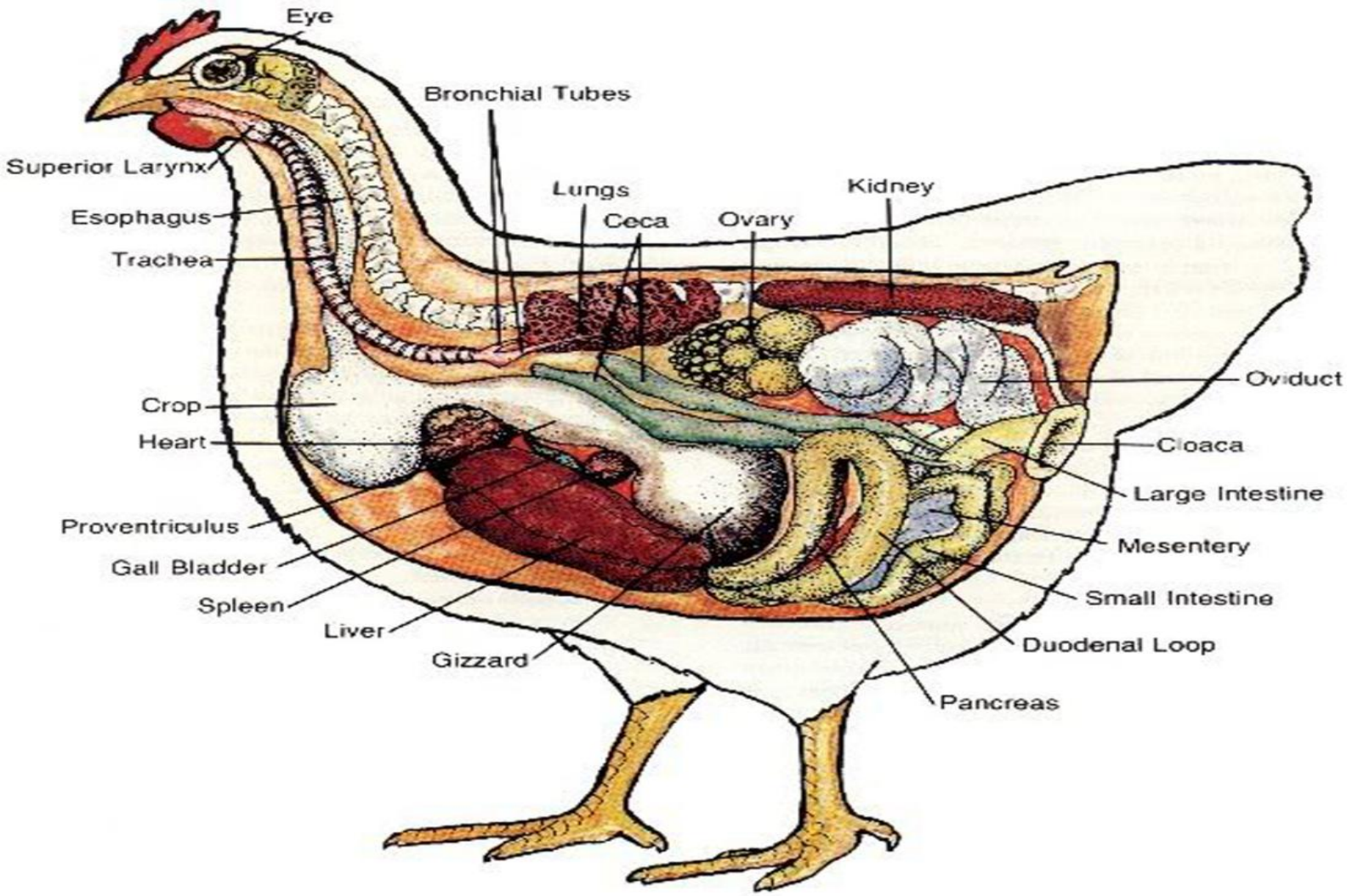


**Figure 3.2: A Chicken Sample Showing the Various Tissues and Organs Analysed,** *Retrieved from Wikipedia, 2011*

Therefore; $n \geq [(2.920 \times 0.53)/0.67)]^2$

$n \geq 10.03 = 10$. This implies that the number of sites used is justified as 10.

The criteria for selection of sampling sites include the following: the presence of households and wells near the dumpsites, and area of population exposure.

### 3.2.2 Refuse characterization (Ikem *et al*., 2002)

To ascertain the percentage compositions of the waste types, 1kg of refuse samples were randomly collected from each dumpsite, then sorted and weighed for refuse characterization.

### 3.2.3 Samples pre –treatment

*a. Soil (Awofolu, 2005)* Soil samples from each site were homogenized and air dried in a circulating air in oven at $30^0$C overnight and then passed through a 2 mm sieve. The sieved soils were placed in polythene bags ready for analyses.Water and leachate samples collected were kept in ice and then transported to the laboratory for the analysis.

*b. Leachates/well water*

Samples for mercury analysis were preserved in 1mL concentrated $H_2SO_4$ and 1mL 5% $K_2Cr_2O_7$ solution for every 100ml samples. The samples for elemental analysis were preserved in 2mL concentrated $HNO_3$ (Aiyesanmi and Imoisi, (2011); APHA, 2005).

*c. Hair and nails*

To eliminate grease and surface contamination the hair and nails samples were rinsed with acetone (Kucera *et al*., 1996) and separately washed in detergent and distilled water (Nowak, 1998; Martin *et al*., 2005) and then kept in an alcohol - ether mixture for 45 mins and dried. The samples were immediately taken to the laboratory and stored in the refrigerator prior to digestion and analysis.

*d. Chicken tissues/organs (Belton, 1998)*

The chickens were slaughtered and various tissues and organs were separated, kept in the polyhene bags and labelled. They were then immediately preserved in a refrigerator prior to digestion.

### 3.2.4 Measurement of physicochemical parameters of waste soil samples

Soil physicochemical properties play a vital role in determining the extent to which the heavy metal pollution of soils occurs. The following were the physicochemical properties measured:

*a. pH (Black, 1965)*

20g of each dried soil samples were weighed seperately into 50ml beaker and 20ml distilled water was added. It was stirred with a glass rod and allowed to stand for 30 minutes. A pre-calibrated HANNA pH meter (Model H1991000) was inserted into the slurry and the pH recorded.

*b. Electrical conductivity (Wilcox, 1950)*

25g each of the air dried soil sample was placed separately into a 250ml beaker. Distilled water was added slowly drop by drop uniformly over the entire soil surface until the soil became wet. A stainless steel spatula was used to form a homogeneous soil

saturated paste. The beaker was then covered with a petri-dish. 50ml distilled water was then added and shaken for 1hour. 40ml of the extract was transferred into 100ml beaker and the conductivity meter electrode was inserted, the electrical conductivities of the soil samples were then recorded in $\mu Scm^{-1}$.

*c. Colour (Black, 1965)*

Refuse waste soil samples were compared to colour standards and suitably graded.

*d. The organic carbon (Black, 1965)*

The organic carbon of soil was determined by wet oxidation, in this method, organic carbon is oxidized by $K_2Cr_2O_7$ in the presence of $H_2SO_4$ leading to the formation of $CO_2$.

$$2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

$$3C + 3O_2 \longrightarrow 3CO_2$$

The soil samples were sieved using a 0.5mm sieve, weighed in duplicate and transferred to a 250ml Erlenmeyer flask. Exactly 10ml of 1M potassium heptaoxodichromate (V1) was pipetted into each flask and swirled gently to dispose the soil followed by adding 20ml concentrated tetraoxosulphate (VI) acid. The flask was swirled gently until soil and reagents were thoroughly mixed. The mixture was then allowed to stand for 30 minuts on a glass plate. 100ml of distilled water was added followed by addition of 3-4drops of ferroin indicator, after which it was titrated with 0.5M ferrous sulphate solution. A blank titration was similarly carried out and the percentage organic carbon was calculated from the equation:

$$\frac{(MeK_2Cr_2O_7 - MeFeSO_4) \times 1.331 \times 100 \times F}{\text{Mass (g) of soil (dried)}}$$

F = Correction factor (1.33)

$M_e$ = Molarity of solution transferred x ml of solution used
%Organic matter in soil = % organic carbon X 1.729.

*e. Particle size distribution (Bouyocos, 1951)*

50g of sieved soil sample was placed in 250ml plastic beaker. 100ml of 50% sodium hematophosphate (calgon) solution was added to the soil mixture and stirred with glass rod. 100ml of distilled water was added to the mixture, stirred and allowed to stand for 30minutes with occasional stirring. It was transferred to a 250ml plastic container and shaken on mechanical shaker for 10minutes and then into 1L measuring cylinder and made up to mark. The temperature readings were taken after 40seconds and 8hours, respectively. A blank consisting of 0% calgon in 100ml of distilled water was made, diluted to 1litre in a measuring cylinder and hydrometer temperature readings taken.

$$\% \text{ clay} = \frac{(\text{corrected 8 hours readings} - \text{blank}) \times 100}{\text{weight of soil sample taken}}$$

$$\%\text{Silt} = \frac{[(\text{corrected 40 sec. readings} - \text{Blank}) \times 100] - \%\text{clay}}{\text{weight of soil sample taken}}$$

% Sand = 100 – (% clay + % silt)
Corrected readings (g/l) = $(R-R_L) + 0.36T$
R = Hydrometer reading of soil suspension
$R_L$ = Blank readings
0.36g/L is added to soil suspension for every reading degree above $20^0$C

*f. Chloride (APHA, 2005)*

10g of soil sample was added to 40ml of distilled water, then stirred with glass rod and allowed to stand overnight. 20ml of the extract was then pipetted into 25ml conical flask and 4 drops of 5% $K_2CrO_4$ indicator was added. The resulting mixture was titrated with 0.01moldm$^{-3}$ $AgNO_3$ using micro-burette to the end–point.

$$mgCl^{-}kg^{-1} = \frac{\text{titre (ml)} \times \text{molarity of } AgNO_3 \times \text{extractant volume}}{\text{weight of sample} \times \text{aliquot volume (ml)}}$$

*g. Sulphate – sulphur ($SO_4^{2}$ - S) (IITA, 1979).*

2.14g of $KH_2PO_4$ was dissolved in 1litre of distilled water to give 500ppm phosphorous solution which was used as the extracting solution. 5g of air dried soil sample was weighed into a 250ml conical flask and 25ml of extracting solution added. It was shaken on mechanical shaker for 30minutes, centrifuged and the supernatant decanted. 0.5434g of anhydrous $K_2SO_4$ was dissolved in 1litre of distilled water in volumetric flask to give 100ppm of $SO_4^{2}$-S stock solution (1ml = 100µgS). 250ml of the stock solution was diluted to 1litre giving intermediate solution (1ml = 25µgS).This was used to prepare working standards of 5, 10, 15, 20 and 25µgS. Absorbances were measured with chroma colorimeter (model 257) and calibration curve of absorbances against concentrations was plotted. Absorbance of the sample solution was measured with the colorimeter along with that of the blank and the concentrations of the $SO_4^{2-}$- S were determined by extrapolation from the calibration curve and calculated as shown in the equation below.

$$mgSO_4^{2-}\text{- S } kg^{-1} = \frac{\text{mg } SO_4^{2-} \text{ from curve x extractant volume}}{\text{weight of sample x aliquot volume (ml)}}$$

*h. Nitrate–Nitrogen (Allen, 1974; Agbenin, 1995)*

150g of KCl was dissolved in distilled water in a beaker and transferred into 1litre volumetric flask and the solution was made up to 1litre to give 2moldm$^{-3}$ KCl solution. 2g of sulphamic acid ($NH_2SO_3H$) was dissolved in 100ml of 2moldm$^{-3}$ KCl solution to act as an extracting agent. 5g of the air - dried soil sample was weighed into a 250ml conical flask and 25ml portion of the extracting agent was added. The flask was shaken for 1hour on a mechanical shaker to make the soil suspension. The suspension was filtered through whatman no. 42 filter paper to give the soil extract. 10ml of the filtrate was

pipetted into a Kjeldahl flask and 0.2g MgO was added. It was digested to drive away $NH_3$ as $NH_3$-N and 1ml of sulphamic acid solution was added to destroy $NO_2$-N. 0.2g of provided Devarda's alloy was added to convert $NO_3$–N to $NH_4$-N. 5ml of boric acid ($H_3BO_3$) indicator was transferred into a 50ml Erlenmeyer flask and 30ml level was marked on the flask which was then placed under the condenser of a steam distillation apparatus. Steam distillation of the filtrate commenced immediately and was stopped when the distillate reached the 30ml level on the Erlenmeyer's flask. The distillate was titrated with standard 0.01moldm$^{-3}$ $H_2SO_4$ from a micro burette until colour changed from green to permanent pink.

1ml 0.01 moldm$^{-3}$ $H_2$ $SO_4$ = 70g/lit $NH_4$- N = 70g /lit $NO_3$ – N = 0.07mg $NO_3$ – N.

$$mgNO_3\text{-}Nkg^{-1} = \frac{\text{mg } NO_3\text{-N (from titre) x extractant volume}}{\text{weight of sample x aliquot of sample}}$$

*i. Nitrite – Nitrogen, $NO_2^-$ – N (Agbenin, 1995)*

10ml of soil extract from above was subjected to the same treatment but without the addition of Sulphamic acid. 0.01Moldm$^{-3}$ $H_2SO_4$ was used for the titration and amount of ($NO_3$ + $NO_2$) – N was obtained. The concentration of $NO_3$–N was subtracted from this amount to get the concentration of the $NO_2$–N for each sample.

*j. Phosphate –Phosphorous, $PO_4^{3-}$ – P (Agbenin, 1995)*

15ml of 1moldm$^3$ $NH_4F$ and 25ml of 0.5moldm$^{-3}$ KCl was mixed with 460ml of distilled water and the mixture stored in a glass bottle to give the extracting solution. 0.2197g of $KH_2PO_4$ was oven dried at 105$^0$C for 1hour, dissolved in distilled water and diluted to 1000ml in a volumetric flask (1ml = 0.05ppm of p). Working standards of 5, 10, 15, 20 and 25µg$PO_4^{3-}$-P, were prepared. Absorbances were read with colorimeter at 690nm

and a calibrations curve of absorbance versus concentration was plotted. 35 ml of the extracted solution was added and then shaken for 1minute, and filtered into dry beaker. Filtration was repeated until filtrate was clear. 10ml of the filtrate was shaken and 0.4ml of ammonium molybdate reagent (Denige's reagent) and 2 drops of stannous chloride were added. Absorbance was measured after 11 minutes for all samples at 690nm and concentrations recorded from the curve and calculated as shown below.

$$mgPO^{3}_{4}\text{–}Pkg^{-1} = \frac{\text{conc. (from curve) x extracting volume}}{\text{aliquot of volume x sample weight}}$$

*k. Cation Exchange Capacity (Black, 1965)*

10g of soil sample was weighed into 100ml plastic beaker, 40ml of 1.0moldm$^{-3}$ ammonium acetate solution (pH 7) was added and the suspension stirred with glass rod and left overnight. The mixture was then filtered with light sunction using 55mm Buchner funnel (coning size No. 40). The residue from filtration was leached with four 25ml portions of 0.25moldm$^{3}$ $NH_4Cl$ solution (pH 7) and one 25ml portion of 0.25 moldm$^{-3}$ $NH_4Cl$ (pH 7). The solution was discarded and electrolyte washed out of the sample with 150 ml ethanol. Sample was allowed to drain completely and leached gradually with acidified NaCl to a volume of 250ml. 50ml of 2% boric acid was measured into 250ml conical flask. The acidified NaCl leachate was poured into 500ml Kjeldahl flask and 10ml of 1.0moldm$^{3}$ NaOH plus anti-bumping granules were added to prevent any explosion. The leachate was distilled over the boric acid and 1.5mol/dm$^{3}$ of $NH_4$ – borate distillate was titrated with standard 0.1 moldm$^{3}$ HCl.

$$CEC\ (Cmolkg^{-1}) = \frac{\text{(titre – blank) x M x100}}{\text{weight of sample (g)}}$$

M = Molarity of ammonium acetate

The blank titre was obtained using same procedure but without the sample and was used as a correction factor.

3.2.5 Measurement of physico-chemical parameters of water

*a. Dissolved oxygen by Winklerazide modification, a titrimetric method (APHA, 2005)*

Standardization was carried out by taking 100 to 150 ml distilled water in an Erlenmeyer flask. 2g KI was dissolved followed by addition of 1ml 6N $H_2SO_4$ and 20ml iodate solution. The solution was diluted to 200ml and the liberated iodine was titrated against thiosulphate titrant to pale straw colour. 2 drops of starch was added and the titration continued to the first appearance of blue colour. The molarity of the thiosulphate was calculated as follows.

$$M = \frac{20 \times 0.0126}{V}$$

Where: V = volume of thiosulphate used
M = molarity of the thiosulphate used

b. Electrical Conductivity (APHA, 2005)

The conductivity cell was rinsed with three portions of 0.01M KCl solution. The resistance of a fourth portion was measured and the temperature was noted. The readings were recorded in µs/cm and the level of the sample aliquots in each case was kept above the vent holes in the cell and no air bubble was allowed in the cell. The cell was rinsed thoroughly after each measurement with double distilled de-ionised water.

When sample conductivity is measured with instruments having temperature compensation, the readout automatically is corrected to $25^0$C. If the instrument does not have internal temperature compensation, conductivity at $25^0$Cis calculated as:

$$\text{Electrical conductivity } (\mu s/cm) = \frac{Cm \times kc}{0.0191(t - 25) + 1}$$

Where:

$K_C$ = the cell constant, 1/cm

$C_m$ = measured conductance of the sample (µS/cm); t = observed temperature of sample ($^O$C). The value of temperature correction (0.0191 x (t - 25) + 1).

*c. Phosphate (APHA, 2005)*

The HI83200 spectrophotometer was used for the analysis of phosphate in the water samples, the reagent used was phenoldisulphonic acid. The sample tube was rinsed with the solution and then filled with 10ml of the sample and then placed in the spectrophotometer. The timer was then pressed with the read altogether, when the timer ends the concentration of the phosphate ($PO_4^{3-}$-P) in the sample and was reecorded in mg/L.

*d. Nitrate (APHA, 2005)*

The HI83200 Bench spectrophotometer (Hanna Instruments) was used in the analysis of nitrate, the reagent used was phenoldisulphonic acid. The sample tube was rinsed with the solution and then filled with 10ml of the sample, placed in the spectrophotometer and shaken vigorously for exactly 10 seconds. Mixing was done while taking care not to induce air bubbles so that powder will not dissolve, the time and way of shaking could sensitively affect the measurements. The timer and read were pressed, when the timer, the instrument displays the results in mg/L of nitrate.

*e. Sulphate (Ademoroti, 1996)*

Sulphate in water samples was determined using Turbidimetric method: 100ml of sample was measured and transferred quantitatively into 250ml Erlenmeyer flask. 5ml of conditioning reagent was then added and the mixture was thoroughly mixed using a magnetic stirrer. The absorbance was measured and the corresponding $SO_4^{2-}$ concentration determined by extrapolation from the calibration curve.

*f. Total suspended solids (AWWA, WEF, 2000)*

A glass fibre filter paper was inserted into the funnel assembled and clip together using a slightly sunction then washed with 100ml of distilled water, after it is free from excess water. The paper was removed carefully and then placed on a watch glass, heated in an oven at $105^0$C for 1hour, cooled in a desiccator and weighed. The funnel was then placed in an assemble form with the filter paper. 100ml of well mixed sample was measured and filtered under slightly sunction and ensuring that all solids are transferred to the paper, the residues were washed three times with 5ml of distilled water after each filtration. The paper was carefully removed and then placed on a watch glass and dried in an oven at 105□C for 1 hour and then allowed to cool in a desiccator and the paper was weighed. The difference in the final weighed of the filter paper with the initial weighed gives the total suspended solid. *g. Total Hardness (AWWA, WEF, 2000)*

25ml of the sample was diluted to 50ml with distilled water, 2 ml buffer solution was added to give a pH of 10.0 to 10.1. 10ml sample solution was then titrated with EDTA using 2 drops of the indicator (bromothyol) solution, the colour change from reddish tinge to blue.

$$\text{Total Hardness (EDTA), mg/L } CaCO_3 = \frac{A \times B \times 1000}{\text{mL of sample}}$$

Where:

A = mL EDTA titrated for sample

B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant

### 3.2.6 Total metal determinations of soil samples (Awofolu, 2005)

5.0g of the soils were weighed into 100ml beaker and 10ml concentrated nitric acid were added. The mixture in the beaker was covered with a watch glass and refluxed for 45 minutes. The watch glass was removed and the contents were evaporated to dryness. 5ml aqua-regia was added and the mixture was again evaporated to dryness after which 10ml 1M nitric acid added and the suspension filtered. The filtrate was then diluted to volume with distilled water in a 50ml volumetric flask. Triplicate digestions of each sample together with blank were carried out.

### 3.2.7 Total metal determinations of water and leachate samples (APHA, 2005)

50ml of water sample was placed in a beaker, 3ml of concentrated $HNO_3$ was added and covered with a watch glass. The beaker was then placed on a hot plate and cautiously evaporated to less than 5ml. The digest was then allowed to cool and the wall of the flask was rinsed with de-ionised water. 5ml of conc $HNO_3$ was added again to the digest and then place on a hot plate. The temperature was raised to allow a reflux to occur which was noticed when the digest was light in colour. 5ml of HCL was then added based on anticipated final volume of 50ml.The solution was then heated for additional 15min to dissolve any precipitate or residue. The digest was then cooled, filtered and made up to 50ml with distilled water

3.2.8 Total metal determinations of chickens' samples (Belton, 1998)

2.0g of each sample (oesophagus, lungs, bones, kidney, intestine, head, gizzard, feather, wattles, skin, heart, muscles, legs, liver and brain) was weighed into a beaker and then pre-digested with 10ml concentrated $HNO_3$ on a hot plate at $135^0$C until liquor was clear. Then 10ml of $HNO_3$, 1ml concentrated $HClO_4$ and 2ml $H_2O_2$ were added and heated on a hot plate still maintaining the temperature of $135^0$C for 1hour until the liquor became colourless. The digests were filtered into 25ml standard flask and diluted to mark with 1M $HNO_3$.

3.2.9 Total metal determinations in human urine (Esimai and Awoleye, 2009)

To the 100ml of the urine sample 1% $HNO_3$v/v was added then the samples were taken to the laboratory for analysis.

3.2.10 Total metal determinations in human blood samples (Babalola *et al.,* 2010)

10ml of the blood sample was measured and placed in a tube followed by addition of 1ml concentrated nitric acid containing 0.1% Triton X100 and then the solution was thoroughly mixed. The test tubes were plugged with cotton wool and left on the bench overnight. The mixture was then heated in a water bath at $100^0$C for 20 min and allowed to cool. The digested blood samples were transferred to a measuring cylinder and the volume made up to 25ml with distilled water.

3.2.11 Total metal determinations in hair and nails (Ayodele *et al.,* 2009)

1.0 g of each sample was digested in 10 $cm^3$ concentrated $HNO_3$ and the resulting solution was evaporated to dryness and redissolved in 0.1 M nitric acid. The solution was

then filtered with whatman No. 42 filter paper and made up to 25ml. Metal concentrations were determined by flame atomic absorption spectrophotometer attached to IBM computer (Varian AA650FS) the digestions were repeated in triplicate for each sample.

3.2.12 Chemical fractionation of heavy metals in soil samples

Chemical speciation of heavy metals was carried out on the waste soil samples collected from the dumpsites according to the method described by Finzgar *et al.*(2007). This modified method fractionates heavy metals into six geochemical fractions. The extractions were carried out with initial mass of 1.0g air dried waste soil samples in polypropylene centrifuge tubes of 50ml capacity. However, $Mg(NO_3)_2$ was used instead of $MgCl_2$ to avoid an increase in the solubility of heavy metals within the soil solution matrix (Shuman, 1985):

The extractions of soil samples were carried out on three sub- samples as follows:

1. Water Soluble Fraction: 1 g of the air dried soil sample (2mm sieve) was mixed with 10ml of de-ionized water with continuous agitation for 1hr, the mixture was centrifuged and the supernatant decanted and made up to 50ml with de-ionized water prior to analysis.

2. Exchangeable phase: Residue from step 1 was shaken at room temperature with 16ml of 1M $Mg(NO_3)_2$ at pH 7.0 for 1hr, the mixture was then centrifuged and supernatant filtered and made up to 50ml with distilled de–ionized water.

3. Oxidisible phase (bound to organic matter): Residue from 2 + 10ml $H_2O_2$ 8.8M + 6 ml $HNO_3$ 0.02 M, were shaken for 5hr + 1hr at $98^0$C. Then 10ml of 3.5M $CH_3COONH_4$ was added as an extracting agent, then the mixture was centrifuged and supernatant filtered made up to 50ml with distilled water prior to analysis.

4. Acid soluble phase (bound to carbonates): 25 ml of 0.05M $Na_2EDTA$ was added to the residue from 3, shaken for 6hrs and the mixture was centrifuged and the supernatant was filtered and made up to 50 ml with distilled water prior to analysis.

5. Reducible phase (bound to Fe-Mn Oxides): Residue from 4 + 17.5ml of 0.1M $NH_2OH.HCl$ + 17.5ml of 3.5M $CH_3COONH_4$ was shaken for 1hr, the mixture centrifuged, the supernatant filtered and made up to 50ml with distilled water prior to analysis.

6. Residual phase (bound to silicates and detrital materials): Residue from 5 was digested by using HCl – $HNO_3$/HF (0.35:12$^{w}/_{V}$ soil solution ratio) in acid digestion in Teflon Cup. It was then ashed - dried for 2hrs and evaporated to dryness. The residue was diluted to 50ml with distilled de-ionized water prior to analysis.

After each successive extraction, the sample was centrifuged at 3000 rpm for 15 minutes. The supernatant was removed with pipette and filtered with whatman No.42 filter paper. The residue in each case was washed with distilled de-ionized water followed by vigorous hand shaking and then 15mins centrifugation before the next extraction (Shuman, 1985).

3.2.14 Chemical fractionation of heavy metals in water and leachates samples (Backstrom *et al.*, 2003).

**Fraction I (Dissolved):** 50ml of the water/leachate samples were decanted from the sample vessel and filtered through 0.50µm Teflon filters before acidification with 5ml of 2% $HNO_3$

**Fraction II (Mobile):** 50ml of the water/leachate sample was decanted from the sample vessel and acidified with 5ml of 2% $HNO_3$ followed by filtration through 0.5µm Teflon filters after 24hr

**Fraction III (Total):** 5ml of 2%$HNO_3$ was added directly into the sample vessel and shaken rigorously to ensure the suspension of all particulate matter. The solution was then filtered after 24hr through 0.5µm Teflon filters.

**Fraction IV (Particulate):** The particulate concentration was calculated as the difference between Fractions III and I.

3.2.15 Chemical analysis of metal-ions

The metal ions in the digests of soils, leachates, chickens, dumpsites residents' blood, urine, hair and well water samples were determined using atomic absorption spectrophotometer (varian model AA650FS) at Multi-user Science Research Laboratory, Ahmadu Bello University. The operating conditions of the AAS machine are given in Table 3.3.

3.2.16 Gaseous pollutants and other field data

The concentrations of the gaseous pollutants (CO, $H_2S$, $SO_2$, $NO_2$, FL, $NH_3$) and particulates were determined using mobile gas sensors manufactured by CROWCON – GASMETER, Model HRD 1000. Humidity and the temperature were determined by TES, 1360 equipment (Temp/Humid/MT). The pieces of equipments were sourced from Kaduna State Environmental Protection Agency (KEPA), Nigeria

3.2.17 Quality assurance protocol All reagents used were of analytical grade, distilled de-ionized water was used. All the glasswares and polythene sample bottles were washed with liquid soap, rinsed with water, soaked in 10% $HNO_3$ for 24hrs and then rinsed thoroughly with distilled de-ionized

**Table 3.3: The operating conditions for AAS Analysis for some heavy metals**

| Element | Lamp current (mA) | Wavelength (nm) | Slit width (mm) | Gas Mixture ($2300^0$C) | Flow rate(L/min) | Burner height (mm) |
|---|---|---|---|---|---|---|
| Cd | 3 | 324.8 | 3 | nitrous-acetylene | 2.3 | 4 |
| Cu | 4 | 228.8 | 4 | nitrous-acetylene | 4 | 4 |
| Hg | | | 2 | nitrous-acetylene | 2.6 | 4 |
| Pb | 5 | 283.3 | 7 | nitrous-acetylene | 1.5 | 5 |
| Zn | 3 | 213.9 | 5 | nitrous-acetylene | 2.4 | 4 |

water and dried (Todorovi *et al*., 2001). The analytical results obtained were validated with spiked samples.

*a. Preparation of multi-element standard solution (MESS)*

0.2740g of $Cd(NO_3)_2.4H_2O$ was weighed out and then transferred in a 100ml beaker followed by the addition of 5ml de-ionized water for dissolution. This solution was then transferred to 500ml volumetric flask. Similarly, 0.07606g of $Cu(NO_3)_2.3H_2O$ was weighed out, dissolved in 2ml water in a beaker and then transferred into the same flask, the beaker was then rinsed thoroughly with water into the flask. Furthermore, 0.1556g of ZnO was also weighed and dissolved in 2ml concentrated $HNO_3$ in a beaker and transferred into the same 500ml volumetric flask. In addition, 0.0040g $Pb(NO_3)_2$, was weighed out and dissolved in 2ml $HNO_3$ in a beaker, water was then added and transferred into the same flask. 0.0068g $HgCl_2$ in 5ml was also weighed and 2ml concentrated $HNO_3$ was added in the same beaker, water was then added to the beaker and then the solution was transferred into the same 500ml volumetric flask. The flask was made up to the mark with distilled water to give 5, 250, 200, 10 and 40mg/L solutions of lead, zinc, cadmium, mercury and copper ions, respectively.

*b. Spiking experiment*

20ml of the Multi element standard solution (MESS) was drawn with graduated pipette and used to spike 2g, 100ml, 1.0ml, 1.0g, 1.0g and 5g of chicken, urine, blood, hair, nails and soil samples, respectively. These were then digested as described in the procedures above for the samples in triplicates together with their blanks and then run on AAS. Concentrations of the metals in spiked and unspiked samples were used to calculate the percentage recoveries in order to validate the method as follows:

Amount of metal used to spike a sample

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

1000

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

Amount of metal in unspiked sample

= Vol. of digest of unspiked sample x conc. of metal in digest of unspiked sample
1000

= $Y_0$mg of metal in Zg of unspiked sample

Amount of metal in spiked sample

= Volume of digest of spiked sample x conc. of metal in digest of spiked sample
1000

= $Y_1$mg of metal in Zg of sample spiked.

Estimate of amount of metal used to spike a sample

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

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

% Recovery of metal = Amount of metal used to spike a sample determined x 100
Amount of metal used to spike a sample calculated

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

3.2.18 Preparation of stock solution

I. Cadmium: Solution was prepared by dissolving 0.274g $Cd(NO_3)_2.4H_2O$ in 5ml concentrated $HNO_3$. The solution was made up to 1litre with distilled deionized water in a volumetric flask giving 1000mg$L^{-1}$ Cadmium solution.

II. Copper solution: This was prepared by dissolving 3.8031g of $Cu(NO_3)_2.3H_20$ in 5ml concentrated $HNO_3$ and making up to 1litre with distilled deionized water giving 1000mg$L^{-1}$ copper solution.

III. Lead solution: This was prepared by dissolving 1.5985g $Pb(NO_3)_2$ in distilled deionized water and making up to 1litre giving 1000mg$L^{-1}$ Lead solution.

IV. Zinc solution: This was prepared by dissolving 1.2444g of ZnO in 5ml of water adding 25ml concentrated $HNO_3$ and making up to 1litre with distilled deionized water giving 1000mg$L^{-1}$ Zinc solution.

V. Mercury: Solution was prepared by dissolving 0.068g $HgCl_2$ in5ml concentrated $HNO_3$. The solution was made up to 500ml with distilled water in a volumetric flask giving 100mg$L^{-1}$ mercury solution.

*a. Calibration curve*

A calibration of absorbance against concentration for each metal ion was prepared by serial dilution of stock solution of the metal ion as shown in appendices LXII to LXVI for Zn, Pb, Cu, Cd and Hg respectively which yielded a good linearity. This implies that the instrument responded very well to the standard analyte of interest and thus, would respond to the analyte in the sample. The calibration curves were used for the determination of metal concentrations in samples.

3.2.19 Electro-analytical determinations of metal ions

*a. Reagents*

All the chemical reagents used for the calibration plots and design of the electrode were of analytical grades (AnalaR) from sigma Aldrich chemicals (Gellingham, UK). The electro-analytical measurements were made in 100mM $NaNO_3$(saturated) supporting electrolyte and a milli- (Q) plus filter Nano pure water made from RO, model

D11931 (Barnstead International, Dubuque, IOWA, USA) ion exchanger and a nominal resistivity of 18.2MΏcm was used for the preparations of the reagents.

*b. Preparation of bismuth electrodes*

Bismuth powder of particle size 150μm (high purity > 99.99%) was used as the electrode material. The preparation of the electrode was made by filling a sealed capillary with bismuth powder to about 3cm with the help of injection syringe, a copper wire of diameter 1.13mm and a length of 11cm was inserted into the glass capillary of 13cm long for electrical contact. The bismuth powder was then heated under vacuum and then cooled to room temperature. The electrode disc was exposed with the help of the electrical grinder at the Glass Blowing Unit of the School of Chemistry, Newcastle University, Newcastle Upon Tyne and Wear, United Kingdom. The whole process is summarised in Fig. 3.3.

*c. Electrode polishing*

Mechanical and electrochemical cleaning processes were used to polish Bi electrodes while only electrochemical process was used to clean the reference electrode. Fine grade alumina with particle size 0.1 to 0.05μm was used. The slurried alumina was prepared in de-ionized water and spread on the smooth plastic glass plate to form a paste. The electrode was polished many times by circular motion and was eventually cleaned primarily by rinsing with de-ionized water followed by propan-2-ol before finally dipped into de-ionized water for 3minutes and dried by nitrogen.

The electrode was assessed by recording the voltammograms of the supporting electrolyte ($NaNO_3$) until repeatable voltammograms were exhibited after about 4cycles and very low background current (Mahmud, 2013). The electrochemical method adopted for the pre-treatment of the electrode surfaces was - 0.2 to 1.5V vs Ag/AgCl in 0.1M $H_2SO_4$

so as to oxidize the contaminants formed on the electrode surface such as metal oxides or adsorbed species. The electrode was removed and immersed in de-ionized

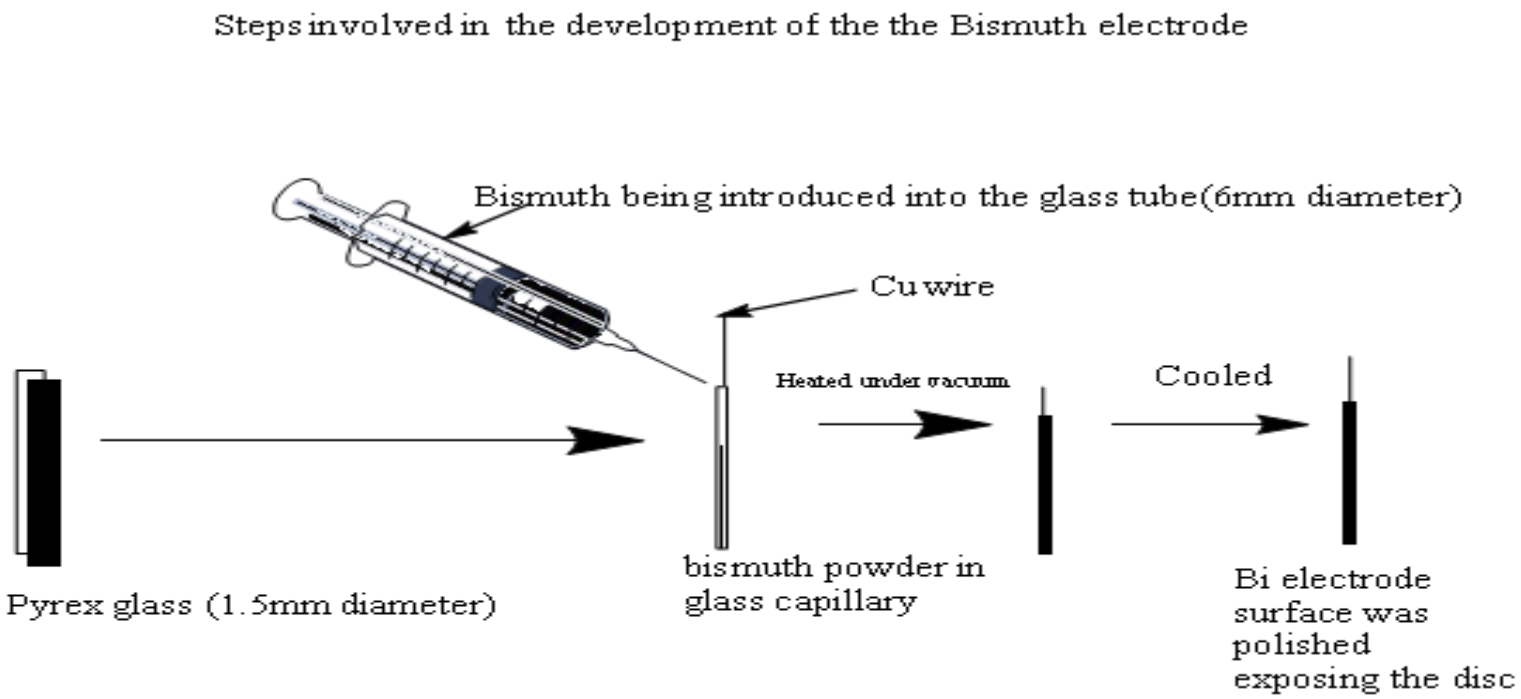


**Fig. 3.3 The steps involved in the development of bismuth powder-based electrode**

water for 3 minutes. This was dried by blowing with nitrogen gas and the electrode was assessed by recording the voltammograms of 0.1M $H_2SO_4$ (Mahmud, 2013).

*d. Preparation of standard metal ions for calibration plots*

The stock solutions (1mM) of the metal ions (Pb, Cu, Cd, Hg and Zn) were prepared by dissolving 0.03315, 0.0241, 0.03085, 0.03426 and 0.29749g of $Pb(NO_3)_2$, $Cu(NO_3)_2.3H_2O$, $Cd(NO_3)_2.4H_2O$, $Hg(NO_3)_2.H_2O$ and $Zn(NO_3)_2.6H_2O$ in 1liter of supporting electrolyte (100mM saturated $NaNO_3$) which were then used to prepare the lower concentrations of the metal ions (0.2, 0.4, 0.6, and 1.0µM) by serial dilution of the stock solutions. 100mM of $NaNO_3$ is formed by dissolving 8.5g of $NaNO_3$ in 1liter of de-ionized water. The peak currents of the standard solutions were measured by the square wave voltammetry and used for the calibration plots after being purged in nitrogen for at least 8 minutes.

*e. Instruments and measurements*

The potentiostat with the model number CHI700B was used for the square wave voltammetric measurements. A three electrode system (shown in Fig. 3.4) comprising of bismuth working electrode, platinum as a counter electrode and Ag/AgCl as reference electrode (using saturated $NaNO_3$ as supporting electrolyte) was used for the electrochemical processes with a magnetic stirrer for stirring the solution to keep the solution homogeneous throughout the deposition and cleaning steps. All the measurements were carried out in triplicate at room temperature.

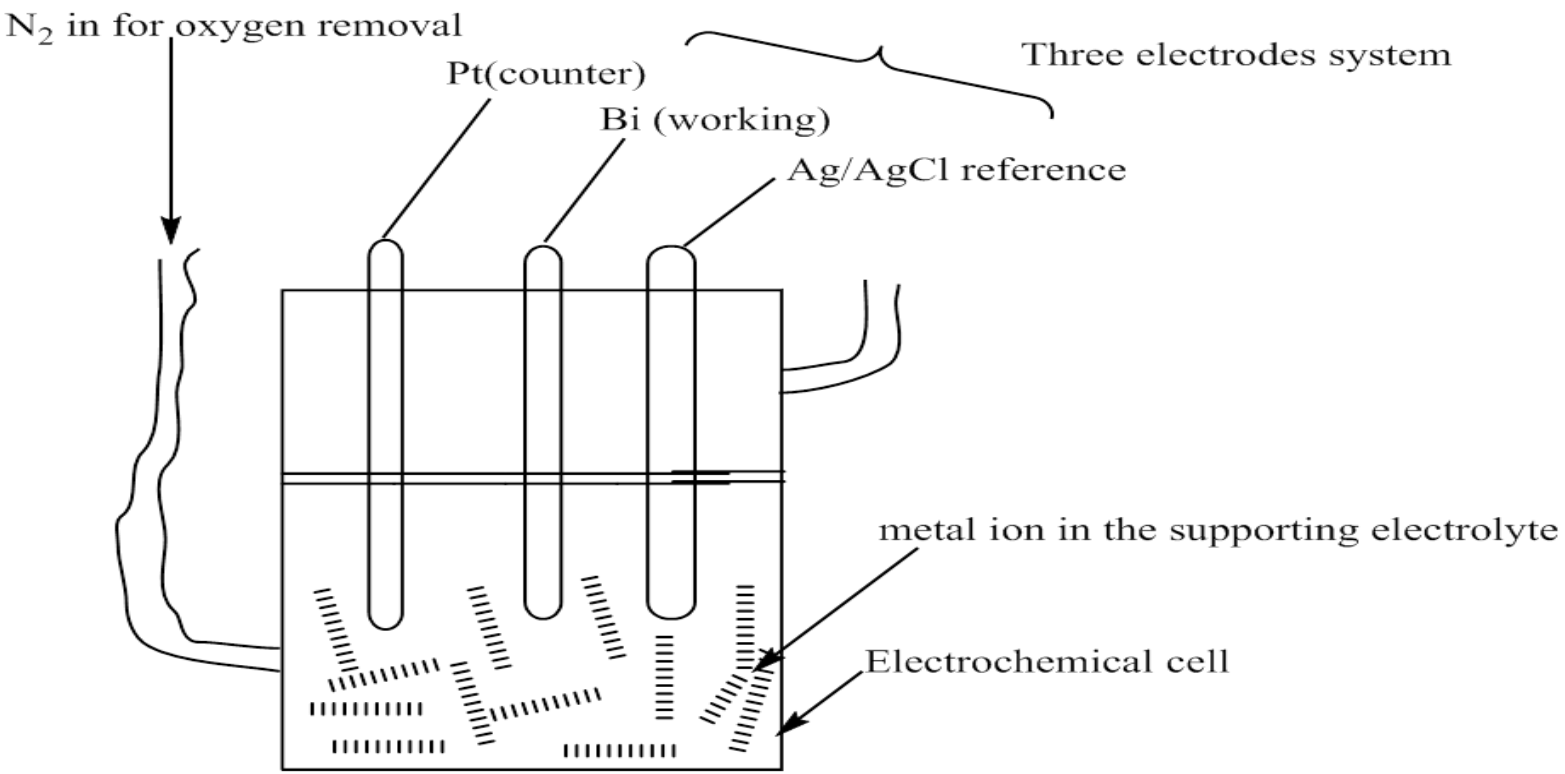


**Fig. 3.4: Schematic diagram of the three electrode cell used for the electrochmical analysis**

*f. Characterisation of the peak due to reduction of hydrogen ions*

In order to characterize the peak due to hydrogen ion reduction, 10ml of the supporting electrolyte and 10ml of 0.015M NaOH solution was used in the electrochemical cell using Bi, Pt and Ag/AgCl as working, counter and reference electrodes, respectively. The scan parameters used were similar to those used in section c above and the concentrations of the metal ions were determined from the calibration plots (Mahmud, 2013). The characterization was aimed at identifying peaks due to hydrogen ion reduction only so as to distinguish them from those of other metal ions.The microscopic studies were carried out using 1cm piece of the treated and fresh electrode (untreated) to study the effect of the supporting electrolyte on the electrode surface.

*g. Electrochemical atomic, tunneling and optical microscopic studies of bismuth elrctode surface*

5mm of the bismuth electrode was studied using atomic force, optical and electron microscopes before and after the electrode was treated with the supporting electrolyte for surface modification.

*h. Spectroscopic analysis by inductively coupled plasma optical emission spectorometry (ICP-OES)*

RF- power was 1kW, coolant flow (13L/min), nebuliser pressure was 42psi, auxiliary flow was 0.4Lmin and the sample uptake was 1.3L/min. The nebuliser was a standard v-groove PFA micro flow (produces a fine aerosol). The standard solution of each of the metal ions was made in glass volumetric flask using de-ionised water (18.2Ω/cm). The Shilbottle mine water samples collected from the abandoned mine site, Newcastle, United Kingdom were filtered through 0.1μm Millipore and the samples were injected into the 701 ICP-OES (unicam instruments Cambridge, England), quartz aqueous torch with

glassy spray chamber the equipment with flow rate 1.3ml/min and the concentration of the elements Cu, Cd, Pb, Hg, and Zn were determined.

*i. Quality assurance for square wave voltammetry (SWV)* The SWV measurement showed good recoveries of all except zinc metal ion which was having percentage recovery of < 23%. A blank sample which was simply a de-ionized water was used as a correction factor, the true concentration of the samples were taken as the difference between the measured concentrations of the samples to those of the blanks for each metal.

3.2.20 Statistical analysis To test the impact of leachates emanating from the waste soils on groundwater quality, the impact of municipal dumpsites on residents, and the effect of dumpsites on air quality, statistical package for social sciences (SPSS) was used. In addition, the Microsoft Excel spread sheet was used for plotting the charts. The results were analyzed using Pearson's correlation coefficient r, where r is dimensionless index that ranged from -1.0 to + 1.0 inclusive and shows the degree of linear relationship between two sets of data, {X} and {Y} (Uzairu, 2006). If there is perfect linear relationship with positive slope between the two variables we have a correlation coefficient of 1. If there is positive correlation whenever one variable has a high (low) value, so does the other .If there is a perfect linear relationship with negative slope between the two variables, a correlation coefficient of -1. If there is negative correlation wherever one variable has a high (low) value, the other has a low (high) value. A correlation coefficient of 0 means that there is no linear relationship between the variables under consideration.

ANOVA is an analysis of variation present in an experiment. It is a test of the hypothesis that the variation in an experiment is no greater than that due to normal variation of individual's characteristics and error in their measurement. The tests in an ANOVA are based on F- ratio. ANOVA puts all the data into one number (F) and gives one *P*- for the null hypothesis.

# CHAPTER FOUR

## 4.0 RESULTS

### 4.1 Quality Assurance

The percentage recoveries of Pb, Cu, Cd, Zn and Hg for the sequential extraction and total metal determination of refuse waste-soil were presented in Table 4.1. The results of the percentage recoveries by sequential extraction of the soil were 92.63, 100.10, 100.05, 100.75 and 99.5% while those obtained by the total metal determination of the soil were 90.07, 85.02, 97.85, 98.10, and 95.0% for Pb, Cu, Cd, Zn and Hg respectively. Furthermore, the results of recovery experiment for underground water, leachates, blood, urine, hair and nails for the metals are presented in Table 4.2. The percentage recoveries of Pb, Cu, Cd, Hg and Zn in the samples are: 99.38±0.20, 100.005 ± 0.04, 99.40 ± 0.28, 99.75 ± 0.18 and 100.05 ± 0.04% for under groundwater, 99.40 ± 0.28, 98.40 ± 0.99, 99.90 ± 0.07, 99.35 ± 0.25 and 99.98 ± 0.05 for leachates, 95.89 ± 0.06, 102.14 ± 0.10, 99.51 ± 0.28, 92.79 ± 0.01 and 100.35 ± 0.25% for blood, 100.05 ± 0.04, 100.14 ± 0.10, 97.19 ± 0.13, 99.13 ± 0.09 and 100.45 ± 0.32 for urine, 99.25 ± 0.18, 100.05 ± 0.04, 97.25 ± 0.18, 99.05 ± 0.04 and 100.03 ± 0.02 for hair, and 97.35 ± 0.25, 98.33 ± 0.23, 91.25 ± 0.53, 97.40 ± 1.70, 99.45 ± 0.32% for nails, respectively.

### 4.2 Dumpsite Characterization

The results for the characterisation of the refuse dumpsites have been presented in Table 4.3. The results indicated that the dumpsites had polythene bags, wood, plastics and textile materials as their major constituents. Plastic materials in the dumpsites across the sites range from 4.24±0.01% to 44.23±0.01%.

**Table 4.1: Comparative mean percentage recoveries of metals for the sequential extraction and total metal determination.**

| Metals | Sequential extraction (%) | Total metal (%) |
|---|---|---|
| Pb | 92.63 | 90.07 |
| Cu | 100.10 | 85.02 |
| Cd | 100.05 | 97.85 |
| Zn | 100.75 | 98.10 |
| Hg | 99.50 | 95.00 |

**Table 4.2: Means (±SD) of percentage recovery of metals in the spiked samples**

| Sample | Pb | Cu | Cd | Hg | Zn |
|---|---|---|---|---|---|
| **well water** | 99.38±0.27 | 100.05±0.04 | 99.4±0.28 | 99.75±0.18 | 100.05±0.04 |
| **Leachate** | 99.4±0.28 | 98.4±0.99 | 99.9±0.07 | 99.35±0.25 | 99.98±0.05 |
| **Blood** | 95.89±0.06 | 102.14±0.10 | 99.51±0.28 | 92.79±0.01 | 100.35±0.25 |
| **Urine** | 100.05±0.04 | 100.14±0.10 | 97.19±0.13 | 99.13±0.09 | 100.45±0.32 |
| **Hair** | 99.25±0.18 | 100.05±0.04 | 97.25±0.18 | 99.05±0.04 | 100.03±0.02 |
| **Nails** | 97.35±0.25 | 98.33±0.23 | 91.25±0.53 | 97.4±1.70 | 99.45±0.32 |

**Table 4.3: Percentage characterization of the dumpsite soils**

| Material | Site | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SA | SH | KU | JK | AJ | NTC | DD | PR | RA | BG |
| Plastics | 13.11±0.14 | 21.19±0.01 | 13.03±0.01 | 11.14±0.01 | 44.23±0.01 | 16.33±0.01 | 10.22±0.04 | 8.05±0.08 | 4.24±0.01 | 12.4±0.02 |
| Papers | 21.43±0.06 | 0.85±0.01 | 11.50±0.07 | 1.73±0.04 | 10.42±0.05 | 26.74±0.08 | 11.20±0.01 | 5.47±0.04 | 24.10±0.01 | 18.18±0.18 |
| Textiles | 18.36±0.01 | 13.10±0.01 | 18.12±0.02 | 42.11±0.01 | 23.73±0.01 | 23.10±0.01 | 14.01±0.01 | 30.60±0.01 | 14.25±0.01 | 16.38±0.01 |
| Polythene Bags | 17.59±0.01 | 16.30±0.04 | 18.50±0.01 | 12.06±0.01 | 17.68±0.04 | 30.06±0.06 | 58.83±0.06 | 16.99±0.01 | 27.15±0.01 | 18.35±0.01 |
| Wood | 13.81±0.01 | | 15.18±0.01 | 27.32±0.04 | 3.95±0.01 | 3.79±0.01 | 5.715±0.01 | 30.34±0.01 | 30.27±0.01 | 10.79±0.02 |
| Metals | 15.70±0.07 | 0.45±0.071 | | | | | | | | |
| Hairs | | | | | | | | | | 10.84±0.01 |
| Bones | | | | | | | | 8.51±0.01 | | |
| Waste Leaves | | 48.11±0.13 | 23.68±0.02 | 5.65±0.01 | | | | | | 10.24±0.01 |
| Rubber Tubes | | | | | | | | | | 2.84±0.01 |
| Charcoal | | | | | | | | | | 0.07±0.007 |

Other important solid wastes recorded across the sites were plastics papers, textiles, polythene bags and wood which ranged from 0.85±0.01 (SH) to 26.74±0.08% (NTC), 13.1±0.01% (SH) to 42.11±0.01% (JK), 16.33±0.04 (SH) to 58.83±0.06 (DA), and 3.79±0.01% (NTC) to 30.34±0.01% (PR), respectively.

### 4.3 Gaseous Pollutants and other field data at the dumpsites

The levels of $H_2S$, $SO_2$, CO, $NO_2$, Fl and $NH_3$ across the seasons were presented in Figures 4.1 and 4.2, respectively. From the Figures, the concentration of $H_2S$ range from 0.00135 (CTR) to 0.0315 (SA) ppm and 0.0005 (CTR) to 0.0037 ppm (RA) in the dry and wet seasons. The concentration of $SO_2$ ranges from 0.0005 ppm (CTR) to 0.0032 ppm (SA) and 0.0011(CTR) to 0.039 ppm (SA) in dry and wet seasons respectively. As shown in the figure, the concentration of CO is 1.500 (CTR) to 11.40 ppm (RA) and 1.5(CTR) to 10.50 ppm (SH) in wet and dry seasons, respectively. Also, levels of $NO_2$ recorded across the sites for the wet and dry seasons ranges from BDL (CTR) to 0.00605 (NTC) and 0.00185(CTR) to 0.00365 ppm (PR), respectively. Similarly, the concentration ranges recorded for Fl across the sites and seasons were 0.0005 (CTR) to 0.0045 ppm (JK and PR) and 0.0015 (CTR) to 0.0625 ppm (SA) for wet and dry seasons, respectively. Also, the concentration of ammonia-nitrogen for wet and dry seasons were 0.0005(CTR) to 0.005 (PR) and 1.50 (CTR) to 8.65 ppm (SA), respectively.

Figures 4.3 and 4.4 showed the distribution of particulates in ambient air samples at the vicinity of dumpsites across the sites and seasons respectively. The concentrations of the particulates matter, relative humidity and temperature ($^{O}C$) in the study in the wet and dry seasons were 7750.141 (SH) to 19,305$\mu gm^{-3}$ (RA) and 355 (CTR) to 1525 $\mu gm^{-3}$ (SA);

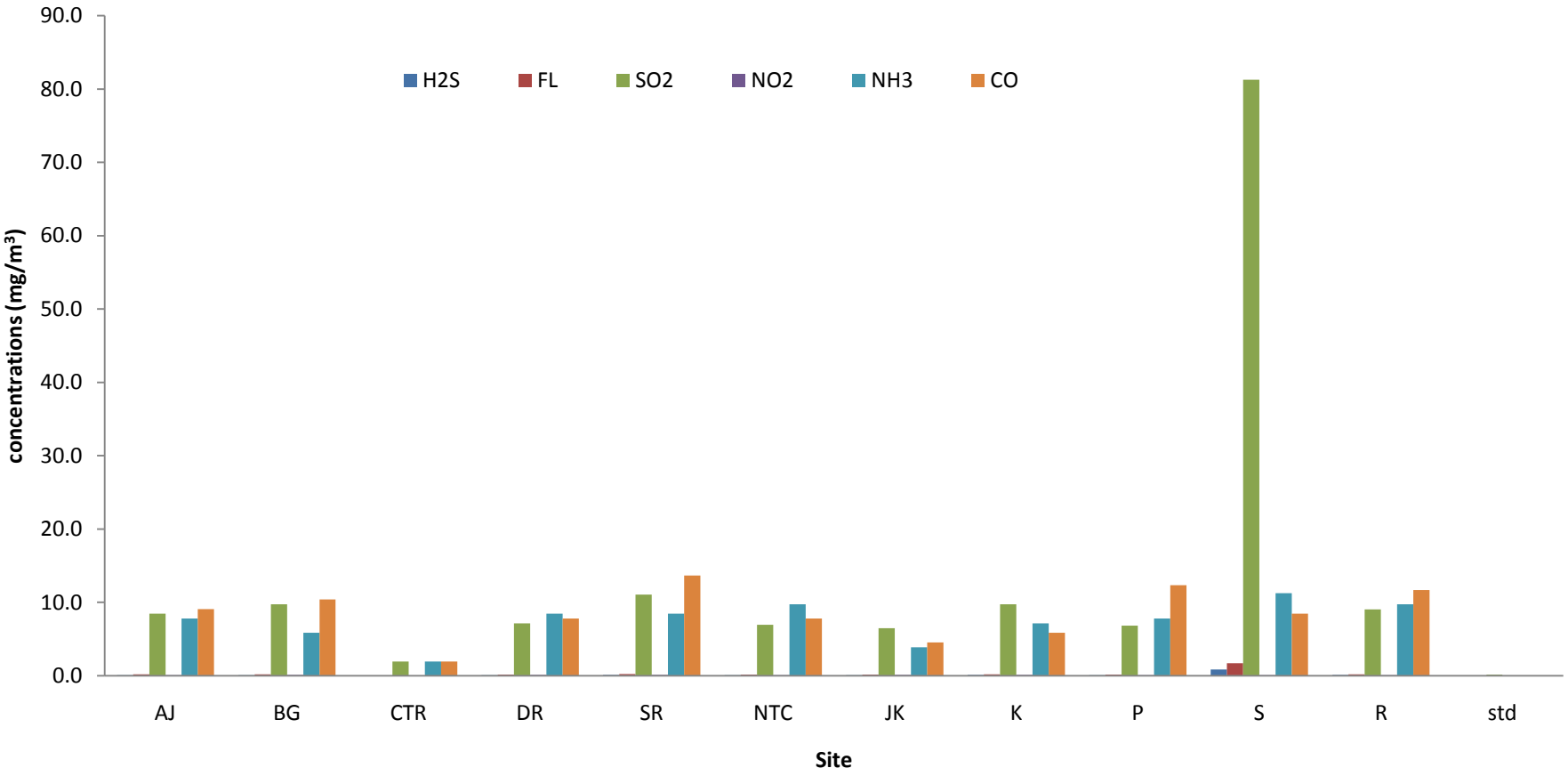


**Figure 4.1: Concentrations of gaseous pollutants at the vicinity of the dumpsites in the wet season**

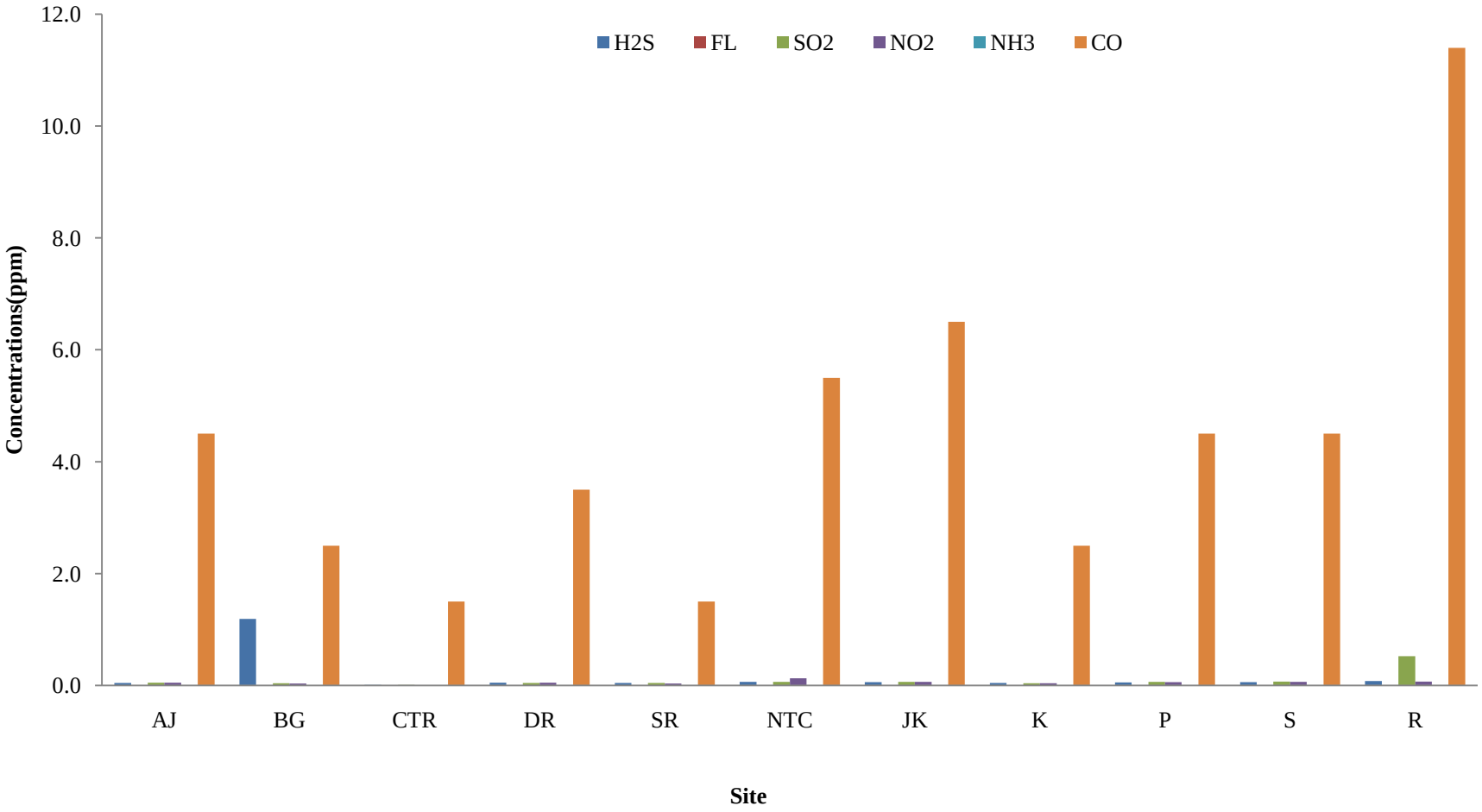


**Figure 4.2: Concentrations of gaseous pollutants at the vicinity of the dumpsites in the dry season**

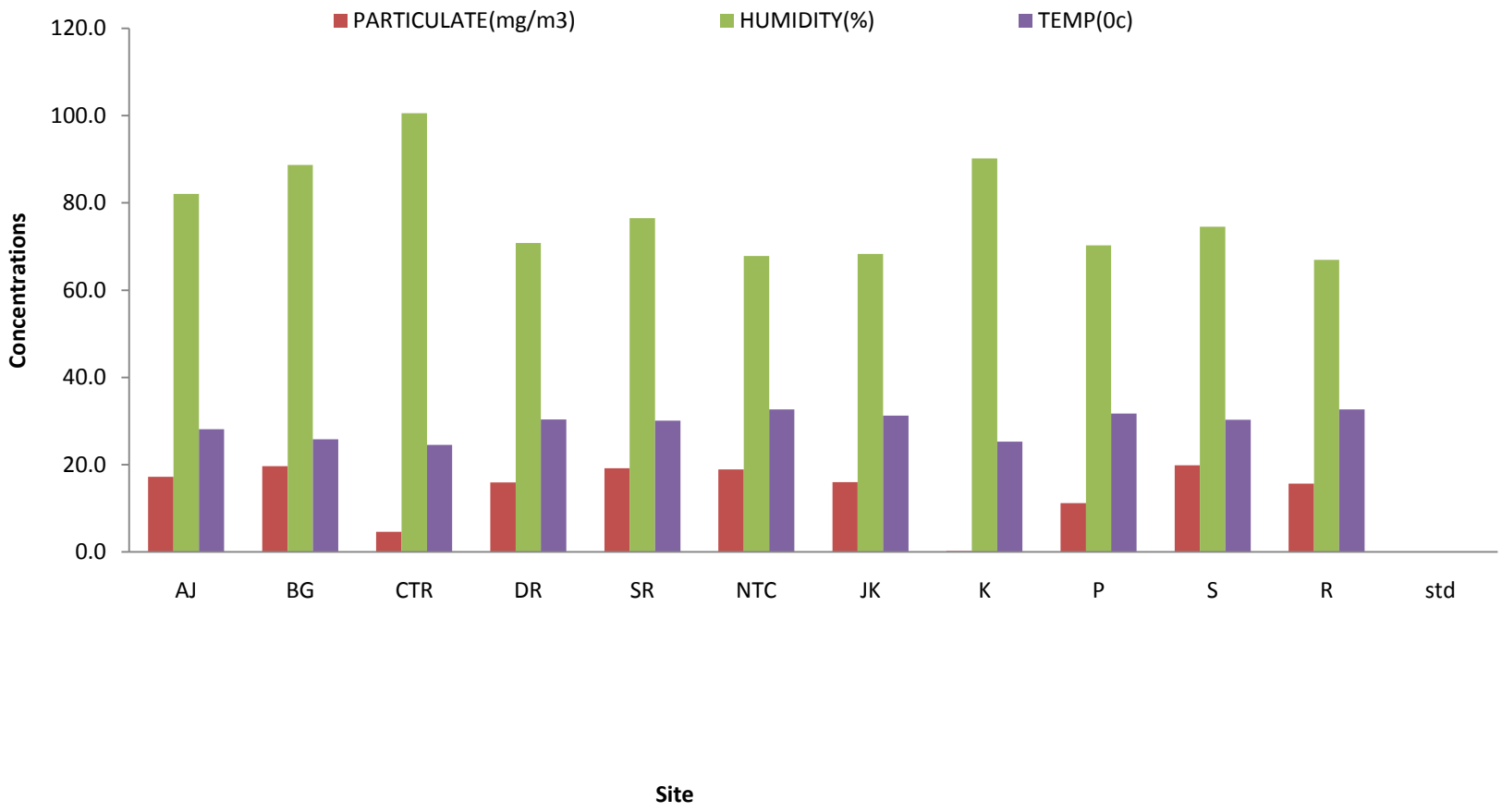


**Figure 4.3: Mean concentrations of particulate, relative humidity and temperature for the wet season**

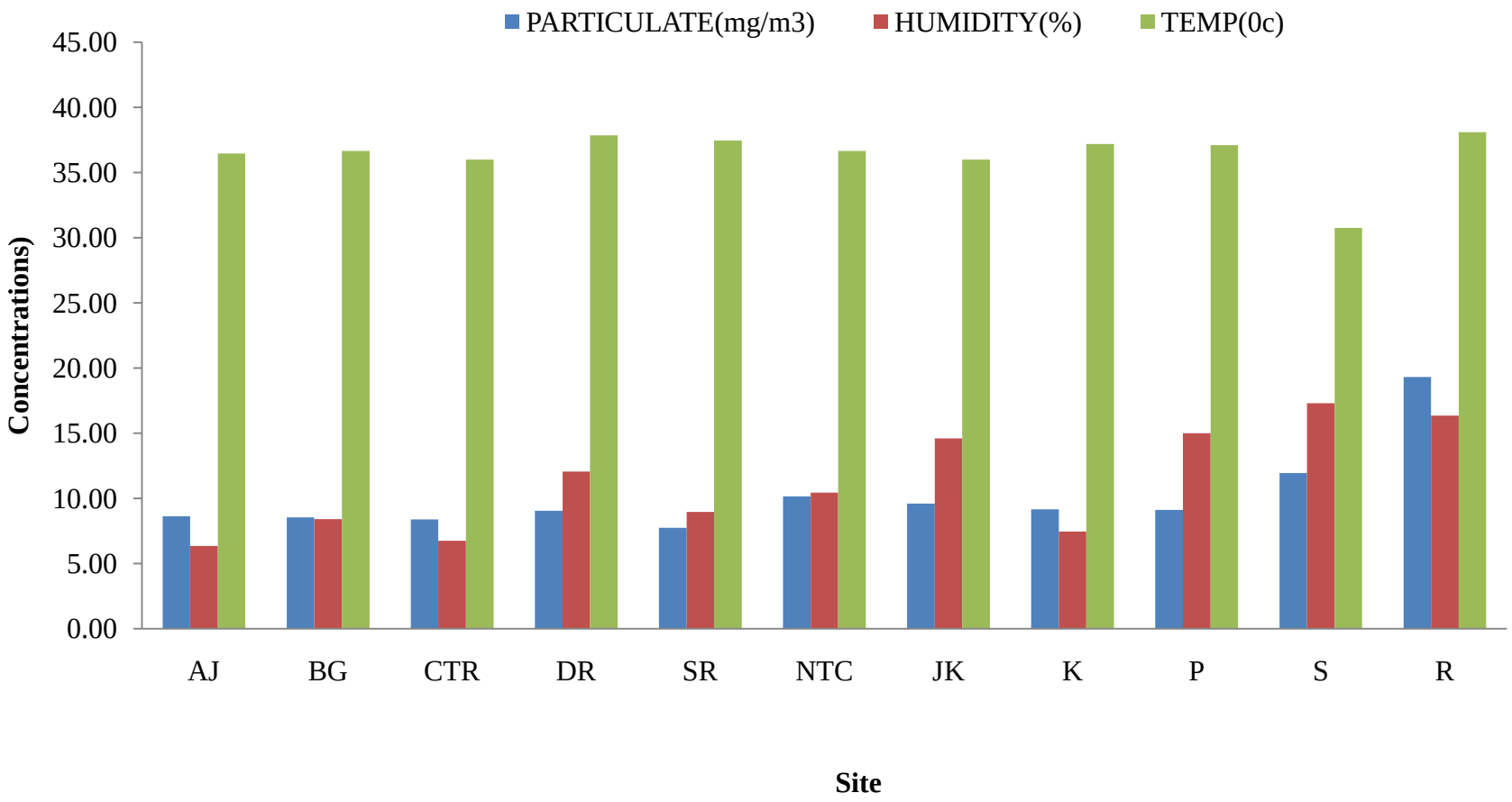


**Figure 4.4: Mean concentrations of particulate, relative humidity and temperature for the dry season**

51.500 (RA) to 77.350%( CTR) and 6.350 (AJ) to 30.750$^{0}$C (SA) to 38.100 and 27.250 (CTR) to 36.300$^{O}$C (RA), respectively.

Tables 4.4a and 4.4b revealed the correlation coefficients of gaseous pollutants for the wet and dry seasons across the sites for FLD vs COD, $SO_2$D, $NO_2$D, $NH_3$D, PartD, HumidD, TempD, COR, $H_2$SR, FLR, $SO_2$R, $NO_2$R, $NH_3$R, PartR and TempR were 0.601, 0.845, 0.460, 0.874, 0.637, 0.100, 0.178, 0.041, 0.023, 0.043, 0.246, 0.341, 0.253, and 0.666, respectively.

Similarly, the correlation coefficients of 0.045, 0.171, 0.200, 0.269, and 0.324 were recorded for the correlations of $H_2$SD Vs TempD, COR, $NO_2$R, PartR and HumdR respectively as presented in Table 4.4.

Also, the correlation coefficients of 0.308, 0.602, 0.701, 0.316, 0.622, 0.065, 0.184, 0.019, 0.040, 0.441, 0.226, 0.198 and 0.712 were recorded for the correlations of FLD vs $SO_2$D, $NO_2$D, $NH_3$D, PartD, HumidD,TempD, COR, $H_2$SR, $SO_2$R, $NO_2$R, $NH_3$R, PartR and TempR, respectively as presented in the Table 4.4.

As presented in the Table 4.4, the correlation coefficients of 0.223, 0.124, 0.938, 0.483, 0.246, 0.319, 0.142, 0.336, 0.137 and 0.449 were recorded for the correlation of $NO_2$D Vs NH3D, PartD, HumD, COR, $NO_2$R, $NH_3$R, PartR and TempR, respectively as presented in the Table.

Similarly, the correlation coeffiecients of 0.622, 0.308, 0.385, 0.225, 0.122,0.091, 0.198, 0.35,0.526, 0.374, and 0.658 were recorded for the correlations of $NO_2$D Vs $NH_3$D, PartD, HumD, COR, $H_2$SR, FLR, $SO_2$R, FLR, $NO_2$R, $NH_3$R, PartR, and TempR, respectively.

The correlation coefficients of 0.184, 0.501, 0.033, 0.250, 0.063, 0.043, 0.120, 0.214, 0.438, 0.138, and 0.679 were recorded for the correlations of $NH_3D$ Vs PartD, HumD, TempD, COR, $H_2SR$, FLR, $SO_2R$, $NO_2R$, $NH_3R$, PartR, and TempR respectively as presented In the Table.

Similarly, as presented in the Table, the correlation coefficients of PartD Vs HumD, TempD, CORD, $H_2SR$, FLR, $SO_2R$, $NO_2R$, $NH_3R$, PartR, and TempR, respectively were 0.617, 0.003, 0.222, 0.208, 0.197, 0.184, 0.094, 0.411, 0.140 and 0.479, respectively.

Also, the correlation coefficients of 0.243, 0.518, 0.497, 0.512, 0.226, 0.437, 0.338 and 0.734, respectively, were recorded for the correlations of HumD Vs COR, $H_2SR$, FLR, $SO_2R$, $NO_2R$, $NH_3R$, PartR, and TempR, respectively as presented in the Table.

The correlation coefficients of 0.206, 0.218 and 0.035 were recorded for the correlations of TempD Vs COR, $NO_2R$, and TempR, respectively as presented in the Table 4.4. Also, the correlation coefficients for COR Vs $H_2SR$, FLR, $SO_2R$, $NO_2R$, $NH_3R$, PartR and TempR were: 0.043, 0.065, 0.033, 0.048, 0.550, 0.509 and 0.449, respectively.

Also, the correlation coefficients of 0.988, 0.001, 0.487, 0.314 and 0.121 were also recorded for FLR Vs FLD, $NO_2R$, $NH_3R$, PartR, and TempR, respectively as presented in Table 4.4. Similarly, the correlation coefficients of 0.511, 0.347, 0.190, were also recorded for the correlations of $SO_2R$ Vs $NH_3R$, PartR, and TempR, respectively as presented in the table.

Also, the correlation coefficients of 0.376, 0.442, and 0.405 were recorded for the correlations of 0.376, 0.442, and 0.405, respectively as presented in the Table 4.4 for the correlations of $NO_2R$ Vs $NH_3R$, PartR, and TempR, respectively.

**Table 4.4a: The correlation matrix of gaseous pollutants and other field data across the sites and seasons**

| Parametrs | COD | $H_2SD$ | FLD | $SO_2D$ | $NO_2D$ | $NH_3D$ | PARTD | HUMD | TEMPD |
|---|---|---|---|---|---|---|---|---|---|
| COD | 1 | | | | | | | | |
| $H_2SD$ | -0.221 | 1 | | | | | | | |
| FLD | 0.601** | -0.255 | 1 | | | | | | |
| $SO_2D$ | 0.845** | -0.119 | 0.308 | 1 | | | | | |
| $NO_2D$ | 0.460* | -0.176 | 0.602** | 0.223 | 1 | | | | |
| $NH_3D$ | 0.365 | -0.384 | 0.701** | 0.124 | 0.622** | 1 | | | |
| PARTD | 0.874** | -0.164 | 0.316 | 0.938** | 0.308 | 0.184 | 1 | | |
| HUMD | 0.637** | -0.234 | 0.622** | 0.483* | 0.385 | 0.501* | 0.617** | 1 | |
| TEMPD | 0.100 | 0.045 | 0.065 | 0.246 | -0.046 | 0.033 | 0.003 | -0.346 | 1 |
| COR | 0.178 | 0.171 | 0.184 | 0.319 | 0.225 | 0.250 | 0.222 | 0.243 | 0.206 |
| $H_2SR$ | 0.041 | -0.093 | 0.019 | -0.026 | 0.122 | 0.063 | 0.208 | 0.518* | -0.915** |
| FLR | 0.023 | -0.070 | -0.024 | -0.033 | 0.091 | 0.043 | 0.197 | 0.497* | -0.912** |
| $SO_2R$ | 0.043 | -0.108 | 0.040 | -0.060 | 0.198 | 0.120 | 0.184 | 0.512* | -0.922** |
| $NO_2R$ | 0.246 | 0.200 | .0441* | 0.142 | 0.355 | 0.214 | 0.094 | 0.226 | 0.218 |
| $NH_3R$ | 0.341 | -0.186 | 0.226 | 0.336 | 0.526* | 0.438* | 0.411 | 0.437* | -0.185 |
| PARTR | 0.253 | 0.269 | 0.198 | 0.137 | 0.374 | 0.138 | 0.140 | 0.338 | -0.224 |
| HUMR | -0.652** | 0.324 | -0.741** | -0.412 | -0.646** | -0.694** | -0.439* | -0.739** | -0.054 |
| TEMPR | 0.666** | -0.398 | 0.712** | 0.449* | 0.658** | 0.679** | 0.479* | 0.734** | 0.035 |

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

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

**Table 4.4b: The correlation matrix of gaseous pollutants and other field data (continued)**

| Parameters | COR | $H_2SR$ | FLR | $SO_2R$ | $NO_2R$ | $NH_3R$ | PARTR | HUMR | TEMPR |
|---|---|---|---|---|---|---|---|---|---|
| COR | 1 | | | | | | | | |
| $H_2SR$ | 0.043 | 1 | | | | | | | |
| FLR | 0.065 | 0.997** | 1 | | | | | | |
| $SO_2R$ | 0.033 | 0.990** | 0.988** | 1 | | | | | |
| $NO_2R$ | 0.048* | -0.003 | 0.001 | -0.018 | 1 | | | | |
| $NH_3R$ | 0.550** | 0.478* | 0.487* | 0.511* | 0.376 | 1 | | | |
| PARTR | 0.509* | 0.306 | 0.314 | 0.347 | 0.442* | 0.455* | 1 | | |
| HUMR | -0.446* | -0.141 | -0.127 | -0.184 | -0.559** | -0.573** | -0.571** | 1 | |
| TEMPR | 0.449* | 0.137 | 0.121 | 0.190 | 0.405 | 0.568** | 0.556** | -0.973** | 1 |

Similarly, the correlations of $NH_3$ R Vs PartR and TempR recorded across the sites and seasons were 0.455 and 0.568, respectively, while the correlation coefficient of 0.556 was recorded for PartR Vs TempR, respectively, as reflected in Table 4.4.

## 4.4 Physico-Chemical Parameters of Dumpsite Soils

The result of the particle size distribution analysis for the refuse dumpsite soils and the control area is presented in Table 4.5. The particle size distribution of dumpsite - soils were: 7.41 (NTC, JK, KU, PR, SA, AJ, BG) to 11.12 % (DA) for clay, 9.26 (AJ) to 14.822 % (BG) for silt, and 70.41 to 75.97% ( AJ). Furthermore, the values recorded at the control site were 2.59, 14.82 and 51.88% for clay, silt and sand, respectively.

The results of the analyses of physico-chemical properties of the refuse waste soils and control area are presented in Tables 4.6 and 4.7 for the dry and wet seasons. The soil samples from the refuse dumpsites had pH ranges of 7.40 (CTR) to 10.25 (JK) and 6.40 to 9.8 (DA) for the dry and wet seasons respectively. The electrical conductivities (EC) of the dumpsite waste soils range from 0.35 $dscm^{-1}$(CTR) to 11.05 $dscm^{-1}$(RA) and 0.08 (CTR) to 10.10 $dscm^{-1}$ for dry and wet seasons, respectively.

The cation exchange capacity (CEC) of the refuse waste soil range from 33.60 (CTR) to 62.35 Cmol/Kg (KU) and 15.81 (CTR) to 56.01 $CmolKg^{-1}$(DA). The concentrations of $NO_2$-N, of the dumpsite soils range from 0.056 (RA) to 0.530 mg/kg (SH) and 0.035 (CTR) to 0.369 (DA) for the dry and wet season as shown in the tables. Similarly, the concentration ranges of the $NO_3$-N were: 0.026 to 0.164 mg/kg (SH) and 0.011 (CTR) to 0.113 (DA) across the seasons.

The levels of $SO_4^{2-}$-S in the soil as presented in the tables across the seasons, were 1.011 (CTR) to 84.60 (JK) and 2.115 (CTR) to 90.57 mg/Kg (JK), respectively.The

**Table 4.5: Means (±SD) of particle size distribution of the dumpsite waste soils across the sites**

| Parameter | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | AJ | BG | CTR | DR | SH | NTC | JK | K | P | S | R |
| Clay | 7.41±0.41 | 7.41±0.41 | 25.94±1.43 | 11.12±0.61 | 7.41±0.41 | 7.41±0.41 | 7.41±0.41 | 7.41±0.41 | 9.26±0.51 | 7.41±0.41 | 5.56±0.31 |
| Silt | 9.26±0.51 | 14.82±0.82 | 14.82±0.82 | 11.12±0.61 | 11.12±0.61 | 14.82±0.82 | 14.82±0.82 | 12.97±0.72 | 12.97±0.72 | 14.82±0.82 | 14.82±0.82 |
| Sand | 75.97±4.19 | 70.41±3.88 | 51.88±2.86 | 70.41±3.88 | 74.11±4.08 | 70.41±3.88 | 70.41±3.88 | 72.26±3.98 | 70.41±3.88 | 70.41±3.88 | 72.26±3.98 |
| Texture Class | Sandy loamy | Sandy loamy | Sandy loamy | Sandy loamy | Sandy loamy | Sandy loamy | Sandy loamy | Sandy loamy | Sandy loamy | Sandy loamy | Sandy loamy |

**Table 4.6: Physico-chemical parameters of dumpsite waste soil samples in the dry season**

| PARAMETER | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **AJ** | **BG** | **CTR** | **DD** | **JK** | **KU** | **SA** | **SH** | **RA** | **PR** | **NTC** |
| pH | 7.50± 0.14 | 8.15± 0.07 | 7.40± 0.14 | 8.35± 0.07 | 10.30± 0.07 | 9.40± 0.141 | 9.5± 0.141 | 9.8± 0.141 | 8.7± 0.141 | 8.5± 0.141 | 9.05± 0.014 |
| EC ($dscm^{-1}$) | 2.85± 0.07 | 2.45± 0.07 | 0.35± 0.01 | 2.40± 0.14 | 5.60± 0.14 | 9.70± 0.283 | 5.1± 0.141 | 1.4± 0.141 | 11.05± 0.071 | 4.1± 0.141 | 0.7± 0.141 |
| CEC ($CmolKg^{-1}$) | 33.51± 0.01 | 37.80± 0.00 | 33.60± 0.14 | 32.86± 0.02 | 50.30± 0.14 | 62.35± 0.212 | 46.1± 0.042 | 50.37± 0.021 | 51.95± 0.212 | 39.4± 0.021 | 41.21± 0.014 |
| $NO_2$-N ($mgKg^{-1}$) | 0.13± 0.00 | 0.11± 0.00 | 0.08± 0.00 | 0.12± 0.00 | 0.14± 0.02 | 0.53± 0.001 | 0.13± 0.001 | 0.53± 0.001 | 0.056± 0.001 | 0.106± 0.001 | 0.047± 0.001 |
| $NO_3$-N ($mgKg^{-1}$) | 0.04± 0.00 | 0.03± 0.00 | 0.03± 0.00 | 0.04± 0.00 | 0.04± 0.00 | 0.161± 0.001 | 0.04± 0.001 | 0.164± 0.004 | 0.017± 0.000 | 0.031± 0.001 | 0.016± 0.002 |
| $SO_4$-S ($mgKg^{-1}$) | 12.09± 0.01 | 22.63± 0.01 | 1.01± 0.00 | 22.62± 0.03 | 84.60± 0.14 | 54.35± 0.014 | 30.2± 0.014 | 39.23± 0.014 | 14.21± 0.014 | 36.24± 0.014 | 30.61±` 0.014 |
| $PO_3^{3-}$P ($mgKg^{-1}$) | 78.76± 0.01 | 120.80± 0.01 | 15.77± 0.02 | 66.45± 0.07 | 87.70± 0.21 | 42.18± 0.247 | 38.6± 0.141 | 50.74± 0.014 | 23.64± 0.007 | 39.39± 0.014 | 94.65± 0.212 |
| $Cl^{-1}$ ( $mgKg^{-1}$) | 4.40± 0.14 | 6.00± 0.14 | 1.00± 0.14 | 7.50± 0.14 | 15.90± 0.07 | 2.6± 0.141 | 10.6± 0.141 | 13.4± 0.141 | 42.8± 0.141 | 7.7± 0.141 | 25.7± 0.141 |
| OM ( $mgKg^{-1}$) | 6.00± 1.41 | 4.06± 0.01 | 0.43± 0.02 | 5.23± 0.03 | 1.25± 0.35 | 11.6± 0.283 | 5.08± 0.014 | 11.5± 0.141 | 0.9± 0.283 | 3.27± 0.014 | 1.68± 0.014 |
| $CO_3^{2-}$ ( $mgKg^{-1}$) | BDL | 0.50± 0.141 | 0.00 | 0.95± 0.21 | BDL | 2.1± 0.141 | 2.5± 0.141 | 2.05± 0.071 | BDL | 1.9± 0.141 | BDL |

**Table 4.7: Physicochemical parameters of dumpsite waste soil samples during the wet season**

| Parameters | SITES | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **AJ** | **BG** | **CTR** | **DD** | **JK** | **KU** | **SA** | **SH** | **RA** | **PR** | **NTC** |
| pH | 7.60± 0.14 | 7.70± 0.14 | 6.40± 0.141 | 9.800± 0.141 | 9.20± 0.14 | 8.350± 0.212 | 7.850± 0.071 | 10.00± 0.141 | 8.50± 0.141 | 9.50± 0.141 | 8.40± 0.141 |
| EC ($dscm^{-1}$) | 3.10± 0.14 | 4.600± 0.14 | 0.08± 0.014 | 7.050± 0.071 | 6.10± 0.14 | 0.80± 0.141 | 2.200± 0.141 | 1.16± 0.021 | ±0.5 0.148 | 3.60± 0.141 | 6.60± 0.14 |
| CEC ($CmolKg^{-1}$) | 35.5± 0.007 | 37.5± 0.021 | 15.81± 0.014 | 56.01± 0.007 | 49.6± 0.14 | 31± 0.141 | 32.00± 0.141 | 50.5± 0.141 | 49.08± 0.021 | 39.83± 0.014 | 46.80± 0.14 |
| $NO_2$-N ($mgKg^{-1}$) | 0.130± 0.0007 | 0.210± 0.0707 | 0.035± 0.0012 | 0.369± 0.0007 | 0.14± 0.001 | 0.09± 0.001 | 0.120± 0.001 | 0.017± 0.0001 | 0.175± 0.005 | 0.139± 0.004 | 0.11± 0.001 |
| $NO_3$-N ($mgKg^{-1}$) | 0.09± 0.0007 | 0.06± 0.0021 | 0.011± 0.0001 | 0.113± 0.0014 | 0.04± 0.0014 | 0.03± 0.001 | 0.030± 0.001 | 0.017± 0.0001 | 0.052± 0.002 | 0.041± 0.0014 | 0.03± 0.0007 |
| $SO_4$-S ($mgKg^{-1}$) | 3.01± 0.014 | 24.2± 0.014 | 2.12± 0.002 | 57.37± 0.014 | 90.6± 0.014 | 9.07± 0.007 | 21.10± 0.01 | 40.55± 0.212 | 10.12± 0.014 | 32.75± 0.212 | 22.7± 0.021 |
| $PO_3^{3-}$P ($mgKg^{-1}$) | 148.00± 0.01 | 49.200± 0.212 | 28.890± 0.021 | 28.1± 0.141 | 74.4± 0.021 | 84.1± 0.071 | 34.10± 0.01 | 60.39± 0.014 | 31.53± 0.035 | 47.27± 0.021 | 61.3± 0.014 |
| $Cl^{-1}$ ( $mgKg^{-1}$) | 4.600± 0.141 | 6.400± 0.141 | 0.600± 0.141 | 15.750± 0.071 | 17.600± 0.283 | 6.250± 6.576 | 6.30± 0.14 | 14.500± 0.141 | 45.650± 0.212 | 8.500± 0.141 | 27.20± 0.141 |
| OM ( $mgKg^{-1}$) | 5.37± 0.594 | 4.36± 0.021 | 0.110± 0.002 | 14.14± 0.021 | 11.1± 0.042 | 3.28± 0.021 | 4.50± 0.028 | 1.14± 0.014 | 6.40± 0.141 | 0.800± 0.141 | 5.5± 0.283 |
| $CO_3^{2-}$ ( $mgKg^{-1}$) | BDL | 1.75± 0.212 | BDL | BDL | 4.95± 0.212 | BDL | 2.05± 0.071 | BDL | 0.75± 0.071 | BDL | 2.15± 0.212 |

ranges of $PO_3^3$—P in the dumpsite soils were 15.765 to 120.76 (BG) and 28.10 (DA) to 148.76 mg/kg (AJ) for the respective dry and wet seasons.

Similarly, the chloride contents of the dumpsite waste soils range from 1.00 (CTR) to 42.80 (RA) and 0.60 (CTR) to 45.65 mg/kg (RA) for the dry and wet seasons, respectively. The levels of organic matter (OM) in the refuse dumpsite soils range from 0.425 (CTR) to 11.600 (KU) and 0.110(CTR) to 14.14% (DA) for the dry and wet seasons respectively. The concentrations of $CO_3^{2-}$ ion across the sites range from BDL (AJ, CTR, JK, and NTC) to 2.50 (SA) and BDL (AJ, CTR, DA, SH, KU and PR) to 4.95 % (JK).

### 4.5 Total Metal Contents in the Dumpsite Soil

Table 4.10 and 4.11 showed the total metal concentrations of Zn, Pb, Cu, Cd and Hg in the dumpsite soils. The concentration ranges of Zn in the refuse waste soils for the dry and wet seasons across the sites were: 194.15 (CTR) to 1,135.30 (SA) and 115.10 (CTR) to 553.44 (SH) mg/kg respectively. Also, concentration ranges of Pb were 14.41 (BG) - 77.17 (RA) and 1.20 (BG) - 5.13 mg/kg (CTR) for wet and dry seasons as presented in Tables 4.7 and 4.8, respectively. Simialrly, the concentration ranges of Cu in the dry and wet seasons were: 1.123 (BG) - 899.50 (RA) and 5.90 (BG) - 60.70 mg/kg (JK), respectively. Furthermore, Cd concentration in the dry and wet seasons were : 1.02 (BG) - 3.48 (RA) and 0.72 (CTR) to 2.96 mg/kg (AJ), respectively. The concentration for Hg recorded in the dumpsite-soil in the dry and wet seasons were: 169.60 (JK) - 731.00 and 33.39 (CTR) - 233.90 mg/kg (BG), respectively.

**Table 4.8: Total metal concentrations (mg/kg) of the dumpsite waste soils during the dry season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NTC | SD |
| Zn | 347.00± 6.96 | 333.50± 3.32 | 194.15± 6.53 | 251.40± 8.44 | 429.40± 7.37 | 932.30± 5.63 | 1135.30± 8.44 | 395.00± 6.39 | 462.10± 24.11 | 276.10± 6.46 | 761.60± 11.93 | 300 |
| Pb | 22.00± 1.10 | 14.41± 0.35 | 20.89± 4.92 | 27.01± 5.39 | 23.60± 4.06 | 18.10± 1.34 | 27.01± 1.44 | 20.50± 2.49 | 77.17± 2.95 | 20.68± 2.75 | 38.17± 5.97 | 100 |
| Cu | 3.52± 0.63 | 1.12± 0.32 | 15.75± 0.54 | 17.25± 0.66 | 13.02± 0.67 | 4.28± 0.76 | 4.61± 0.92 | 7.98± 1.04 | 899.50± 1.08 | 8.82± 0.71 | 19.12± 0.57 | 100 |
| Cd | 2.05± 0.03 | 1.02± 0.01 | 1.75± 0.02 | 2.14± 0.03 | 2.17± 0.03 | 2.46± 0.03 | 2.98± 0.04 | 3.36± 0.05 | 3.48± 0.05 | 2.28± 0.03 | 1.83± 0.03 | 3.00 |
| Hg | 731.00± 1.41 | 120.30± 1.98 | 189.38± 1.93 | 216.50± 12.36 | 169.60± 6.36 | 207.60± 2.65 | 212.08± 2.04 | 283.40± 9.95 | 192.60± 1.95 | 203.20± 9.28 | 214.60± 1.46 | 0.13 |

**Table 4.9: Total metal concentrations (mg/kg) of the dumpsite waste soils during the wet season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Meta | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT | STD |
| Zn | 169.40± 6.14 | 162.60± 5.90 | 115.10± 7.80 | 122.00± 4.45 | 209.00± 7.59 | 454.50± 16.48 | 553.44± 20.07 | 192.50± 6.98 | 225.30± 8.17 | 134.60± 4.88 | 371.00± 13.46 | 300 |
| Pb | 1.172± 0.77 | 1.197± 0.95 | 5.130± 2.42 | 2.29± 1.93 | 3.40± 1.69 | 4.722± 2.50 | 1.443± 5.63 | 1.95± 7.99 | 2.44± 1.49 | 2.98± 1.72 | 1.35± 0.65 | 100 |
| Cu | 9.749± 0.35 | 5.895± 2.78 | 6.025± 2.84 | 6.58± 3.11 | 60.70± 28.64 | 34.49± 16.26 | 37.29± 17.58 | 1.24± 0.58 | 14.91± 7.03 | 15.54± 7.33 | 46.0± 21.69 | 100 |
| Cd | 2.96± 0.11 | 1.29± 1.27 | 0.72± 0.58 | 1.59± 1.56 | 1.79± 1.76 | 2.34± 2.29 | 2.72± 2.67 | 0.96± 0.94 | 2.28± 2.23 | 2.22± 2.18 | 1.93± 1.90 | 3.00 |
| Hg | 125.50± 2.76 | 233.90± 1.50 | 33.39± 4.32 | 85.60± 6.52 | 68.60± 4.47 | 100.80± 7.26 | 111.73± 7.00 | 183.00± 12.40 | 114.82± 2.19 | 130.62± 2.37 | 90.86± 1.25 | 0.13 |

## 4.6. Concentrations of Heavy Metals in the Dumpsites Particulate Dust

### 4.6.1 Heavy metals in dumpsite particulate dust

The levels of metals in the dust samples emanating from the dumpsites in the dry and wet seasons were presented in Tables 4.10 and 4.11, respectively. The range of Zn in the dust particulates during the dry season range from 1.40 (JK) to 88.60 mg/kg (SH) while the range of BDL (CTR) to 210.60mg/kg (SA) was recorded for Zn during the wet season as presented in the Tables. Also, the range of 1.42(CTR) to 78.260 mg/kg (SH) was recorded for Pb during the dry season while the range of 2.26 (CTR) to 9.55 mg/kg(SA) was recorded during the wet season as reflected in the Table 4.11.

Similarly, the concentration ranges of Cd recorded in both the wet and dry seasons were 0.609 (CTR) to 3.74 mg/kg (RA) and BDL (CTR) to 0.39 mg/kg (NTC), respectively. The levels of Cu recorded during the wet season range from 1.310 (CTR) to 390.500 mg/kg (JK), across the sites as presented in Table 4.10. Also, the concentration range of 0.241 (KU) to 311.5 mg/kg (NTC) was recorded for Cu in the dry season across the sites. Also, the concentration range of Hg recorded during the dry season was 10.30 (JK) to 25.69 mg/kg (AJ) while the range of BDL (CTR) to 24.710 mg/kg (NTC) was recorded as presented in the Tables 4.10 and 4.11.

### 4.6.2 Correlation matrices of metals in soils and Particulate Dust

Correlation coefficients of CdD, ZnR, PbR, CuR, CdR, PbDustR, CdDustR, HgDustR were 0.12, 0.173, 0.968, 0.722, 0.761, 0.149, 0.006, 0.152, 0.222, 0.535, 0.509, 0.112, 0.243 and 0.176, respectively, as presented in the Tables 4.12a and 4.12, respectively.

Similarly, the correlations of 0.937, 0.481, 0.009, 0.009, 0.145, 0.041, 0.037, 0.320, 0.515, 0.692, 0.202, 0.528, 0.079, 0.786 for PbD Vs CuD, CdD, ZnR, CuR, CdR, ZndUSTD, PbDustD, CuDustD, CdDustD, HgDustD, PbDustR, CuDustR and CdDustR, respectively as presented in the Table 4.12

Also, the correlation coefficients 0.502, 0.058, 0.203, 0.418, 0.306, 0.817, 0.280, 0.504, and 0.820 were recorded for CuD Vs CdD, CdR, ZnDustD, PbDustD, CuDustD, CdDustD, HgDustD, PbDustD, CuDustD, CdDustD, HgDustD, PbDustR, CuDustR and CdDustR, respectively as presented in the Table 4.12.

The correlation coefficients for CdD Vs HgD, ZnR, PbR, CuR, ZnDustD, PbDustD, CuDustD, CdDustD, HgDustD, PbDustR and CdDustR, respectively were 0.102, 0.077, 0.309, 0.073, 0.320, 0.403, 0.570, 0.148, 0.062, 0.547, and 0.640, respectively as presented in the Table.

Similarly, the correlation coefficients of 0.200, 0.158, 0.350, and 0.096 were recorded for HgD Vs CdR, PbDustD, HgDustD, and CdDustD, respectively as presented in the Table 4.12 were recorded for the correlations of HgD Vs CdR, PbDustD, HgDustD, and CdDustD, respectively as presented in the Table. The correlation coefficients of ZnR Vs PbR, CuR, CdR, CuDustD, CdDustD, HgDustD, ZnDustR, PbDustR, CuDustR, CdDustR, and HgDustR were: 0.074, 0.727, 0.205, 0.127, 0.155, 0.049, 0.461, 0.462, 0.088, 0.117, and 0.062, respectively.

The correlation coefficients of 0.553, 0.047, 0.286, 0.144, 0.826, 0.721, and 0.148 were recorded for the correlations of PbR Vs Cu, ZnDustD, PbDustD, CdDustD, ZnDustR, PbDustR, CuDustR, CdDustR, and HgDustR, respectively as presented in Table 4.12.

The correlation coefficients of 0.450, 0.122, 0.089, 0.234, 0.311, 0.210, 0.217, and 0.241, respectively were recorded for the correlations of CuR Vs CuDustD, CdDustD, HgDustD, ZnDustR, PbDustR, CuDustR, CdDustR and HgDustR, respectively.

Also, the correlation coefficients for CdR Vs HgR, PbDustD, CdDustD, ZnDUstR, PbDustR and CdDustR were: 0.544, 0.161, 0.055, 0.066, 0.132 and 0.079, respectively as revealed in the Taable. The correlation coefficients of 0.259 and 0.034 were recorded for HgR Vs ZnDustD, ZnDustR, respectively, as presented in the Table 4.12.

## 4.7 Chemical Fractionation of Metals in the Dumpsite Soils

The concentrations of Zn, Pb, Cu, Cd and Hg in different fractions based on sequential extraction method are presented in Figures 4.7 to 4.19.

**(a) Zinc**

Figures 4.7 to 4.8 and appendices XII and XIII showed the bioavailable, residual and non-residual fractions of Zn in the refuse waste soil. The range of the percentage of the bioavailable fractions of the dumpsite - soil during the wet season across the sites was: 4.00(NTC) to 43.56 % (DD). However, the non-residual and residual fractions ranged from 56.44(CTR)-95.88 % (NTC) and 10.04 (KU) to 43.56% (DD), respectively. The percentage of the bioavailable fraction of zinc during the dry season range from 8.19 (NTC) to 79.08 % (BG).

**Table 4.10 Concentrations of metals ($mgkg^{-1}$) in the dust particulates for dry season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NTC |
| Zn | 47.000± | 96.900± | 6.950± | 72.690± | 1.402± | 51.210± | 59.340± | 88.660± | 78.750± | 96.250± | 22.259± |
| | 2.250 | 4.604 | 0.330 | 3.453 | 0.067 | 2.433 | 2.819 | 4.212 | 3.741 | 4.572 | 1.057 |
| Pb | 59.900± | 35.040± | 1.422± | 65.350± | 45.760± | 41.840± | 58.727± | 14.010± | 78.260± | 74.270± | 6.018± |
| | 2.845 | 1.665 | 0.068 | 3.105 | 2.174 | 1.988 | 2.790 | 0.666 | 3.718 | 3.528 | 0.286 |
| Cd | 0.967± | 1.151± | 0.609± | 1.538± | 1.383± | 2.496± | 1.509± | 0.957± | 3.744± | 1.354± | 0.667± |
| | 0.046 | 0.055 | 0.029 | 0.073 | 0.066 | 0.119 | 0.072 | 0.046 | 0.178 | 0.064 | 0.032 |
| Cu | 28.630± | 77.120± | 5.790± | 29.510± | 42.380± | 0.241± | 27.389± | 52.010± | 149.500± | 36.580± | 311.500± |
| | 1.360 | 3.664 | 0.275 | 1.402 | 2.013 | 0.011 | 1.301 | 2.471 | 7.106 | 1.738 | 14.796 |
| Hg | 25.690± | 19.200± | 26.05± | 18.953± | 10.300± | 27.490± | 16.9110± | 22.000± | 25.310± | 18.210± | 19.700± |
| | 1.220 | 0.912 | 1.238 | 0.900 | 0.489 | 1.306 | 0.803 | 1.045 | 1.202 | 0.865 | 0.940 |

**Table 4.11 Concentrations of metals ($mgkg^{-1}$) in the dust particulates for wet season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NTC |
| Zn | 46.556± | 97.330± | BDL | 65.060± | 50.990± | 35.940± | 210.600± | 41.060± | 18.460± | 60.610± | 16.750± |
| | 2.212 | 4.624 | | 3.091 | 2.422 | 1.707 | 10.007 | 1.951 | 0.877 | 2.880 | 0.796 |
| Pb | 3.405± | 2.283± | 2.260± | 4.044± | 4.537± | 3.008± | 9.549± | 2.989± | 7.856± | 4.141± | 3.105± |
| | 0.162 | 0.108 | 0.108 | 0.192 | 0.216 | 0.143 | 0.454 | 0.142 | 0.373 | 0.197 | 0.148 |
| Cd | 0.357± | 0.242± | BDL | 0.281± | 0.212± | 0.348± | 0.358± | 0.309± | 0.774± | 0.319± | 0.391± |
| | 0.017 | 0.011 | | 0.013 | 0.010 | 0.017 | 0.017 | 0.015 | 0.037 | 0.015 | 0.015 |
| Cu | 12.045± | 2.844± | 1.310± | 3.840± | 390.500± | 2.728± | 11.360± | 3.811± | 16.090± | 3.347± | 298.700± |
| | 0.572 | 0.135 | 0.062 | 0.182 | 18.552 | 0.130 | 0.540 | 0.181 | 0.765 | 0.159 | 14.190 |
| Hg | 4.760± | 14.900± | BDL | 14.630± | 18.400± | 23.300± | 4.034± | 20.950± | 1.355± | 15.980± | 24.710± |
| | 0.226 | 0.712 | | 0.695 | 0.873 | 1.107 | 0.192 | 0.995 | 0.064 | 0.759 | 1.174 |

**Table 4.12a: The correlation matrix of the total metals in the soil and dust particulates across the sites and seasons**

| Metals | ZnD | PBD | CUD | CdD | HgD | ZnR | PbR | CuR | CdR | HgR |
|---|---|---|---|---|---|---|---|---|---|---|
| ZnD | 1 | | | | | | | | | |
| PBD | 0.012 | 1 | | | | | | | | |
| CUD | -0.065 | 0.937** | 1 | | | | | | | |
| CdD | 0.175 | 0.481* | 0.502* | 1 | | | | | | |
| HgD | -0.121 | -0.099 | -0.120 | 0.102 | 1 | | | | | |
| ZnR | 0.968** | 0.009 | -0.074 | 0.077 | -0.161 | 1 | | | | |
| PbR | 0.722** | -0.051 | -0.093 | 0.309 | -0.089 | 0.674** | 1 | | | |
| CuR | 0.761** | 0.145 | -0.034 | 0.073 | -0.110 | 0.727** | 0.553** | 1 | | |
| CdR | 0.149 | 0.041 | 0.058 | -0.234 | 0.200 | 0.205 | -0.120 | -0.184 | 1 | |
| HgR | -0.158 | -0.180 | -0.046 | -0.283 | -0.023 | -0.117 | -0.286 | -0.414 | 0.544** | 1 |
| ZnDustD | -0.118 | 0.037 | 0.203 | 0.320 | -0.061 | -0.255 | 0.047 | -0.166 | -0.118 | 0.259 |
| PbDustD | 0.006 | 0.320 | 0.418 | 0.403 | 0.158 | -0.133 | 0.286 | -0.042 | 0.161 | -0.169 |
| CuDustD | 0.152 | 0.515* | 0.306 | -0.105 | -0.141 | 0.127 | -0.179 | 0.450* | -0.063 | -0.078 |
| CdDustD | 0.222 | 0.692** | 0.817** | 0.570** | -0.202 | 0.155 | 0.144 | 0.122 | 0.055 | -0.157 |
| HgDustD | -0.029 | 0.202 | 0.280 | 0.148 | 0.350 | 0.049 | -0.227 | 0.089 | -0.039 | -0.014 |
| ZndustR | 0.535* | -0.279 | -0.242 | 0.062 | -0.091 | .0461* | 0.826** | 0.234 | 0.066 | 0.034 |
| PbDustR | 0.509* | 0.528* | 0.504* | 0.547** | -0.104 | 0.462* | 0.721** | 0.311 | 0.132 | -0.217 |
| CuDustR | 0.112 | 0.079 | -0.112 | -0.188 | -0.166 | 0.088 | -0.074 | 0.210 | -0.057 | -0.271 |
| CdDustR | 0.243 | 0.786** | 0.820** | 0.640** | 0.096 | 0.117 | 0.148 | 0.217 | 0.079 | -0.109 |
| HgDustR | 0.176 | -0.342 | -0.426* | -0.093 | -0.247 | 0.062 | -0.174 | 0.241 | -0.213 | -0.065 |

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).
S = soil, D = dust particulates

**Table 4.12b: The correlation matrices of the total metals in soil and dust particulates for wet and dry seasons (continued)**

| Metals | ZnDustD | PbDustD | CuDustD | CdDustD | HgDustD | ZndustR | PbDustR | CuDustR | CdDustR | HgDustR |
|---|---|---|---|---|---|---|---|---|---|---|
| ZnDustD | 1 | | | | | | | | | |
| PbDustD | 0.457* | 1 | | | | | | | | |
| CuDustD | -0.110 | -0.258 | 1 | | | | | | | |
| CdDustD | 0.297 | 0.621** | 0.002 | 1 | | | | | | |
| HgDustD | 0.124 | -0.124 | -0.062 | 0.260 | 1 | | | | | |
| ZndustR | 0.293 | 0.338 | -0.261 | -0.038 | -0.429* | 1 | | | | |
| PbDustR | 0.133 | 0.587** | 0.024 | 0.542** | -0.215 | 0.608** | 1 | | | |
| CuDustR | -0.653** | -0.254 | 0.495* | -0.204 | -0.615** | -0.183 | -0.051 | 1 | | |
| CdDustR | 0.439* | 0.619** | 0.340 | 0.821** | 0.213 | 0.031 | 0.604** | -0.136 | 1 | |
| HgDustR | 0.056 | -0.285 | 0.285 | -0.190 | -0.275 | -0.163 | -0.455* | 0.424* | -0.142 | 1 |

Also, during the dry season the percentage of non-residual and residual fractions were 5.30 (BG) to 48.50 % (PR) and 5.30 to 48.50% (PR), respectively.

**(b) Lead**

Figures 4.9 to 4.10 and appendices XIV and XV showed the bioavailable, residual, and non-residual fractions of Pb in the refuse soil. The ranges of the percentages of the bioavailable, non-residual and residual fractions during the wet season were 5.37 (SA) to 30.77 (SH), 8.36 (DD) to 88.44% (SH) and 6.87 to 91.64% (CTR), respectively. During the dry season, the ranges of 9.73 (RA) to 39.65 % (CTR), 64.76(CTR), to 91.29% (BG) and 8.70 (BG) to 34.09 % (SH), were recorded for the bioavailable, non-residual and residual fractions, respectively.

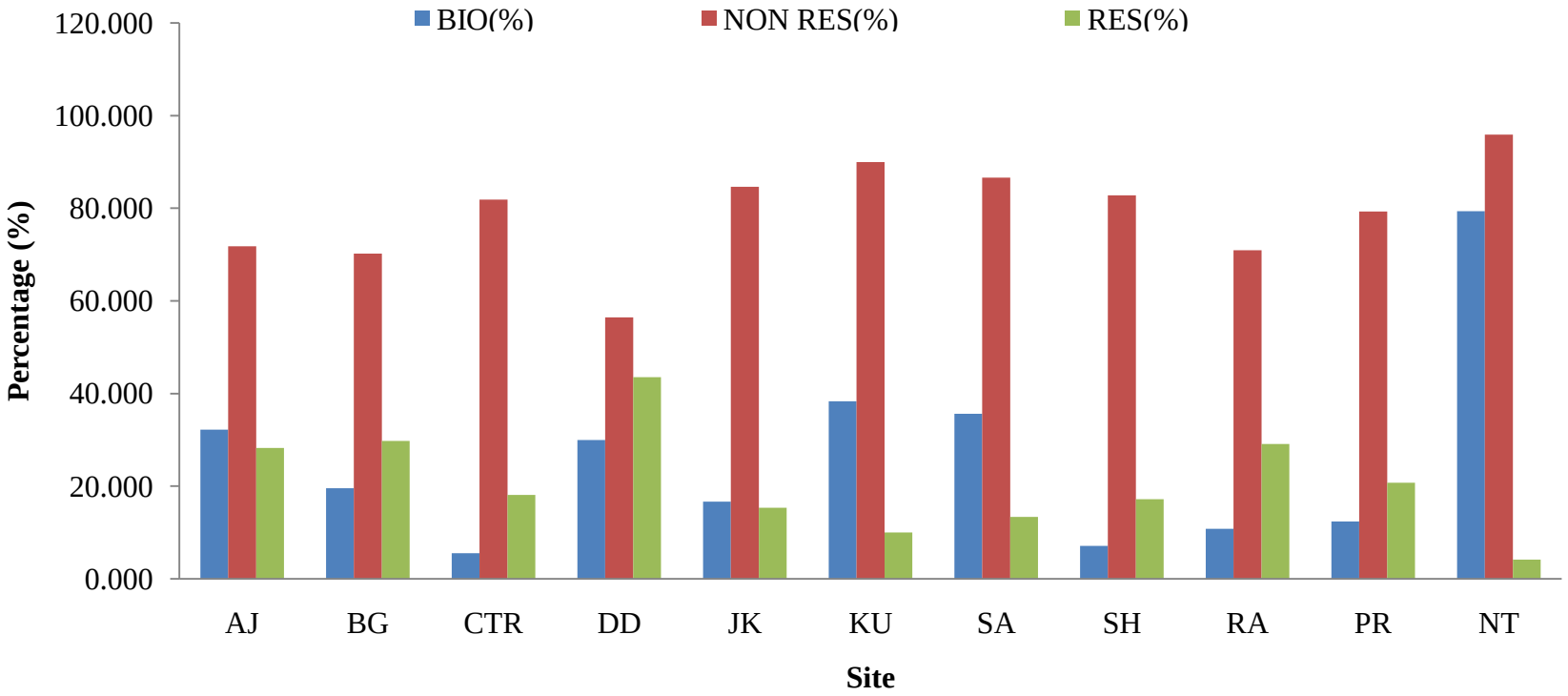


**Figure 4.5: Bioavailable, residual and non-residual (%) Zn during the wet season in the refuse waste soils**

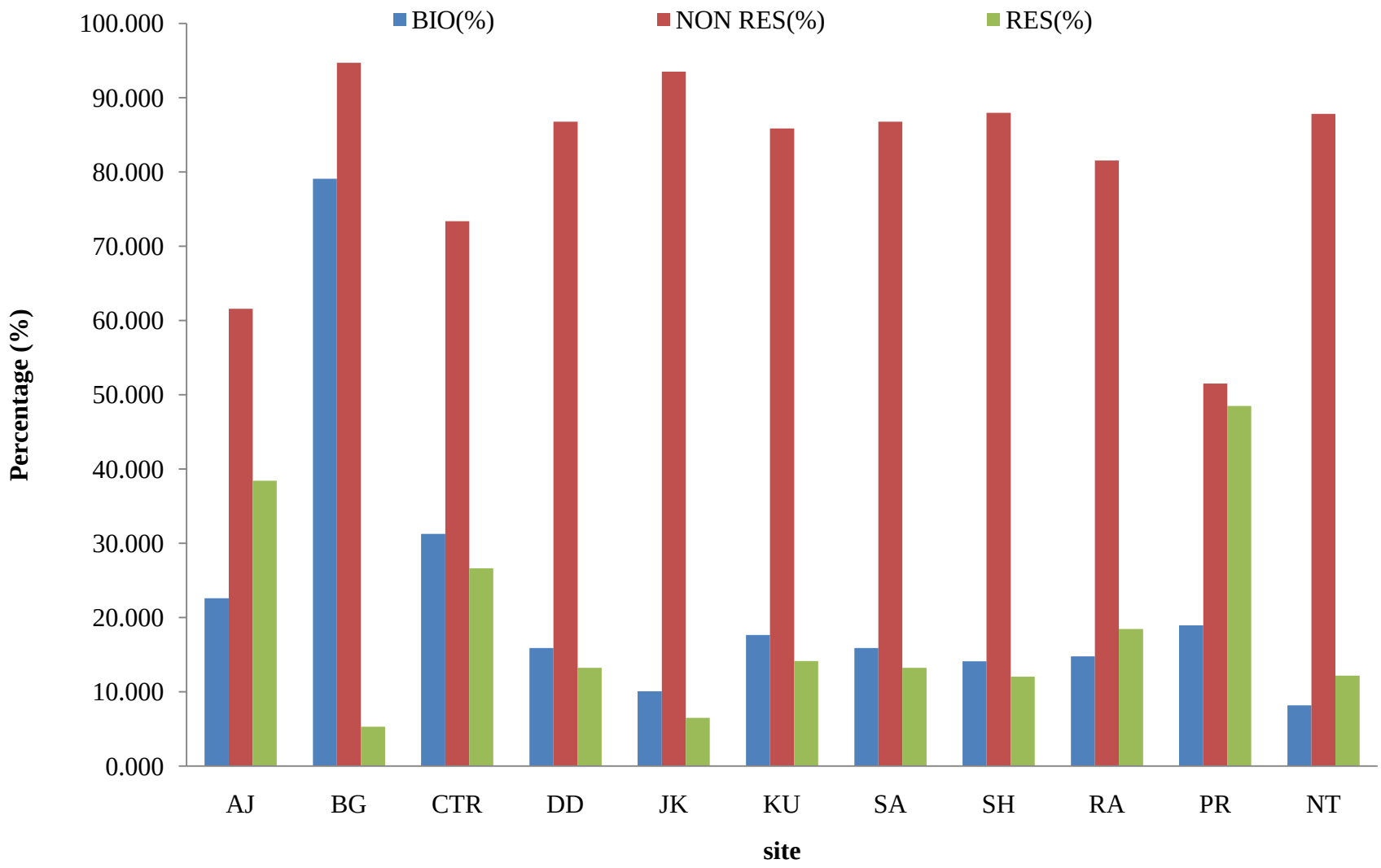


**Figure 4.6: Bioavailable, residual and non-residual(%) zinc ( Zn) during the dry season in refuse waste-soils**

## (c) Copper

The concentrations of Cu in the waste soils dumpsites and a control site for the wet and dry seasons were presented in Figures 4.11 and 4.12. while the extractable fractions were shown in the appendices XVI and XVII. The ranges of the bioavailable, non-residual and residual fractions during the dry seasons were: 0.35 (RA) to 27.68%(BG), 36.74 (AJ) to 98.83% (RA) and 1.169 (RA) to 63.27% (AJ) respectively. Also, the percentages of BDL (RA) to 68.57% (NTC), 10.23 (JK) to 93.94%(KU) and 6.06 (KU) to 89.77% (JK) were recorded during the wet season.

### (d) Cadmium

Figures 4.13 to 4.14 and appendices XVIII and XIX showed the percentages of the residual, non-residual and bioavailable components across the seasons for the wet and dry seasons. The ranges of Cd in the bioavailable, non-residual and residual fractions during the dry season were: 28.14(SH) and 56.74% (AJ), 76.19 (DD) to 86.58% (SH) and 14.65 (PR) to 24.17 % (CTR), respectively. Similarly, ranges of BDL (CTR) to 65.74% (DD), 73.148 (DD) to 89.34 (AJ) and 10.66 (AJ) to 26.85% (DD) were recorded for the bioavailable, non-residul and residual fractions, respectively.

### (e) Mercury

Figures 4.15 and 4.16 showed the percentages of the bioavailable, residual and the non-residual fractions of mercury while the extractable fractions of the metal were presented in appendices XX and XXI for the wet and dry seasons respectively. The percentage range of the bioavailable fraction during the wet season was 24.07 (SH) to 76.85% (BG).

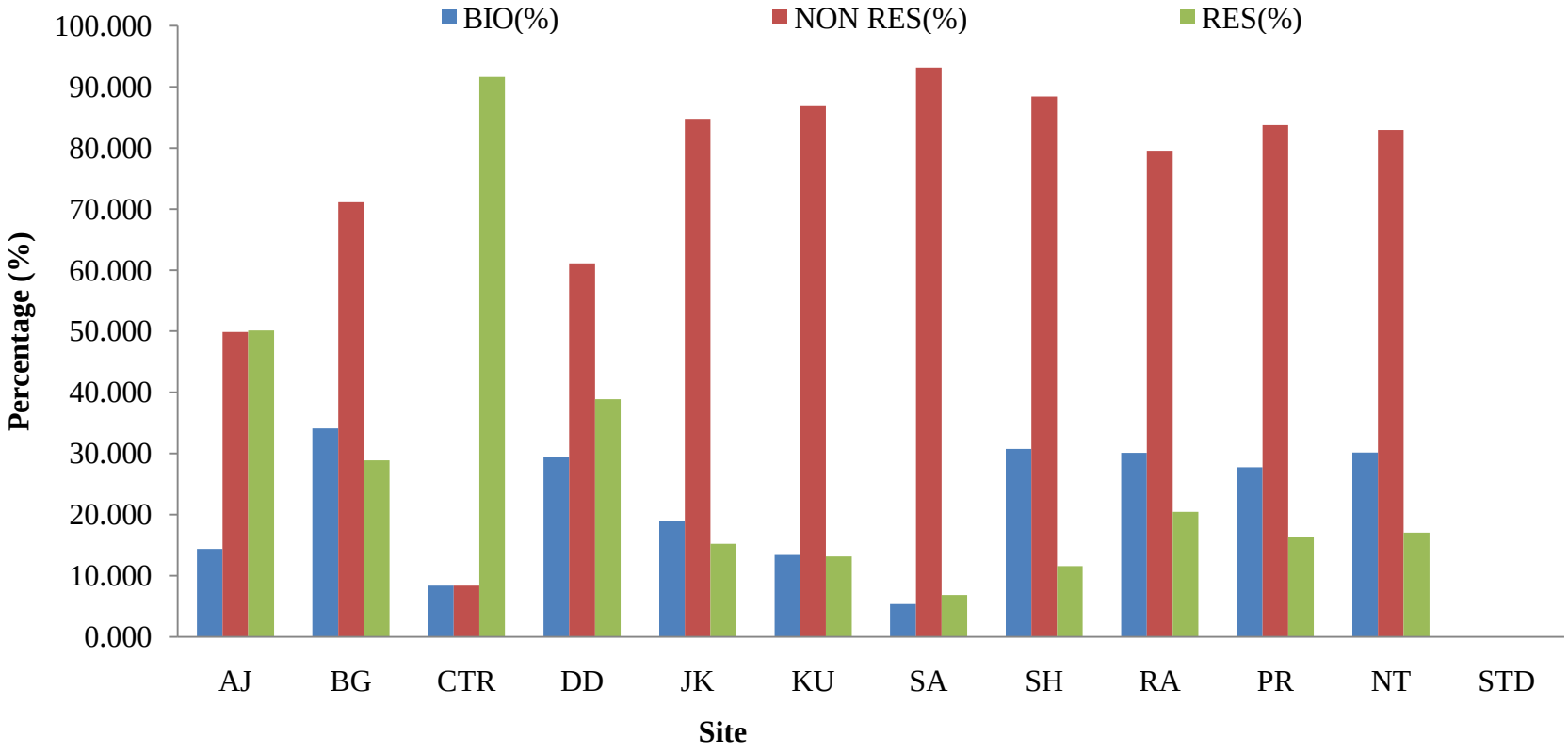


**Figure 4.7: Bioaavilable, residual and non-residual(%) lead in the wet season refuse waste-soils**

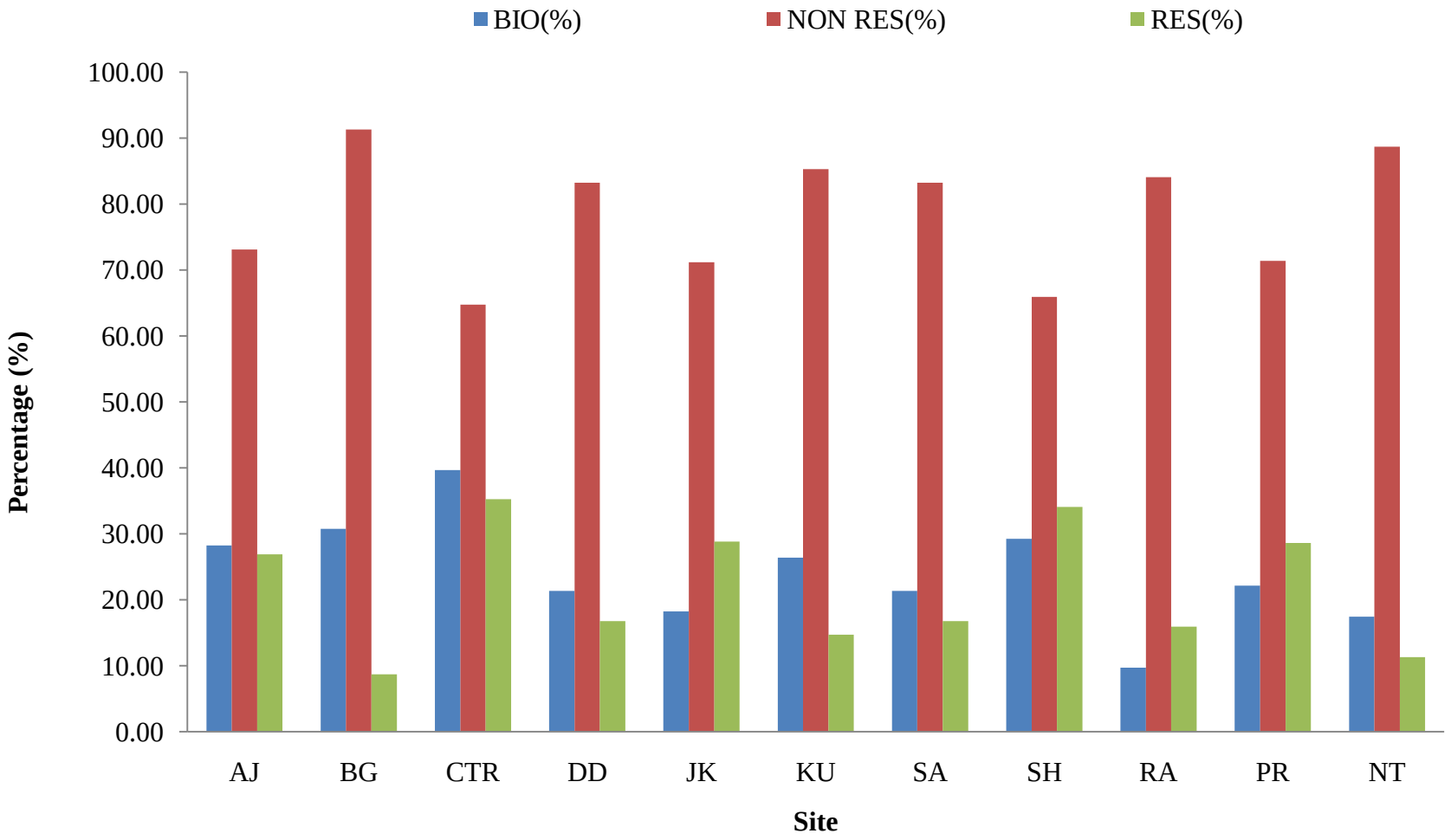


**Figure 4.8: Bioavilable, residual and non-residual (%) lead ( Pb ) during the dry season in the refuse waste-soils**

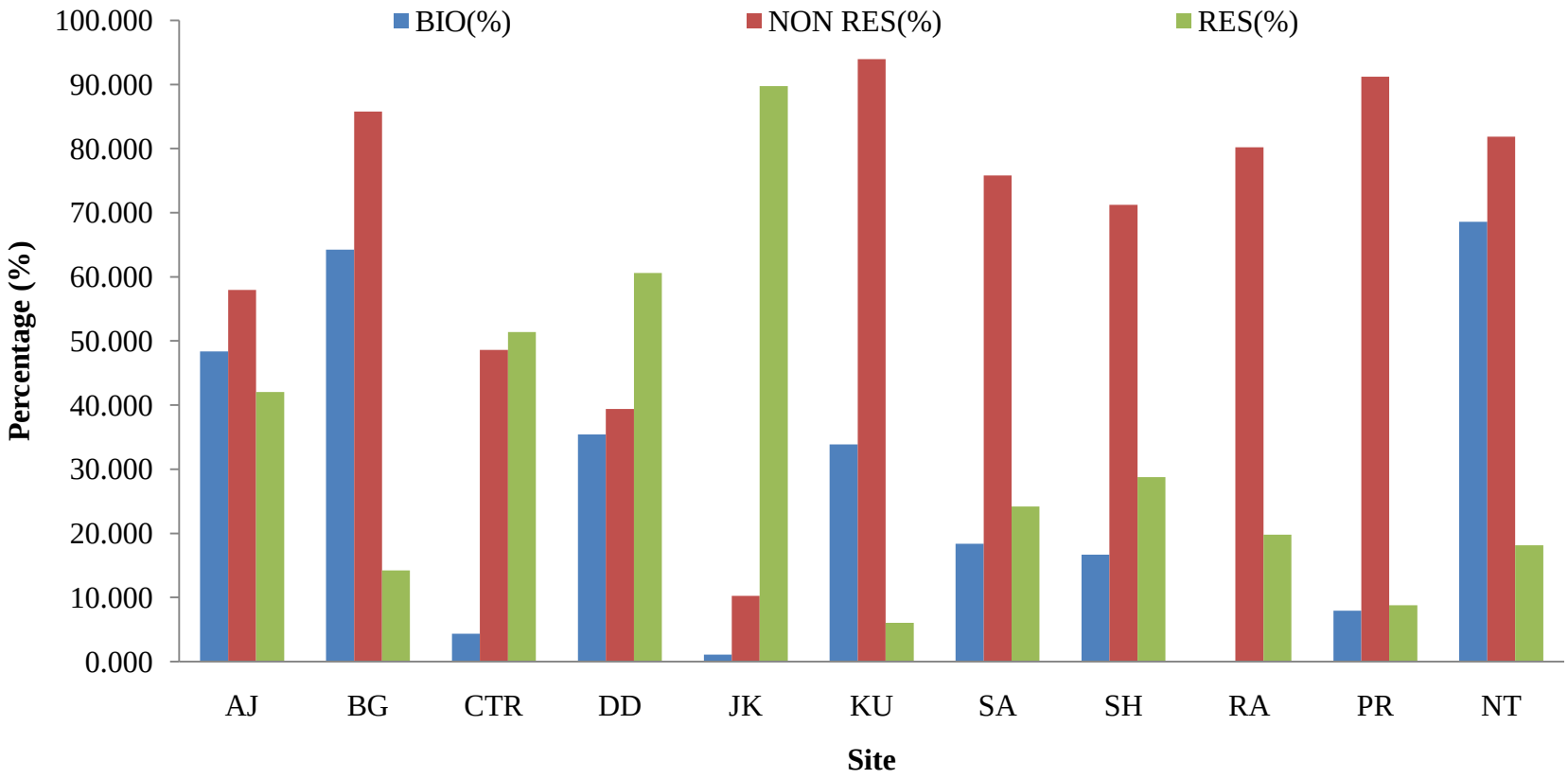


**Figure 4.9: Bioavailable, residual and non-residual fractions copper (Cu) during the wet season in the refuse waste-soils**

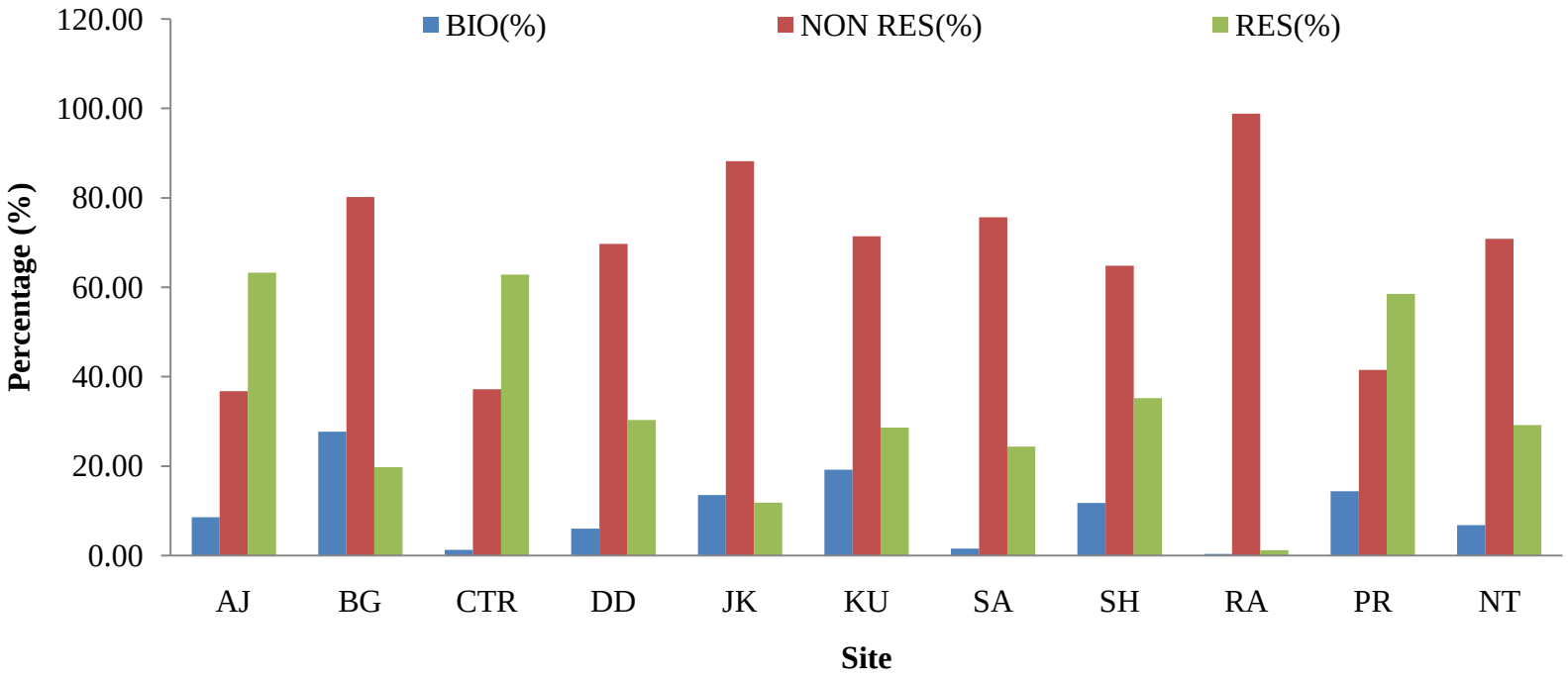


**Figure 4.10: Bioavailable, residual and non-residual (%) fractions of copper (Cu) during the dry season in soil**

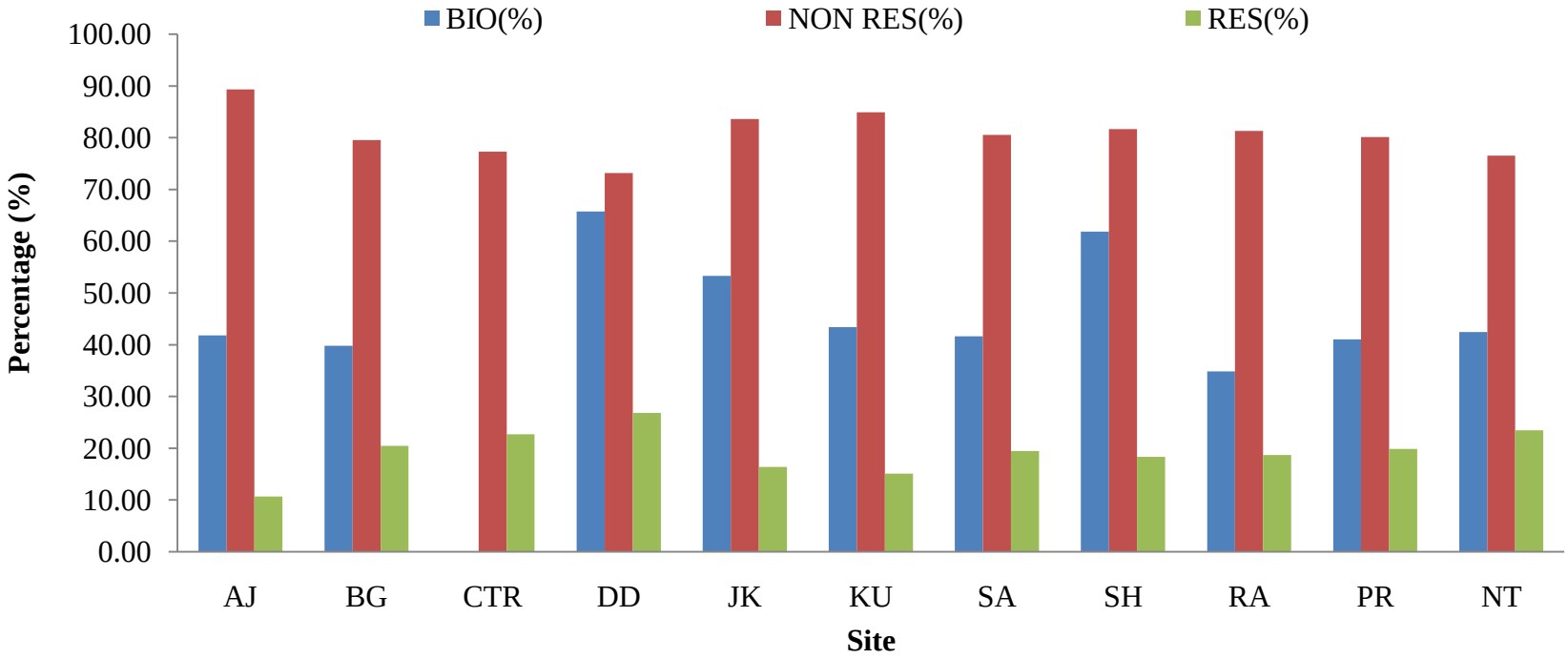


**Figure 4.11: Bioavailable, residual and non-residual cadmium in the wet season refuse waste soils**

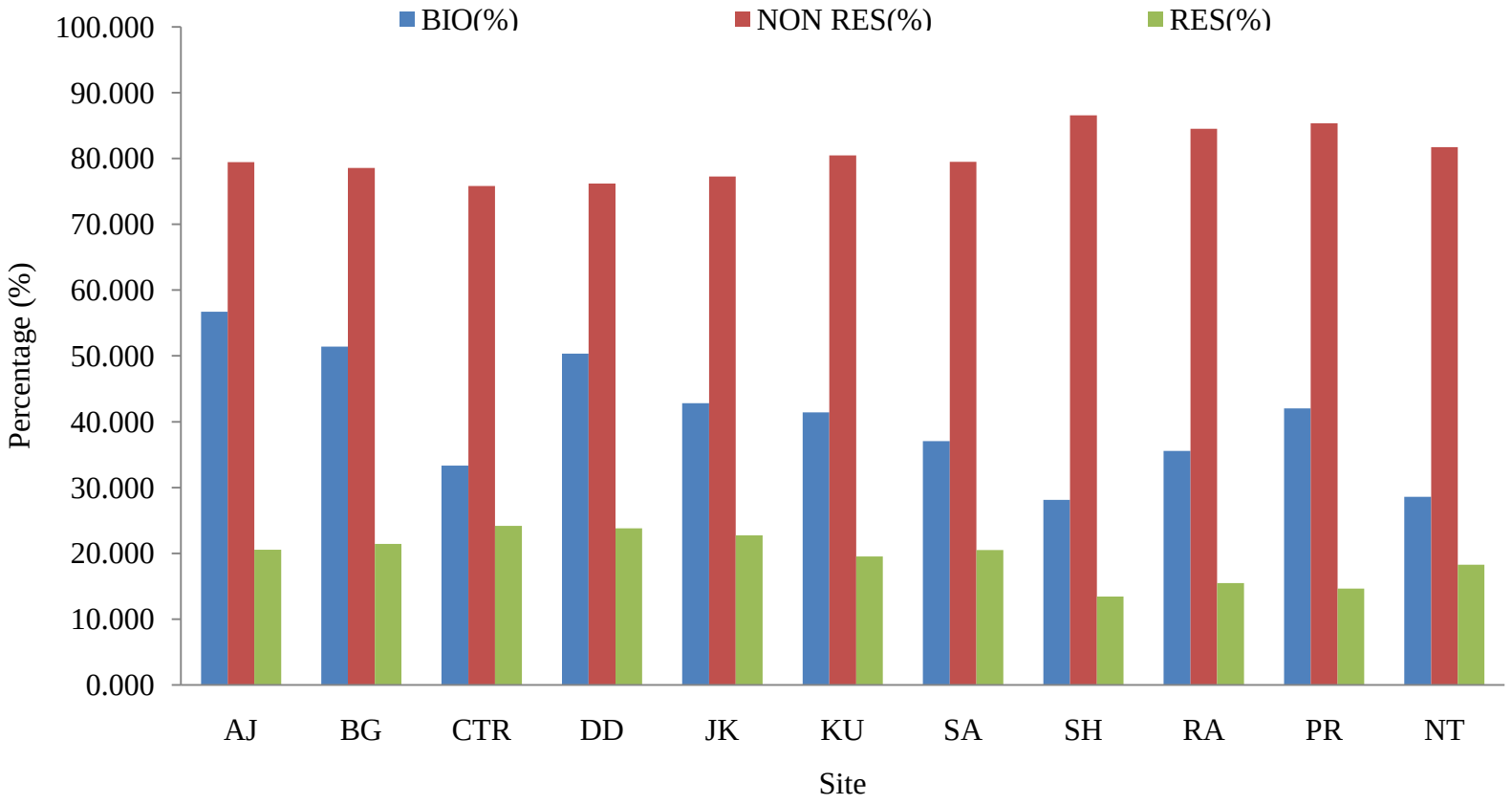


**Figure 4.12: Bioavailable, residual and non-residual (%) cadmium (Cd) in the dry season refuse waste soils**

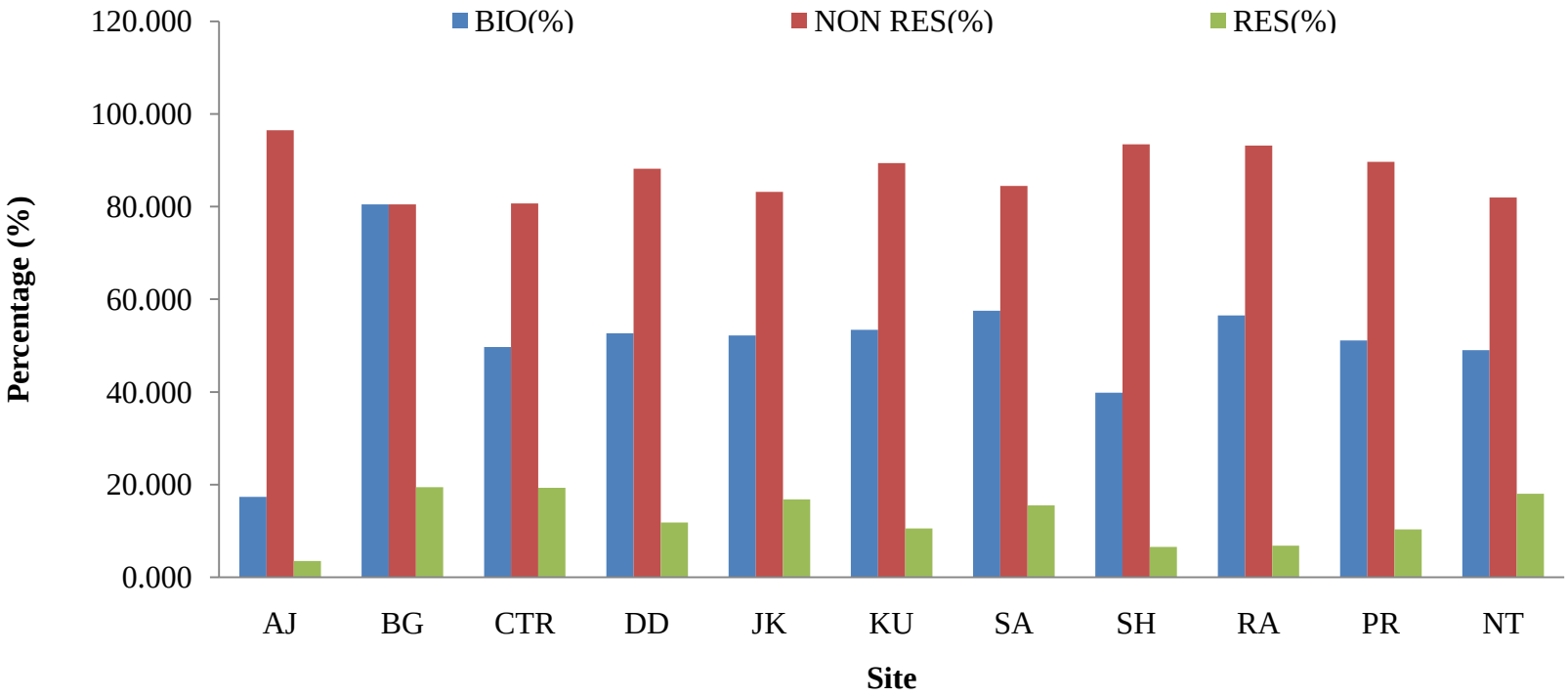


**Figure 4.13: Bioavailable, residual and non-residual fractions of mercury (Hg) during the wet season in refuse waste soils**

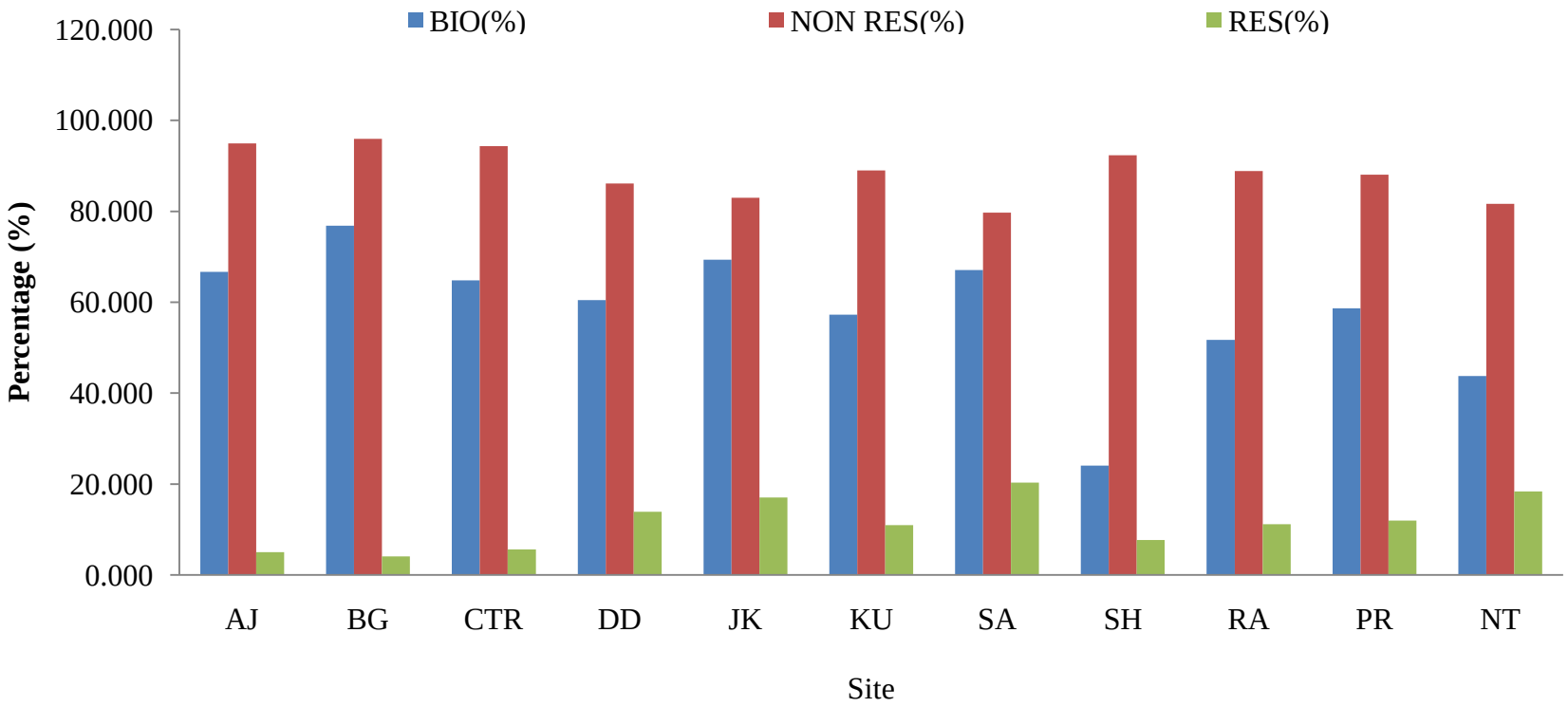


**Fig. 4.14: Bioavailable, residual and non-residual fractions of mercury (Hg) during the dry season for the refuse waste soils**

while the residual and non-residual fractions were 4.058 (BG) to 20.317% (SA) and 79.683 (SA) to 95.942% (CTR). The percentage range of the bioavailable fraction during the dry season was 17.35 to 80.52% (BG) while the non-residual and the residual fractions had 80.523 % (BG) to 96.52 % (AJ) and 3.484 (AJ) to 19.477% (BG), respectively.

**4.8: Water Quality**

4.8.1: Physico-chemical parameters of leachates

The physico-chemical properties of leachates across the sites is presented in Table 4.13. The physico-chemical parameters of leachates and the hand-dug well water were compared in Figures 4.15 to 4.30.

The pH of the dumpsite–leachates range from 6.9(RA) to 7.75(BG, SH), indicating slightly acidic and alkaline conditions of the leachate. The total alkalinity range from 110.5(KU) to 2202 mg $CaCO_3$/L. Nitrate and Nitrite levels were in the range of 0.35 (DD) to 110.5 (SH, RA) and 1.0 (NTC) to 78.50 mg/L (BG) respectively. The concentrations range for ammonia-nitrogen was from 0.205(NTC, KU) to 0.515 mg/L (PR, SH).The Turbidity levels recorded in the leachate samples ranged from 3.0 (KU) to 6.5 NTU (SH, RA). The chloride levels ranged from 7.98 (BG) to 1599.4 mg/L (SH) was obtained. Other anion detected in the Leachates samples was $S04^{2-}$S, with the range of 14.5 (AJ) to 999.5 mg/L (JK). The colour of the leachates ranged from 14.50 CTU (CTR) to 70.50 CTU (AJ). The higher value was recorded at site AJ. The electrical conductivities (EC) of the leachate samples ranged from 81.0 (CTR) to 14,001.5 $\mu scm^{-1}$ (RA).

**Table 4.13a: The Physico-chemical parameters of the dumpsite leachates during the wet season.**

| | SITE | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | AJ | BG | CTR | DD | SH | NTC | JK | KU | PR | SH | RA | STD |
| Temp($^{o}$C) | 22.500± 0.500 | 21.500± 0.707 | 22.500± 0.707 | 21.500± 0.707 | 21.500± 0.707 | 22.500± 0.500 | 21.500± 0.707 | 22.500± 0.707 | 21.500± 0.707 | 22.500± 0.707 | 21.500± 0.707 | 5-50$^{0}$C |
| pH | 7.350± 0.071 | 7.550± 0.212 | 7.050± 0.071 | 7.750± 0.071 | 7.550± 0.071 | 7.750± 0.071 | 7.450± 0.071 | 6.950± 0.071 | 7.450± 0.071 | 7.250± 0.354 | 6.900± 0.141 | 7-9.2 |
| EC(µs/cm) | 2600.500± 0.707 | 271.000± 1.414 | 81.000± 1.414 | 260.5.000± 0.707 | 14000.500± 0.707 | 2500.500± 0.707 | 1751.000± 1.414 | 2450.500± 0.707 | 270.500± 0.707 | 150.500± 0.707 | 14001.500± 0.707 | 1.2-14 |
| TS(mg/L) | 1810.500± 0.707 | 2100.500± 0.707 | 560.500± 0.707 | 1910.500± 0.707 | 7850.500 0.707 | 1630.500± 0.707 | 1981.000± 1.414 | 1421.000± 1.414 | 1331.000± 1.414 | 770.500± 0.707 | 7853.000± 2.828 | 500 |
| SS(mg/L) | 960.500± 0.707 | 1240.500± 0.707 | 370.500± 0.707 | 960.500± 0.707 | 6330.500± 0.707 | 1261.000± 1.414 | 1321.000± 1.414 | 770.500± 0.707 | 861.000± 1.414 | 441.000± 1.414 | 6325.500± 0.707 | 10 |
| DS(mg/L) | 850.500 0.707 | 861.000± 1.414 | 191.500± 0.707 | 950.500± 0.707 | 1521.000± 1.414 | 360.500± 0.707 | 660.500± 0.707 | 641.000± 1.414 | 460.500± 0.707 | 331.000± 1.414 | 1521.500± 0.707 | 500 |
| TH(mg/L) | 9090.500± 0.707 | 3029.500± 0.707 | 23264.500± 48.790 | 6059.000± 1.414 | 4039.000± 1.414 | 6059.000± 1.414 | 3029.000± 1.414 | 1011.000± 1.414 | 6044.000± 22.627 | 4039.000± 1.414 | 4041.000± 1.414 | 100 |
| Alkalinity(mg/L) | 1501.000± 1.414 | 401.000± 1.414 | 999.500± 0.707 | 1100.500± 0.707 | 2200.500± 0.707 | 200.500± 0.707 | 799.000± 1.414 | 110.500± 0.707 | 601.000± 1.414 | 699.500± 0.707 | 2202.000± 1.414 | 100-500 |
| $NO_2^-$-N(mg/L) | 11.500± 0.707 | 78.500± 0.707 | 4.500± 0.707 | 15.500± 0.707 | 63.500± 0.707 | 1.000± 0.000 | 12.500± 0.707 | 1.500± 0.707 | 8.000± 1.414 | 10.500± 0.707 | 63.000± 1.414 | 45 |
| $NO_3^-$-N(mg/L) | 3.800± 0.141 | 7.650± 0.071 | 2.050± 0.071 | 0.350± 0.071 | 110.500± 0.707 | 3.050± 0.071 | 7.050± 0.071 | 5.250± 0.071 | 1.600± 0.141 | 4.050± 0.071 | 110.000± 2.828 | 45 |
| $SO_4^{2-}$ - S(mg/L) | 14.500± 0.707 | 500.500± 0.707 | 24.500± 0.707 | 80.500± 0.707 | 500.500± 0.707 | 24.500± 0.707 | 999.500± 0.707 | 74.500± 0.707 | 59.500± 0.707 | 24.500± 0.707 | 496.000± 1.414 | 200-600 |
| $PO_4^{3-}$-P(mg/L) | 1.450± 0.071 | 18.450± 0.071 | 1.650± 0.071 | 8.800± 0.141 | 14.400± 0.141 | 8.050± 0.071 | 1.650± 0.071 | 20.050± 0.071 | 22.250± 0.071 | 19.750± 0.071 | 14.400± 0.141 | |
| Cl(mg/L) | 99.955± 0.007 | 7.985± 0.007 | 399.860± 0.014 | 549.700± 0.141 | 1599.400± 0.000 | 399.860± 0.014 | 399.860± 0.014 | 549.750± 0.071 | 449.850± 0.014 | 549.700± 0.141 | 1599± 1.414 | 5 -15 |

**Table 4.13b: The Physico-chemical parameters of the dumpsite leachates during the wet season.**

| | SITE | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | AJ | BG | CTR | DD | SH | NTC | JK | KU | PR | SH | RA | STD |
| Colour | 70.500± 0.707 | 29.500± 0.707 | 14.500± 0.707 | 69.500± 0.707 | 69.500± 0.707 | 40.500± 0.707 | 60.500± 0.707 | 40.500± 0.707 | 69.500± 0.707 | 49.500± 0.707 | 68.500± 0.707 | 0.01 |
| Turbidity(NTU) | 5.500± 0.707 | 6.500± 0.707 | 2.500± 0.707 | 4.500± 0.707 | 6.500± 0.707 | 4.500± 0.707 | 2.500± 0.707 | 3.000± 0.000 | 3.500± 0.707 | 2.500± 0.707 | 6.500± 0.707 | 5 -25 |

The temperature range of the leachates measured across the sites was 21.50 (RA, PR, JK, SH, DA, PR) to 22 $^{0}$C (CTR, AJ, NTC, KU and SA). The range of the total dissolved solids across the sites was 191.50 (CTR) to 521.50 mg/L (RA).

4.8.2: Total heavy metal contents in leachates

The five heavy metals investigated were Hg, Zn, Pb, Cu and Cd in the leachates samples were analyzed and the results presented in Figures 4.33 to 4.37. The concentration range of Hg was from BDL (CTR) to 3.680 mg/L (JK) while the range of Pb in the leachate samples across sites was from BDL (CTR, SH) to 1.444 mg/L (BG). Also the concentration range of BDL (CTR) to 1.598 mg/L (DD) was recorded for Cu in the samples across the sites. The concentrations range of Cd was 0.330(JK) to 0.071mg/L (SH) across the sites. Similarly, the range of Zn recorded in the samples across the sites was 0.095 (PR) to 4.941 mg/L (AJ).

4.8.3 Physico-chemical parameters of the well waters

Tables 4.12 and 4.13 showed the physicochemical parameters of the well waters in both the dry and wet seasons, respectively.

The temperature recorded in the well water across sites during the dry season range from 29.0 (SA) to 31.0$^{0}$C (SH) as presented in Table 4.12. Also, the range of 23.59 (BG, SH, JK, PR, RA) to 25$^{0}$C (AJ, CTR, NTC, KU, SA) was recorded during the wet season as prsented in Table 4.13. Similarly, the pH range in the water samples recorded during the dry season across the sites was 6.75 (CTR) to 7.96 (PR) while the range of 4.60 (RA) to 5.10 (NTC, DD) was recorded in the wet season for the pH as presented in Table 4.13.

The levels of electrical conductivities (EC) in the water samples across the sites range from 4.23 (AJ) to 2,568.5µs/cm (KU) in the dry season as presented in Table 4.12. Also, the range of 54 (CTR) to 9334µScm$^{-1}$ (RA) was recorded in the wet season as presented in Table 4.13. Also, the concentration of the total dissolved solids across the sites range from 180.50 to 7,700mg/L for the dry season as presented in Table 4.12 while the levels of total dissolved solids (TDS) in the water samples during the wet season range from 240 (NTC) to 1014.33 mg/L (RA) across the sites as presented in Table 4.13.

The range of the total alkalinity during the dry season was 3.50 (DD, NTC, JK, PR) to 15.50 mg/L as presented in Table 4.12 while the concentration range recorded in the wet season was 73.67 (KU) to 1468 (RA) mg/L as presented in Table 4.13. Also, the levels of Cl recorded in the dry season was 3.48 (SA) to 449.86 mg/L (AJ) as presented in Table 4.12 while the range of 5.30 (BG) to 1066.00 mg/L (SH) was recorded in the wet season as shown in Table 4.13.

Nitrate ($NO_3$-N) contents of the water samples across the sites range from 1.07 (PR) to 73.67 mg/L (SH, RA) in the wet season as presented in Table 4.13. Similarly, as presented in Table 4.12, the levels of $NO_3$-N in the dry season range from BDL (CTR JK) to 115.5 mg/L (AJ) across the sites.

Also, the levels of $NO_3^{-}$N recorded in the water samples during the wet season range from 0.60 (NTC) to 52.30 mg/L as presented in Table 4.13, while the range of 67.5000 (DD) to 147.500 mg/L (BG) was recorded in the well water samples during the dry season across the sites as presented in Table 4.12. The range of 0.97 (AJ) to 14.83 mg/L (PR) was recorded for the $PO4^{3-}$P in the water samples across the sites during the wet

season while the range of 1.05 (SH) to 6.50 (CTR) was recorded across the sites during the dry season, as presented in Table 4.13 and 4.12, respectively.

Simialarly, the concentrations range of 9.70 (AJ) to 666.30 mg/L (JK) $SO_4^{2-}$-S was recorded in the water across the sites during the wet season while the range of 4.500 (SA) to 500.500 mg/kg (KU) was recorded during the dry season as presented in the Table 4.13 and 4.12, respectively. Also, the levels of colour recorded for the well water samples during the wet season across the sites range from 19.67 (BG) to 47.0 TCU (AJ), as presented in Table 4.13 while the levels of colour recorded in the samples during the dry season across the sites range from 4.5 (SA, SH) to 14.50 mg/L (AJ), respectively, as presented in Table 4.12.

Also, the range of 0.015 (SH) to 0.115mg/L (AJ) mg/L was recorded for the $NH_4$ – N across the sites during the dry season as presented in Table 4.12 while the range of 0.137 (SH JK) to 0.340 mg/L (BG, RA) was recorded in the water samples across the sites during the wet season as presented in Table 4.13. Similarly, Table 4.13 showed the levels of turbidity in the well water samples across the sites ranging from 2.0 (KU) to 4.33 NTU (BG, RA) while the levels recorded during the dry season range from 1.75 (RA) to 174.50 NTU (AJ) as presented in Table 4.12.

### 4.8.4 Total heavy metal contents in the well waters for dry and wet seasons

The underground water across the sites near the dumpsites were analyzed for heavy metals such as Hg, Zn, Cd, Cu and Pb. The results of the analyses were compared with those in leachates and presented in Figures 4.33 to 4.41.

The concentration ranges of Zn the water across the sites and seasons (wet and dry) were 0.092 to 0.826 mg/L and 0.019 to 0.774 mg/L (Tables 4.14 and 4.15). Furthermore, the concentration ranges of lead recorded across the sites and seasons (wet and dry) were 0.068 to 0.648 mg/L and 0.008 to 0.564 mg/L (Tables 4.14 and 4.15). The concentration ranges for copper across the sites and seasons (wet and dry) was from BDL (CTR) to 2.589 mg/L (DD) and BDL to 0.654 mg/L (Tables 4.14 and 4.15).

Moreover, the concentration ranges of cadmium recorded across the sites and seasons (wet and dry) were: 0.006 (CTR) to 0.079 mg/L (KU) and 0.004 to 0.038 mg/L (Tables 4.9 and 4.10). The concentration ranges of the analysed mercury in the hand –dug water at the vicinity of the dumpsite across the sites and seasons (wet and dry) were: 0.211 (CTR) to 2.160 mg/L (BG) and 0.211 to 2.601 mg/L (Tables 4.9 and 4.10), respectively.

### 4. 8.5 Quality Indices of the Well Waters at the Vicinity of the Dumpsites

Table 4.14 and 4.15 showed the water quality index assessment of the well waters within the vicinity of the dumpsites for both the wet and dry season. The temperatures and pH across seasons (wet and dry) ranged from 23–25.88 $^{0}$C, 4.6-5.16 and 29.5–30.5, 6.75-7.95 respectively. The water quality indices were more than 300 as shown in Tables 4.14 and 4.15.

### 4.8.6 Correlation matrices of water and leachates

The correlation matrices of the physicochemical parameters of well water and leachtes during the wet season are presented in Table 4.15. The correlation coefficients of 1.0, and 0.266 were recorded for the correlation of TempL Vs TempW and THW, respectively, as presented in the Table 4.15.

**Table 4.14a: The Physico-chemical parameters of well waters during the dry season**

| Parameter | SITE | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AJ | BG | CTR | DD | SH | NTC | JK | KU | PR | SA | RA | STD |
| Temp($^0$C) | 29.500± 0.707 | 29.500± 0.707 | 30.500± 0.707 | 31.000± 1.414 | 31.000± 1.414 | 30.500± 0.707 | 30.500± 0.707 | 30.500± 0.707 | 29.500± 0.707 | 29.000± 1.414 | 29.500± 0.707 | <40 |
| pH | 7.325± 0.007 | 7.785± 0.007 | 6.750± 0.212 | 7.610± 0.014 | 6.515± 1.421 | 7.655± 0.007 | 7.805± 0.007 | 7.505± 0.007 | 7.955± 0.007 | 7.660± 0.014 | 7.515± 0.007 | 7-9.2 |
| EC(µs/cm) | 4.230± 0.014 | 115.850± 0.071 | 115.700± 0.141 | 1052.500± 0.707 | 2231.500± 0.707 | 682.500± 0.707 | 674.500± 0.707 | 2568.500± 0.707 | 415.500± 0.707 | 290.2500± 0.071 | 237.350± 0.071 | 1.2-14 |
| TS(mg/L) | 2320.500± 0.707 | 1190.500± 0.707 | 540.500± 0.707 | 880.500± 0.707 | 1330.500± 0.707 | 580.500± 0.707 | 380.500± 0.707 | 7700.500± 8910.253 | 230.500± 0.707 | 260.500± 0.707 | 180.500± 0.707 | 500-1500 |
| SS(mg/L) | 520.500± 0.707 | 100.500± 0.707 | 420.500± 0.707 | 300.500± 0.707 | 90.500± 0.707 | 170.500± 0.707 | 10.500± 0.707 | 140.500± 0.707 | 150.500± 0.707 | 110.000± 0.000 | 50.500± 0.707 | 10 |
| DS(mg/L) | 2.035± 0.007 | 935.500± 0.707 | 59.250± 0.071 | 141.150± 0.071 | 1072.000± 0.000 | 335.500± 0.707 | 325.500± 0.707 | 1205.500± 0.707 | 137.850± 0.071 | 141.150± 0.071 | 115.850± 0.071 | 500 |
| TH(mg/L) | 10100.500± 0.707 | 14141.500± 0.707 | 212.000± 0.001 | 2020.000± 0.001 | 27272.500± 0.707 | 2020.500± 0.707 | 13131.500± 0.707 | 121.250± 0.071 | 363.650± 0.071 | 313.100± 0.141 | 2777.750± 3213.447 | 100-500 |
| TA(mg/L) | 15.500± 0.707 | 5.500± 0.707 | 3.500± 0.707 | 3.500± 0.707 | 4.500± 0.707 | 3.500± 0.707 | 3.500± 0.707 | 11.500± 0.707 | 3.500± 0.707 | 5.500± 0.707 | 5.500± 0.707 | 100-500 |
| $NO_2^-$N(mg/L) | 88.500± 0.707 | 147.500± 0.707 | 150.500.± 0.707 | 67.500± 0.707 | 95.500± 0.707 | 77.500± 0.707 | 140.500± 0.707 | 71.500± 0.707 | 101.500± 0.707 | 126.500± 0.707 | 96.500± 0.707 | 45 |
| $NO_3$-N(mg/L) | 115.500± 0.707 | 36.250± 0.071 | BDL | 1.750± 0.071 | 0.550± 0.000 | 1.750± 0.071 | BDL | 62.350± 0.071 | 1.050± 0.071 | 5.350± 0.071 | 7.500± 0.707 | 45 |
| $SO_4^{2-}$S(mg/L) | 20.500± 0.707 | 90.500± 0.707 | 19.500± 0.707 | 15.500± 0.707 | 500.500± 0.707 | 50.500± 0.707 | 34.500± 0.707 | 500.500± 0.707 | 65.500± 0.707 | 4.500± 0.707 | 30.500± 0.707 | 200-600 |
| $PO_4^{3-}$P(mg/L) | 2.850± 0.071 | 1.450± 0.071 | 116.500± 0.707 | 2.250± 0.071 | 1.050± 0.071 | 1.050± 0.071 | 1.350± 0.071 | 1.150± 0.071 | 1.650± 0.071 | 1.150± 0.071 | 2.450± 0.071 | 0.7 |
| Cl(mg/L) | 449.855± 0.007 | 56.475± 0.007 | 4.985± 0.007 | 55.975± 0.007 | 399.865± 0.007 | 27.485± 0.007 | 28.980± 0.014 | 499.840± 0.000 | 9.980± 0.014 | 3.480± 0.014 | 9.480± 0.014 | 200-600 |
| $NH_4$-N(mg/L) | 0.115± 0.007 | 0.155± 0.007 | 0.145± 0.007 | 0.15± 0.071 | 0.015± 0.007 | 0.025± 0.007 | 0.045± 0.007 | 0.145± 0.007 | 0.025± 0.007 | 0.025± 0.007 | 0.025± 0.007 | 0.5 |

**Table 4.14b: The Physico-chemical parameters of well waters during the dry season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | AJ | BG | CTR | DD | SH | NTC | JK | KU | PR | SA | RA | STD |
| Colour | 14.500± 0.707 | 5.500± 0.707 | 10.500± 0.707 | 5.500± 0.707 | 4.500± 0.707 | 5.500± 0.707 | 5.500± 0.707 | 5.500± 0.707 | 5.000± 0.000 | 4.500± 0.707 | 5.00± 0.000 | 0.01-0.02 |
| Turbidity(NTU) | 174.500± 0.707 | 2.215± 0.007 | 3.580± 0.014 | 21.500± 0.707 | 6.155± 0.007 | 11.700± 0.001 | 2.840± 0.001 | 39.100± 0.001 | 9.450± 0.000 | 5.950± 0.071 | 1.745± 0.007 | 5-25 |

Temp = Temperature, EC = Electorical conductivities, TS = Total solids, SS = suspended solids, DS = Dissolved solids, TH = Total hardness, Cl = chloride, $NO_2$- N = nitrite nitrogen, $NO_3$-N = nitrate nitrogen, $SO_4^{2}$— S = Sulphate sulphur

**Table 4.15a Correlation matrices of the physicochemical parameters in dumpsite leachates and water across the sites**

| Parameter | TempL | pHL | ECL | TSL | SSL | DSL | THL | ALKL | $NO_2NL$ | $NO_3NL$ | $SO_4SL$ | $PO_4SL$ | ClL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TempL | 1 | | | | | | | | | | | | |
| pHL | -0.093 | 1 | | | | | | | | | | | |
| ECL | -0.246 | -0.220 | 1 | | | | | | | | | | |
| TSL | -0.367 | -0.122 | 0.977** | 1 | | | | | | | | | |
| SSL | -0.346 | -0.139 | 0.983** | 0.997** | 1 | | | | | | | | |
| DSL | -0.430* | -0.023 | 0.846** | 0.913** | 0.877** | 1 | | | | | | | |
| THL | 0.266 | -0.179 | -0.241 | -0.292 | -0.260 | -0.414 | 1 | | | | | | |
| ALKL | -0.263 | -0.163 | 0.803** | 0.819** | 0.810** | 0.783** | 0.098 | 1 | | | | | |
| $NO_2NL$ | -0.450* | 0.022 | 0.602** | 0.720** | 0.698** | 0.757** | -0.303 | 0.509* | 1 | | | | |
| $NO_3NL$ | -0.311 | -0.224 | 0.982** | 0.985** | 0.992** | 0.849** | -0.212 | 0.822** | 0.686** | 1 | | | |
| $SO_4SL$ | -0.463* | 0.046 | 0.373 | 0.455* | 0.445* | 0.461* | -0.375 | 0.274 | 0.520* | 0.405 | 1 | | |
| $PO_4SL$ | -0.143 | -0.121 | 0.093 | 0.131 | 0.132 | 0.109 | -0.552** | -0.209 | 0.289 | 0.159 | -0.147 | 1 | |
| ClL | -0.259 | -0.253 | 0.916** | 0.897** | 0.913** | 0.723** | -0.198 | 0.744** | 0.450* | 0.932** | 0.272 | 0.216 | 1 |
| $NH_3NL$ | -0.492* | -0.007 | 0.283 | 0.417 | 0.419 | 0.366 | 0.238 | 0.459* | 0.603** | 0.435* | 0.302 | 0.186 | 0.377 |
| COLOURL | -0.337 | 0.201 | 0.432* | 0.474* | 0.441* | 0.586** | -0.476* | 0.548** | 0.113 | 0.396 | 0.192 | 0.064 | 0.425* |
| TURBIDL | -0.295 | 0.217 | 0.610** | 0.686** | 0.654** | 0.770** | -0.261 | 0.540** | 0.785** | 0.611** | 0.198 | 0.110 | 0.376 |
| TempW | 1.000** | -0.093 | -0.246 | -0.367 | -0.346 | -0.430* | 0.266 | -0.263 | -0.450* | -0.311 | -0.463* | -0.143 | -0.259 |
| pHW | -0.091 | 1.000** | -0.218 | -0.121 | -0.138 | -0.022 | -0.179 | -0.161 | 0.021 | -0.222 | 0.044 | -0.121 | -0.250 |
| ECW | -0.246 | -0.220 | 1.000** | 0.977** | 0.983** | 0.846** | -0.241 | 0.803** | 0.602** | 0.982** | 0.373 | 0.093 | 0.916** |
| TSW | -0.367 | -0.122 | 0.977** | 1.000** | 0.997** | 0.913** | -0.292 | 0.819** | 0.720** | 0.985** | 0.455* | 0.131 | 0.897** |
| SSW | -0.241 | 0.331 | 0.599** | 0.615** | 0.615** | 0.556** | -0.209 | 0.475* | 0.451* | 0.600** | 0.325 | 0.063 | 0.535* |
| DSW | -0.430* | -0.023 | 0.846** | 0.913** | 0.877** | 1.000** | -0.414 | 0.783** | 0.757** | 0.849** | 0.461* | 0.109 | 0.723** |
| THW | 0.266 | -0.179 | -0.241 | -0.292 | -0.260 | -0.414 | 1.000** | 0.098 | -0.303 | -0.212 | -0.375 | -0.552** | -0.198 |
| ALKW | -0.263 | -0.163 | 0.803** | 0.819** | 0.810** | 0.783** | 0.098 | 1.000** | 0.509* | 0.822** | 0.274 | -0.209 | 0.744** |
| $NO_2NW$ | -0.450* | 0.022 | 0.602** | 0.720** | 0.698** | 0.757** | -0.303 | 0.509* | 1.000** | 0.686** | 0.520* | 0.289 | 0.450* |
| $NO_3NW$ | -0.311 | -0.224 | 0.982** | 0.985** | 0.992** | 0.849** | -0.212 | 0.822** | 0.686** | 1.000** | 0.405 | 0.159 | 0.932** |
| $SO_4SW$ | -0.463* | 0.046 | 0.373 | 0.455* | 0.445* | 0.461* | -0.375 | 0.274 | 0.520* | 0.405 | 1.000** | -0.147 | 0.272 |
| $PO_4PW$ | -0.143 | -0.121 | 0.093 | 0.131 | 0.132 | 0.109 | -0.552** | -0.209 | 0.289 | 0.159 | -0.147 | 1.000** | 0.216 |
| ClW | -0.259 | -0.253 | 0.916** | 0.897** | 0.913** | 0.723** | -0.198 | 0.744** | 0.450* | 0.932** | 0.272 | 0.216 | 1.000** |
| $NH_3NW$ | -0.489* | -0.006 | 0.286 | 0.418 | 0.421 | 0.366 | 0.237 | 0.459* | 0.602** | 0.437* | 0.300 | 0.189 | 0.379 |
| COLOURW | -0.337 | 0.201 | 0.432* | 0.474* | 0.441* | 0.586** | -0.476* | 0.548** | 0.113 | 0.396 | 0.192 | 0.064 | 0.425* |
| TURBIDW | -0.295 | 0.217 | 0.610** | 0.686** | 0.655** | 0.770** | -0.261 | 0.540** | 0.785** | 0.611** | 0.198 | 0.111 | 0.376 |

**Table 4.15b: Correlation matrices of the physicochemical parameters in dumpsite leachates and water across the sites (continued)**

| Parameters | $NH_3NL$ | COLOURL | TURBIDL | TempW | pHW | ECW | TSW | SSW | DSW | THW | ALKW | $NO_2NW$ | $NO_3NW$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $NH_3NL$ | 1 | | | | | | | | | | | | |
| COLOURL | 0.052 | 1 | | | | | | | | | | | |
| TURBIDL | 0.304 | 0.308 | 1 | | | | | | | | | | |
| TempW | -0.493* | -0.337 | -0.295 | 1 | | | | | | | | | |
| pHW | -0.009 | 0.203 | 0.215 | -0.091 | 1 | | | | | | | | |
| ECW | 0.283 | 0.432* | 0.610** | -0.246 | -0.218 | 1 | | | | | | | |
| TSW | 0.417 | 0.474* | 0.686** | -0.367 | -0.121 | 0.977** | 1 | | | | | | |
| SSW | 0.244 | 0.301 | 0.433* | -0.241 | 0.334 | 0.599** | 0.615** | 1 | | | | | |
| DSW | 0.366 | 0.586** | 0.770** | -0.430* | -0.022 | 0.846** | 0.913** | 0.556** | 1 | | | | |
| THW | 0.238 | -0.476* | -0.261 | 0.266 | -0.179 | -0.241 | -0.292 | -0.209 | -0.414 | 1 | | | |
| ALKW | 0.459* | 0.548** | 0.540** | -0.263 | -0.161 | 0.803** | 0.819** | 0.475* | 0.783** | 0.098 | 1 | | |
| $NO_2NW$ | 0.603** | 0.113 | 0.785** | -0.450* | 0.021 | 0.602** | 0.720** | 0.451* | 0.757** | -0.303 | 0.509* | 1 | |
| $NO_3NW$ | 0.435* | 0.396 | 0.611** | -0.311 | -0.222 | 0.982** | 0.985** | 0.600** | 0.849** | -0.212 | 0.822** | 0.686** | 1 |
| $SO_4SW$ | 0.302 | 0.192 | 0.198 | -0.463* | 0.044 | 0.373 | 0.455* | 0.325 | 0.461* | -0.375 | 0.274 | 0.520* | 0.405 |
| $PO_4PW$ | 0.186 | 0.064 | 0.110 | -0.144 | -0.121 | 0.093 | 0.131 | 0.063 | 0.109 | -0.552** | -0.209 | 0.289 | 0.159 |
| ClW | 0.377 | 0.425* | 0.376 | -0.259 | -0.250 | 0.916** | 0.897** | 0.535* | 0.723** | -0.198 | 0.744** | 0.450* | 0.932** |
| $NH_3NW$ | 1.000** | 0.054 | 0.308 | -0.489* | -0.008 | 0.286 | 0.418 | 0.248 | 0.366 | 0.237 | 0.459* | 0.602** | 0.437* |
| COLOURW | 0.052 | 1.000** | 0.308 | -0.337 | 0.203 | 0.432* | 0.474* | 0.301 | 0.586** | -0.476* | 0.548** | 0.113 | 0.396 |
| TURBIDW | 0.305 | 0.308 | 1.000** | -0.295 | 0.215 | 0.610** | 0.686** | 0.433* | 0.770** | -0.261 | 0.540** | 0.785** | 0.611** |

**Table 4.15c: Correlation matrices of the physicochemical parameters in dumpsite leachates and water across the sites continued**

| Parameters | $SO_4$SW | $PO_4$PW | ClW | $NH_3$NW | COLOURW | TURBIDW |
|---|---|---|---|---|---|---|
| $SO_4$SW | 1 | | | | | |
| $PO_4$PW | -0.147 | 1 | | | | |
| ClW | 0.272 | 0.216 | 1 | | | |
| $NH_3$NW | 0.300 | 0.189 | 0.379 | 1 | | |
| COLOURW | 0.192 | 0.064 | 0.425* | 0.054 | 1 | |
| TURBIDW | 0.198 | 0.111 | 0.376 | 0.309 | 0.308 | 1 |

**Table 4.16a: Physico-chemical parameters of well waters for the wet season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameters | AJ | BG | CTR | DD | SH | NTC | JK | KU | PR | SA | RA |
| Temp($^0$C) | 25.000± 0.790 | 23.889± 0.790 | 25.000± 0.790 | 23.889± 0.790 | 23.889± 0.790 | 25.000± 0.790 | 23.889± 0.790 | 25.000± 0.790 | 23.889± 0.790 | 25.000± 0.790 | 23.889± 0.790 |
| pH | 4.900± 0.050 | 5.033± 0.140 | 4.700± 0.050 | 5.167± 0.050 | 5.033± 0.050 | 5.167± 0.050 | 4.967± 0.050 | 4.633± 0.050 | 4.967± 0.050 | 4.833± 0.240 | 4.600± 0.090 |
| EC(µs/cm) | 1733.667± 0.470 | 180.667± 0.940 | 54.000± 0.940 | 173.667± 0.470 | 9333.667± 0.470 | 1667.000± 0.470 | 1167.333± 0.940 | 1633.667± 0.470 | 180.333± 0.470 | 100.333± 0.470 | 9334.333± 0.470 |
| TS(mg/L) | 1207.000± 0.470 | 1400.300± 0.470 | 373.660± 0.470 | 1273.667± 0.470 | 5233.667± 0.470 | 1087.000± 0.470 | 1320.667± 0.940 | 947.333± 0.940 | 887.333± 0.94 | 513.667± 0.47 | 5235.333± 1.89 |
| SS(mg/L) | 640.333± 0.470 | 827.000± 0.470 | 247.000± 0.470 | 640.333± 0.470 | 4220.333± 0.470 | 840.6667± 0.940 | 880.667± 0.940 | 513.667± 0.470 | 574.000± 0.940 | 294.000± 0.940 | 4217.000± 0.470 |
| DS(mg/L) | 567.000± 0.470 | 574.000± 0.940 | 127.667± 0.470 | 633.667± 0.470 | 1014.000± 0.940 | 240.333± 0.470 | 440.333± 0.470 | 427.333± 0.940 | 307.000± 0.470 | 220.667± 0.940 | 1014.333± 0.470 |
| TH(mg/L) | 6060.333± 0.470 | 2019.667± 0.470 | 159.667± 32.530 | 4039.333± 0.940 | 2692.667± 0.940 | 4039.333± 0.940 | 2019.333± 0.940 | 674.000± 0.940 | 4029.333± 15.080 | 2692.667± 0.940 | 2694.000± 0.940 |
| TA(mg/L) | 1000.667± 0.94 | 267.333± 0.94 | 666.333± 0.47 | 733.667± 0.47 | 1467± 0.47 | 133.667± 0.47 | 532.667± 0.94 | 73.667± 0.47 | 400.667± 0.94 | 466.333± 0.47 | 1468.000± 0.94 |
| $NO_2$-N(mg/L) | 7.667± 0.47 | 52.333± 0.47 | 3.0± 0.47 | 10.333± 0.47 | 42.333± 0.47 | 0.667± 0.00 | 8.333± 0.47 | 1.00± 0.47 | 5.33± 0.94 | 7.00± 0.47 | 42.00± 0.94 |
| $NO_3$-N(mg/L) | 2.533± 0.09 | 5.10± 0.05 | 1.367± 0.05 | 0.233± 0.05 | 73.667± 0.47 | 2.033± 0.05 | 4.7± 0.05 | 3.5± 0.05 | 1.067± 0.09 | 2.7± 0.05 | 73.333± 1.89 |
| $SO_4^{2-}$-S(mg/L) | 9.667± 0.47 | 333.667± 0.47 | 16.330± 0.470 | 53.666± 0.47 | 333.666± 0.47 | 16.333± 0.47 | 666.333± 0.47 | 49.667± 0.47 | 39.667± 0.47 | 16.333± 0.47 | 330.667± 0.94 |

**Table 4.16a: Physico-chemical parameters of well waters for the wet season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameters | AJ | BG | CTR | DD | SH | NTC | JK | KU | PR | SA | RA |
| $PO_4^{3-}$P(mg/L) | 0.967± 0.05 | 12.300± 0.05 | 1.100± 0.05 | 5.867± 0.09 | 9.600± 0.09 | 5.367± 0.05 | 1.10± 0.05 | 13.367± 0.05 | 14.833± 0.05 | 13.167± 0.05 | 9.60± 0.09 |
| Cl(mg/L) | 66.630± 0.00 | 5.3200± 0.00 | 266.570± 0.01 | 366.460± 0.09 | 1066.260± 0.00 | 266.570± 0.01 | 266.570± 0.01 | 366.500± 0.05 | 299.900± 0.01 | 366.460± 0.09 | 1066.000± 0.94 |
| $NH_4$-N(mg/L) | 0.157± 0.00 | 0.340± 0.01 | 0.340± 0.01 | 0.297± 0.00 | 0.343± 0.00 | 0.137± 0.00 | 0.237± 0.00 | 0.137± 0.00 | 0.343± 0.00 | 0.217± 0.00 | 0.340± 0.01 |
| Colour | 47.00± 0.47 | 19.667± 0.47 | 9.667± 0.47 | 46.333± 0.47 | 46.333± 0.47 | 27.00± 0.47 | 40.333± 0.47 | 27.00± 0.47 | 46.333± 0.47 | 33.00± 0.47 | 45.667± 0.47 |
| Turbidity | 3.667± 0.47 | 4.333± 0.47 | 1.667± 0.47 | 3.000± 0.47 | 4.333± 0.47 | 3.000± 0.47 | 1.667± 0.47 | 2.000± 0.00 | 2.333± 0.47 | 1.667± 0.47 | 4.333± 0.47 |

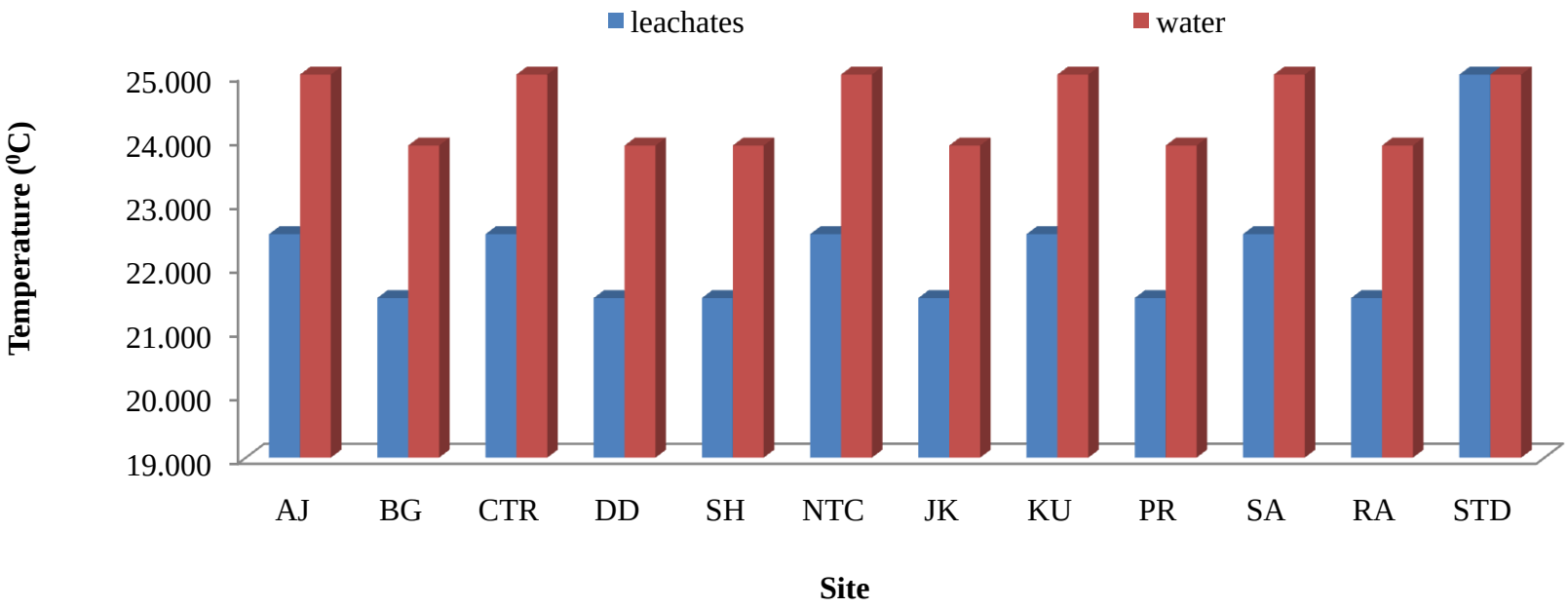


**Figure 4.15: Temperature of the dumpsite-leachates and well waters**

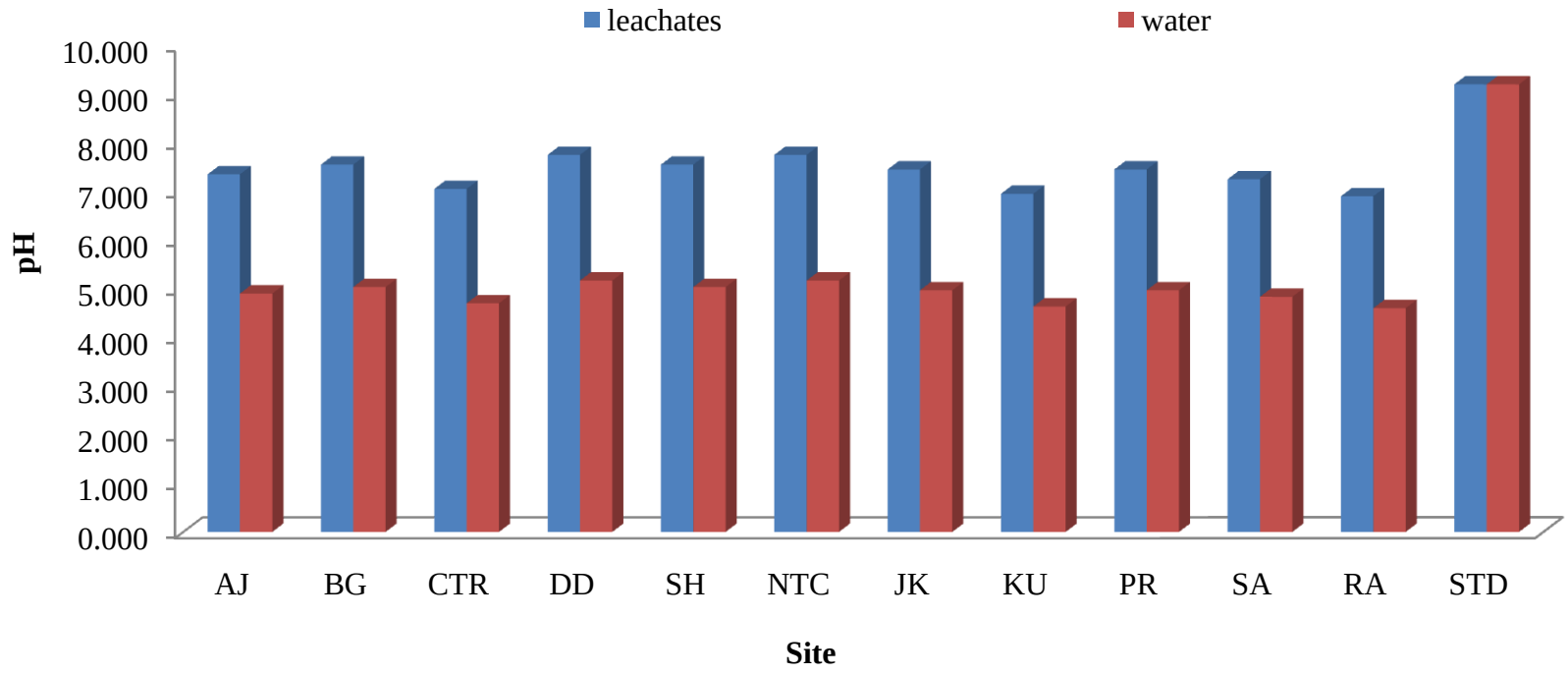


**Figure 4.16: pH of the dumpsite-leachates and well waters**

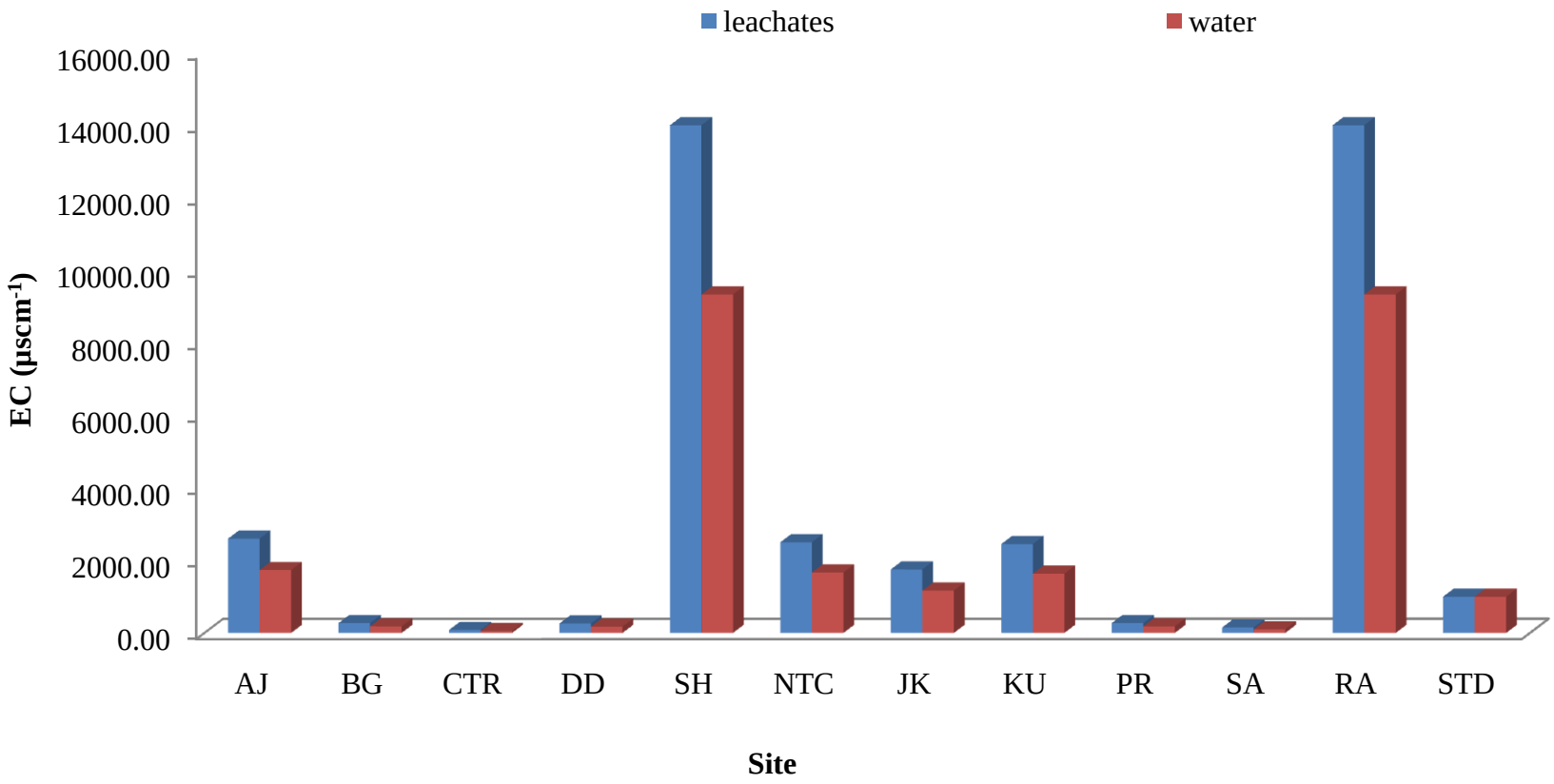


**Figure 4.17: The electrical conductivities of the dumpsite-leachates and well-water**

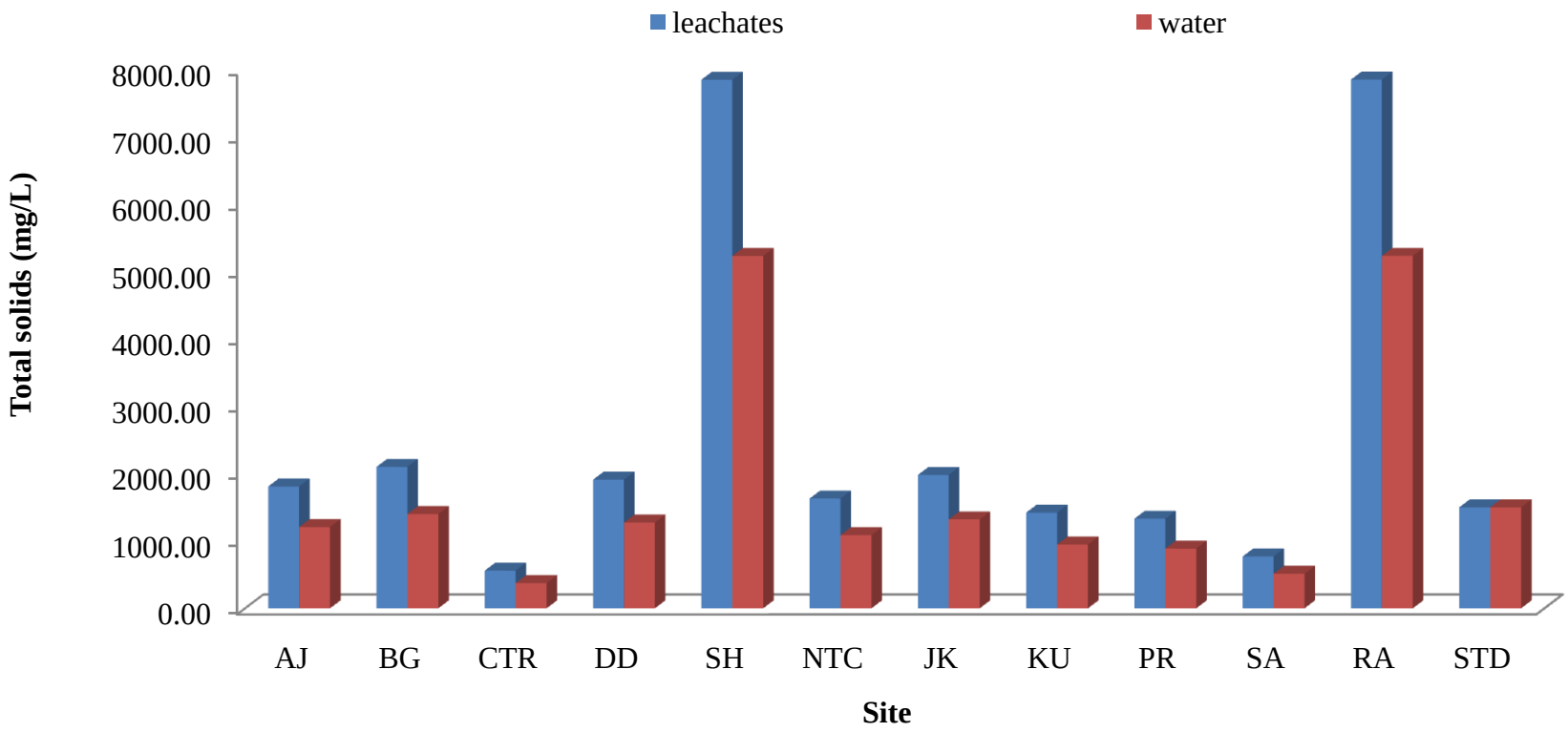


**Figure 4.18: Concentrations of the total solids in the dumpsite-leachates and well water**

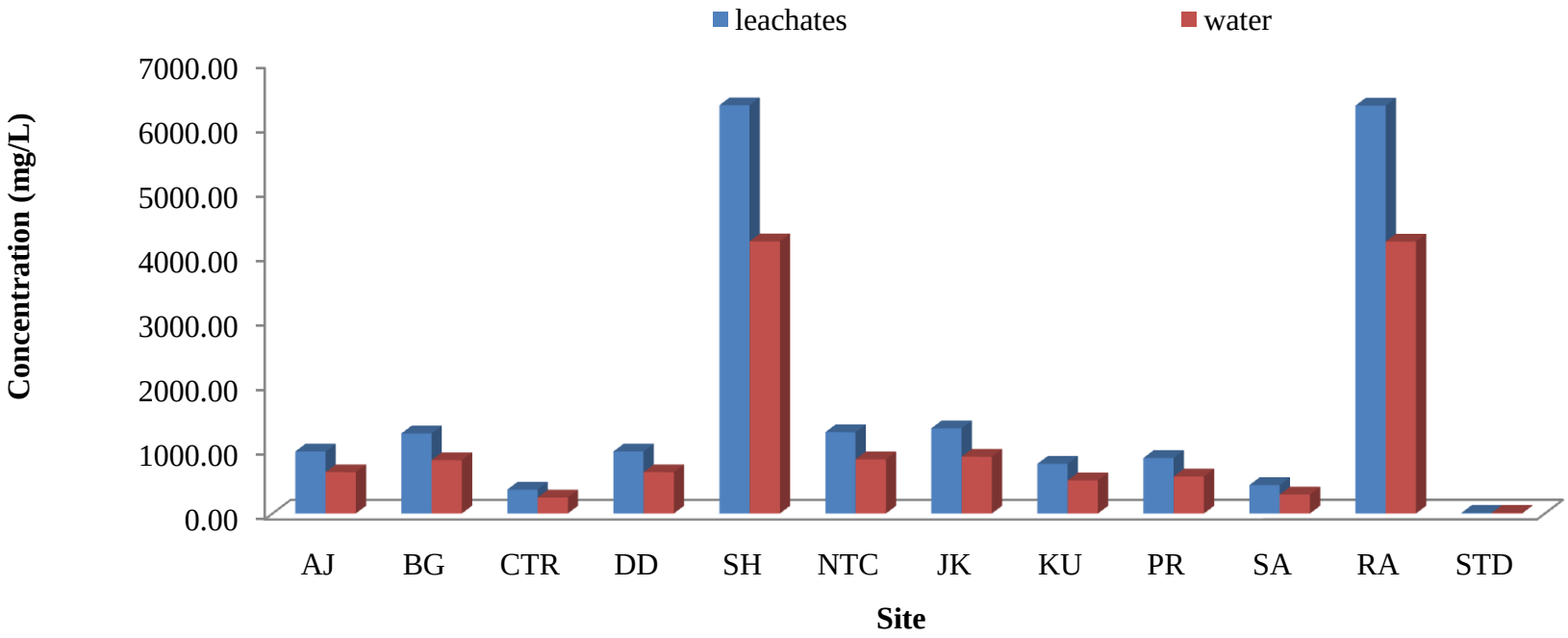


**Figure 4.19: Concentrations of the suspended solids in dumpsite-leachates and well waters**

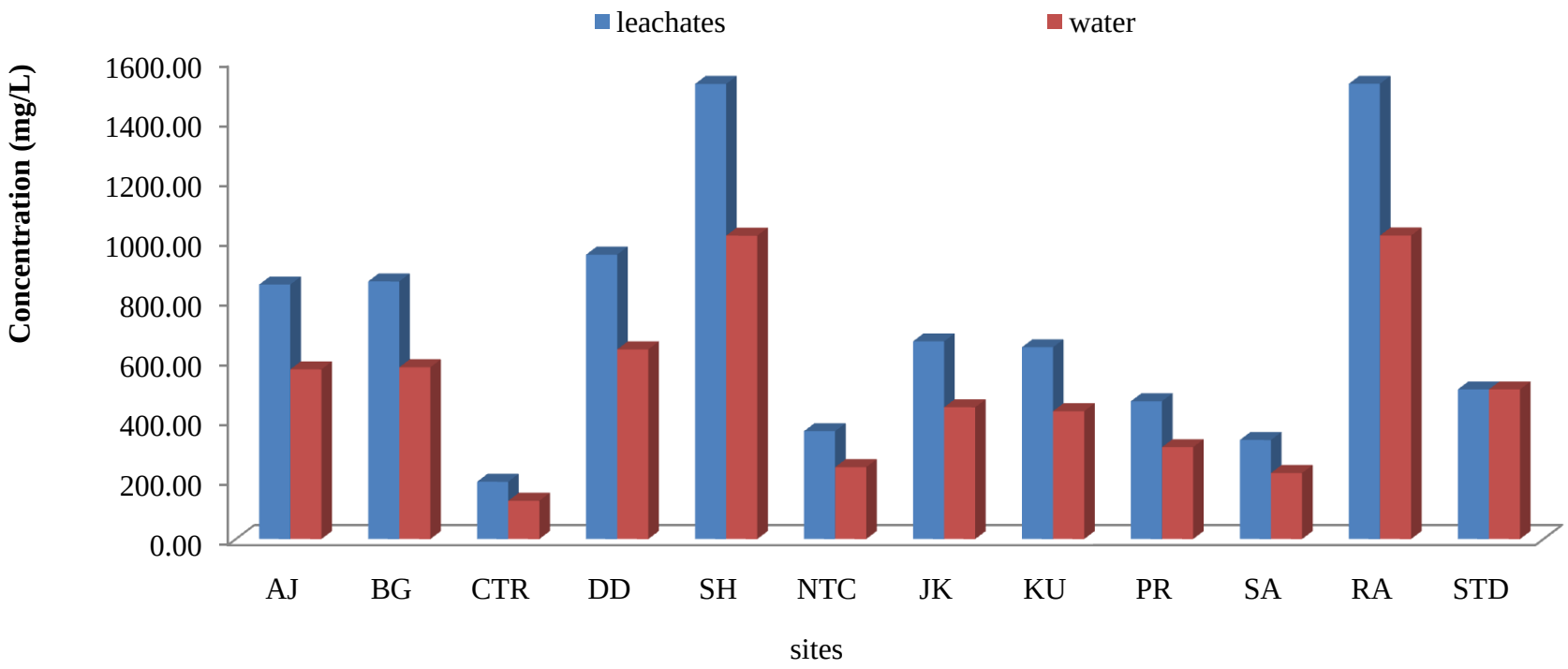


**Figure 4.20: Concentrations of dissolved solids in leachates and water samples**

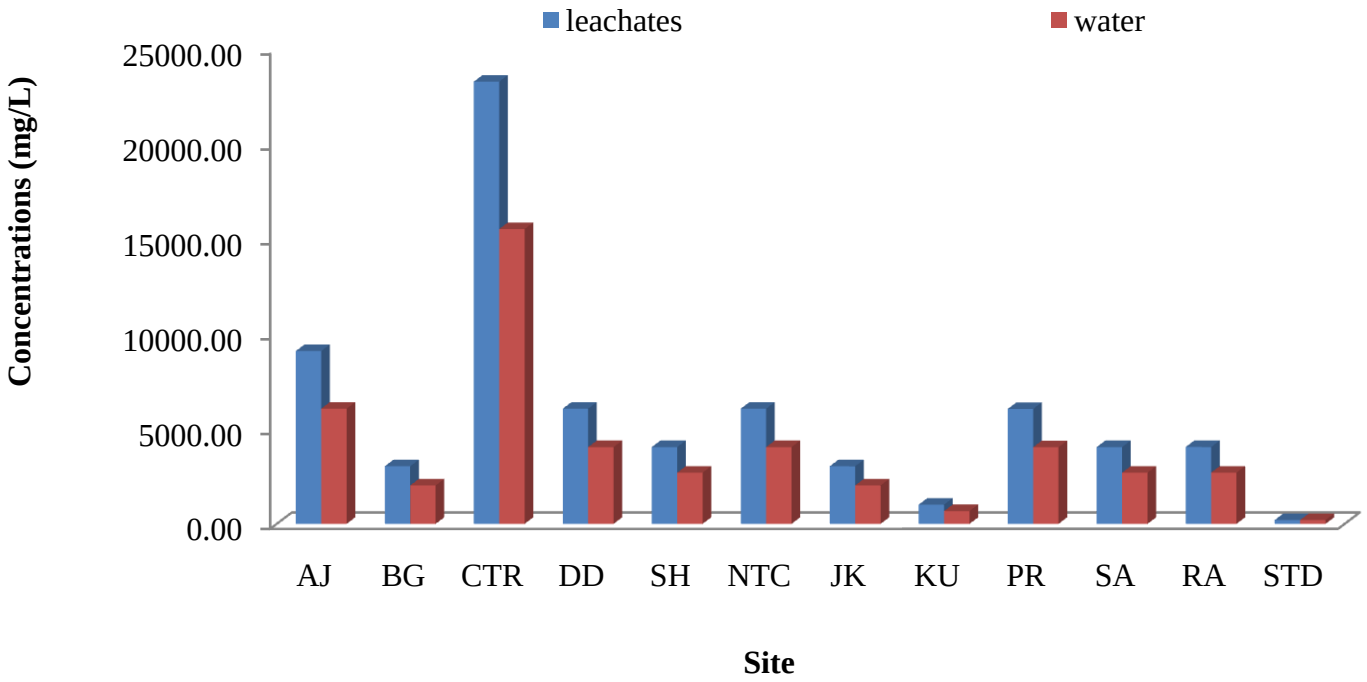


**Figure 4.21: Concentrations of the total hardness in dumpsite-leachates and well waters**

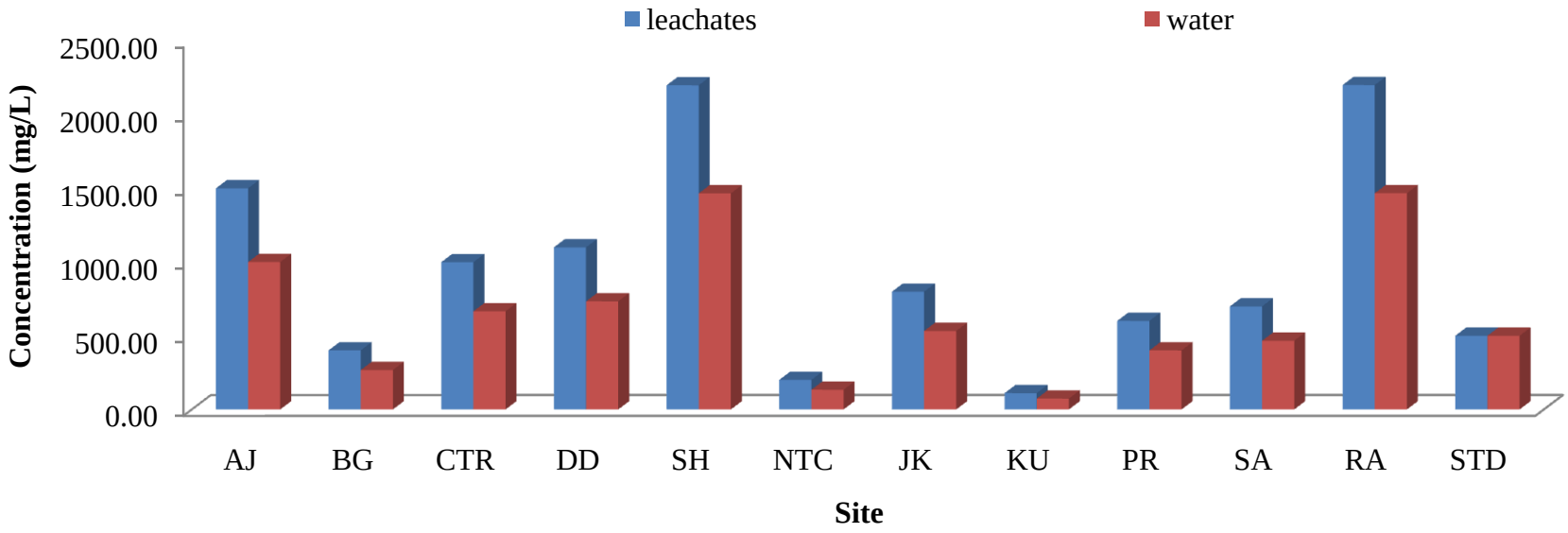


**Figure 4.22: Total alkalinity of the dumpsite-leachates and well waters**

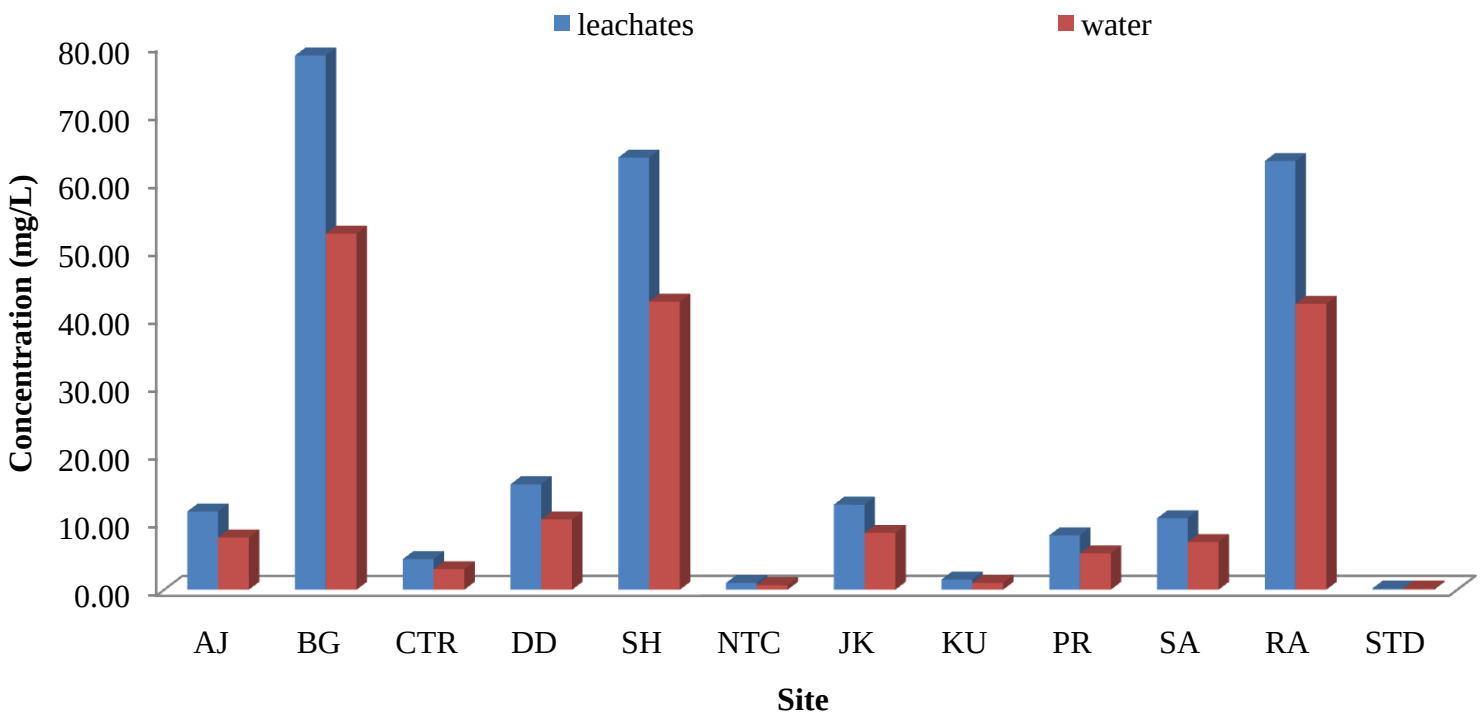


**Figure 4.23: The levels of $NO_2^-$ - N in the dumpsites-leachates and well waters**

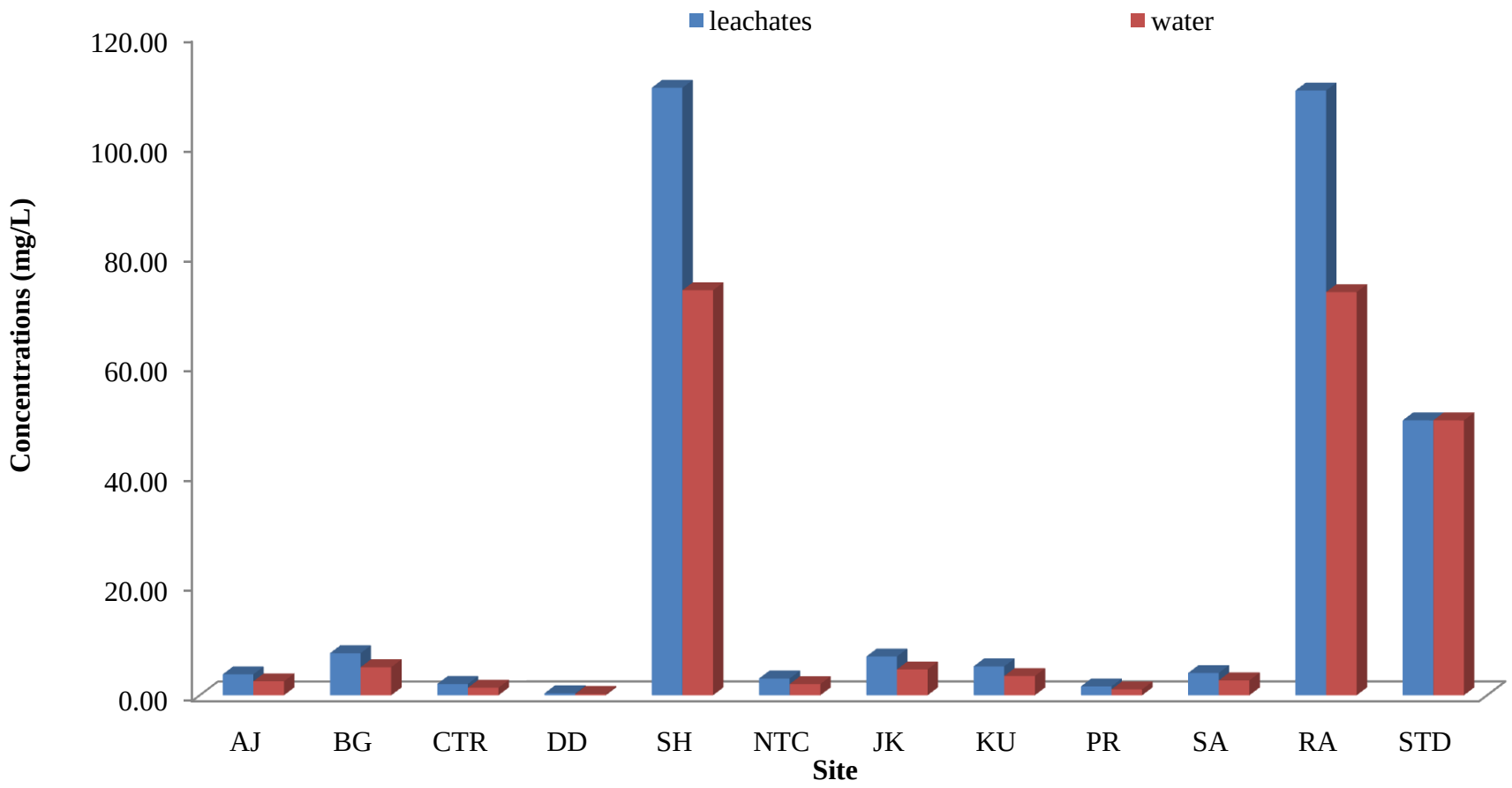


**Figure 4.24: The levels of $NO_3^-$-N of the dumpsites-leachates and well waters**

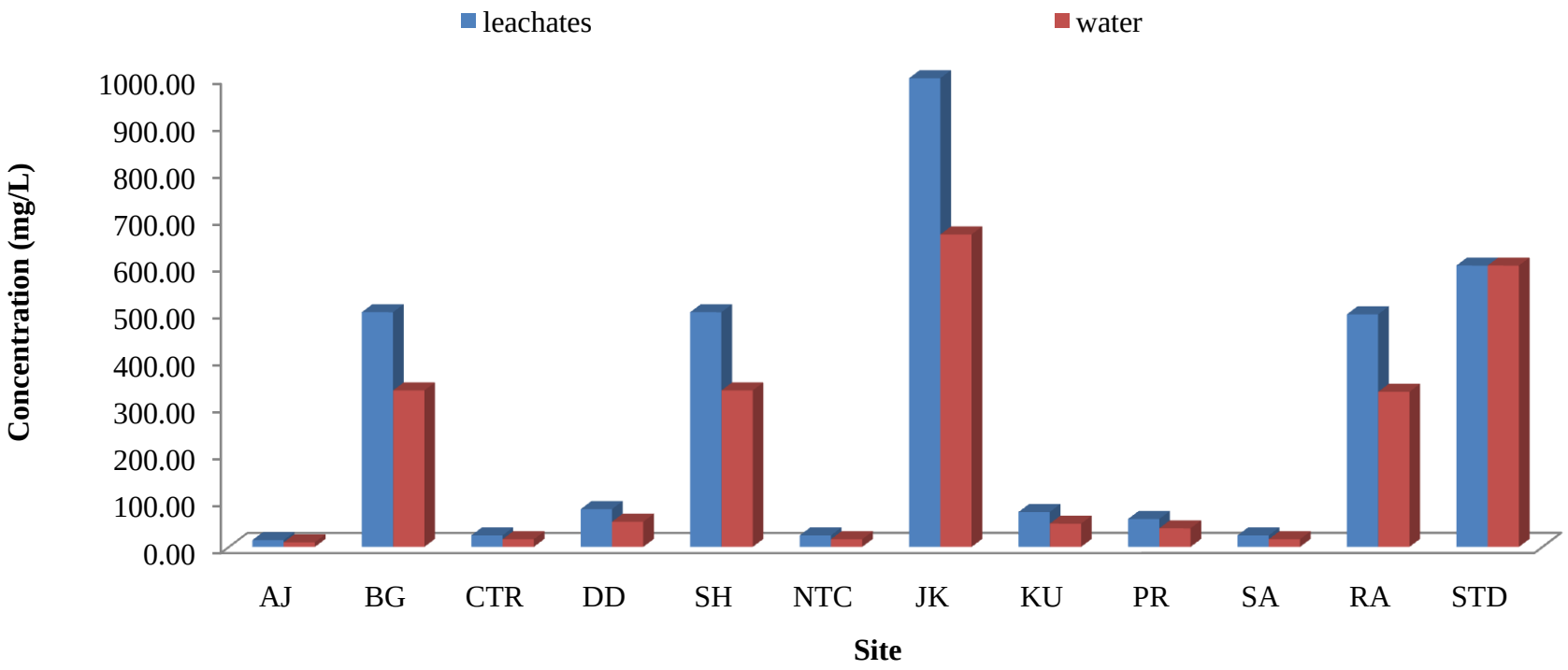


**Figure 4.25: The $SO_4^{2-}$-S of the dumpsite-leachates and well waters**

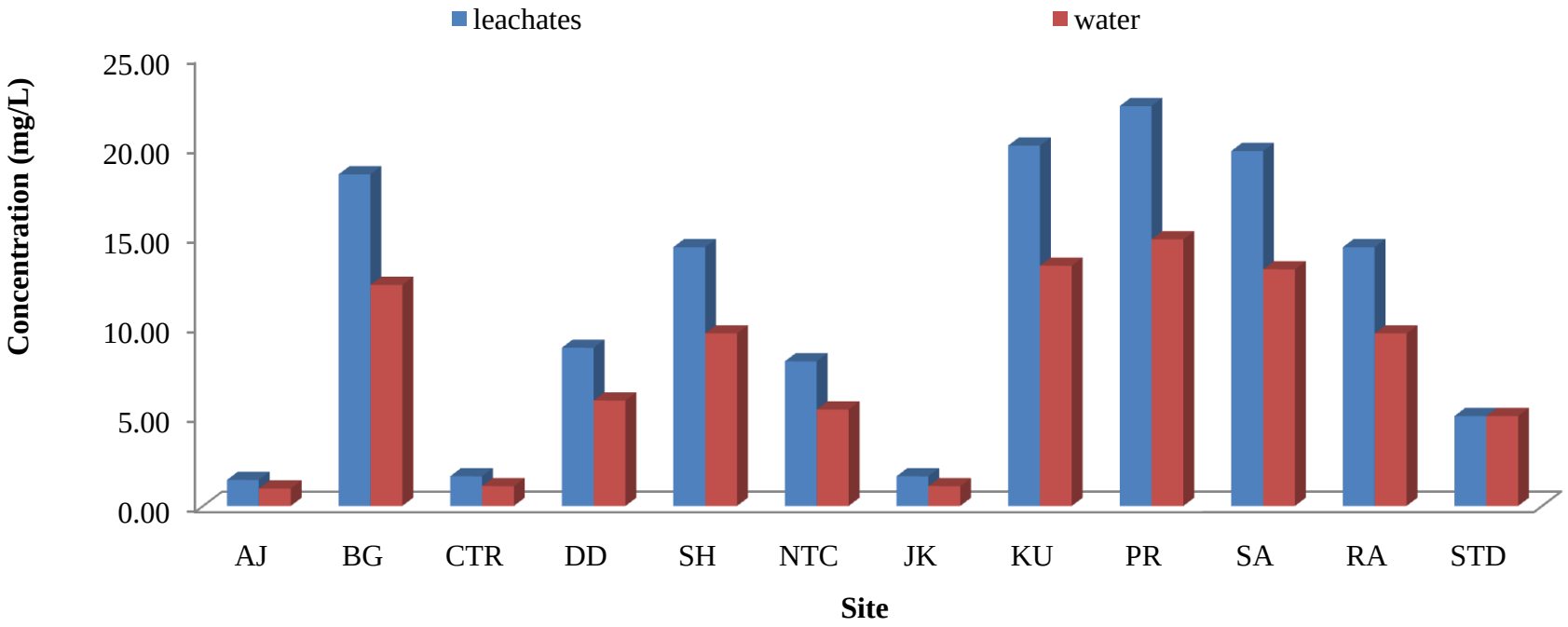


**Figure 4.26: The $PO_4^{3-}$-P of the dumpsites-leachates well waters**

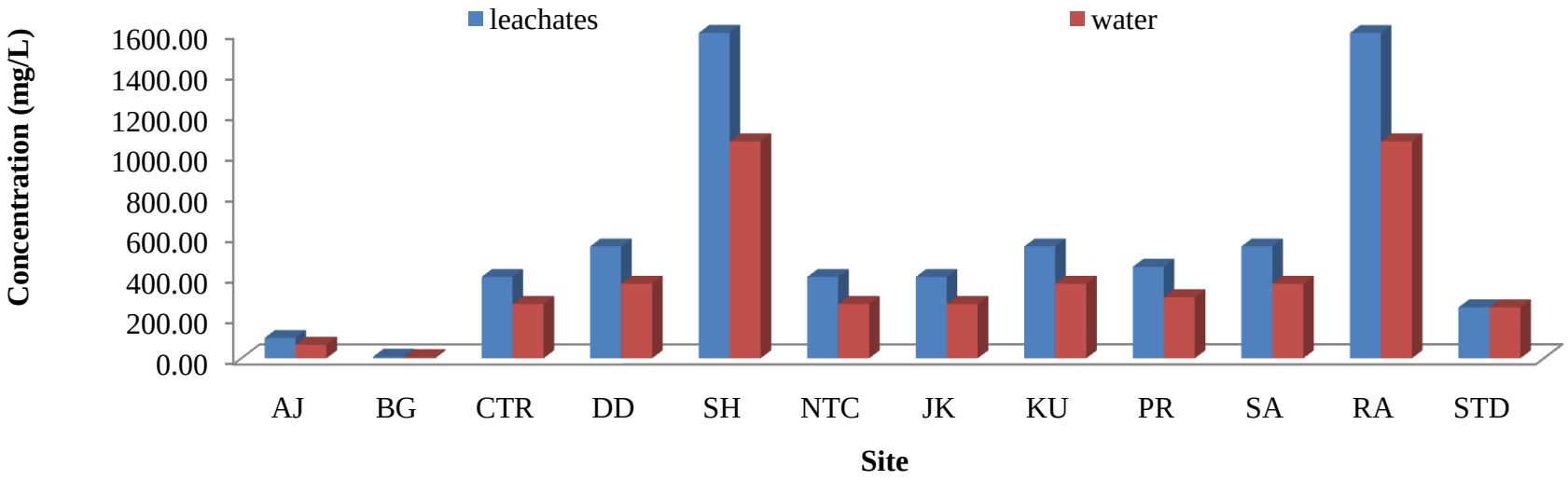


**Figure 4.27: The levels of Cl in the dumpsites-leachates and well waters**

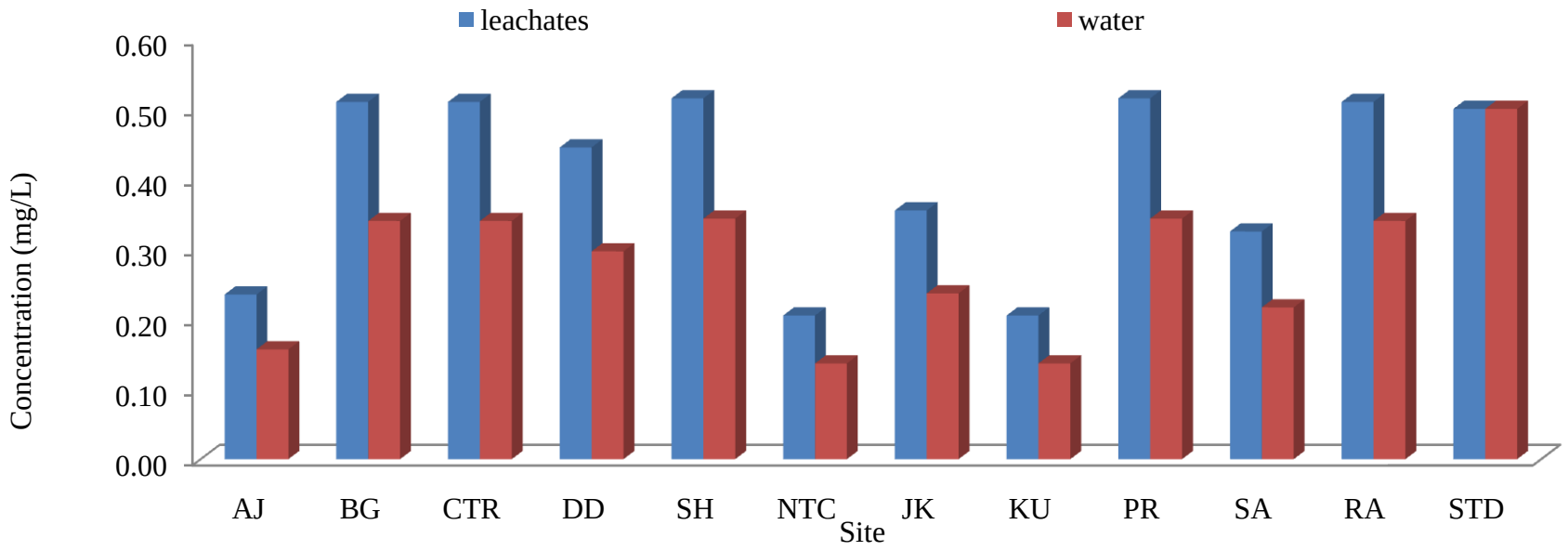


**Figure 4.28: The levels of $NH_4$-N of the dumpsite-leachates and well water**

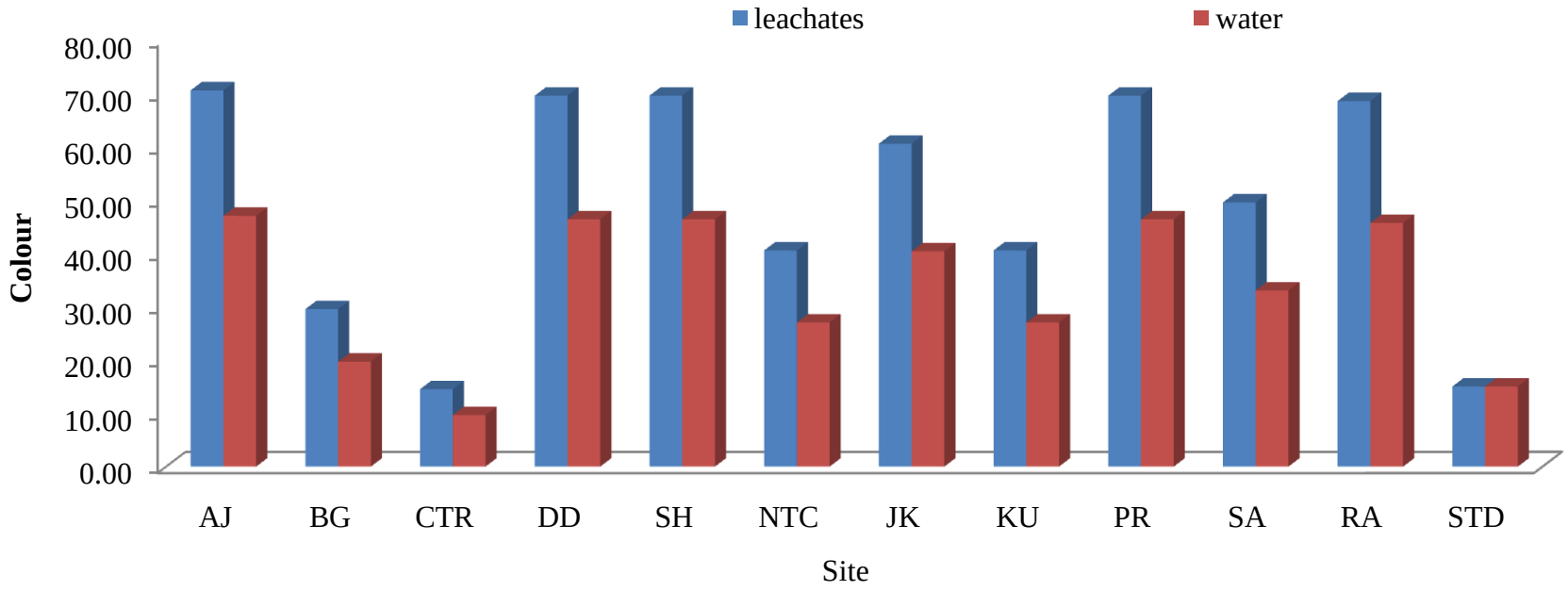


**Figure 4.29: The intensities of colour in the dumpsite-leachates and well waters**

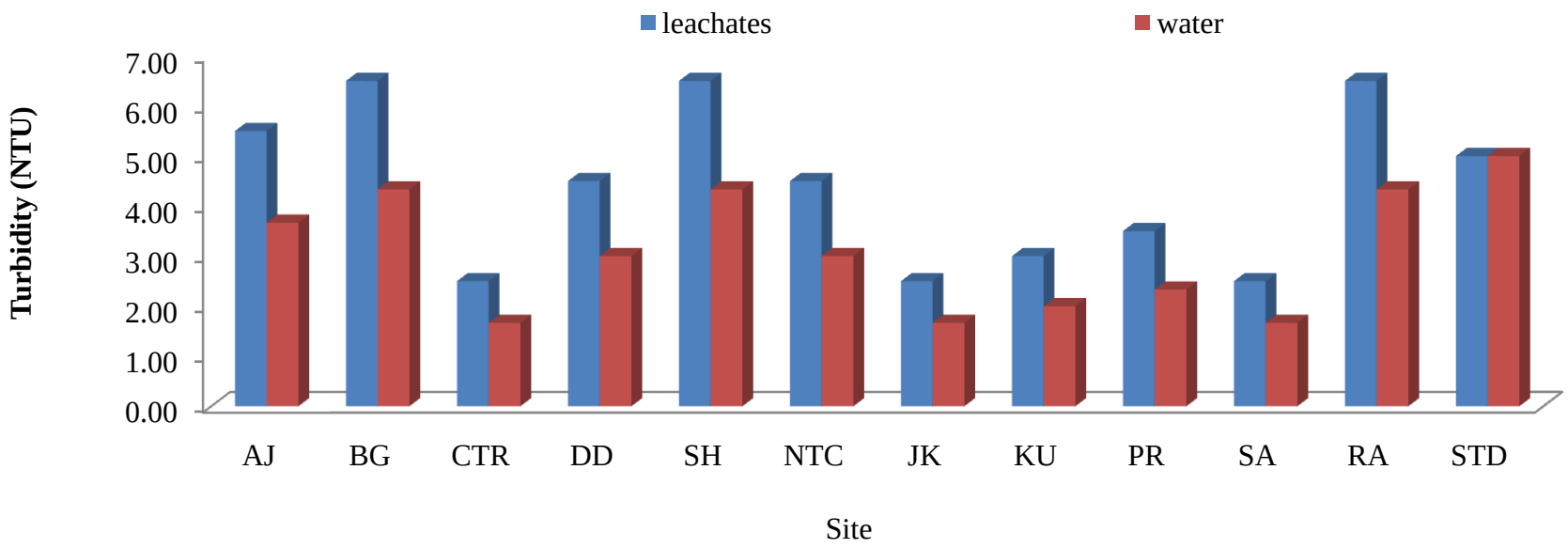


**Figure 4.30: The turbidity levels of leachates and well waters**

Similarly, the correlation coefficients of 0.022, 0.046, 0.201, 0.217, 1.0, 0.331, 0.022, 0.046, 0.201, and 0.217 were recorded for the correlations of pHL Vs $NO_2$NL, $SO_4^{2-}$-SL, ColourL, TurbidL, pHW, respectively, as presented in the Table 4.15.

Similarly, the correlation coefficients for ECL Vs TSL, SSL, DSL, ALKL, $NO_2$NL, $SO_4^{2-}$SW, colourW and TurbidW, respectively as presented in the Table 4.15 were 0.977, 0.983, 0.846, 0.803, 0.846, 0.803, 0.602, 0.982, 0. 373, 0.093, 0.916, 0.283, 0.432, 0.610, 1.0, 0.977, 0.599, 0.846, respectively.

Also, the correlation coefficients of 0.997, 0.913, 0.819, 0.720, 0.985, 0.455, 0.131, 0.897, 0.417, 0.474, and 0.686, respectively, were recorded for TSL Vs SSL, DSL, ALKL, $NO_2$N $NO_3$NL, $SO_4$SL, $PO_4$SL, ClL, $NH_3$NL, ColourL, TurbidL as presented in Table 4.15.

The correlation coefficients of 0.977, 1.00, 0.615, 0.913, 0.819, 0.720, 0.985, 0.455, 0.131, 0.897, 0.418, 0.474, and 0.686, respectively for the correlations of TSL Vs ECW, TSW, SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW and TurbidW, respectively, as presented in Table 4.15.

Also, the correlation coefficients of 0.877, 0.810, 0.698, 0.992, 0.445, 0.132, 0.913, 0.419, 0.441, 0.654, 0.983, 0.997, 0.615, 0.877, 0.810, 0.698, 0.992 and 0.445 were recorded for SSL Vs DSL, ALKL, NO2NL, NO3NL, SO4SL, P 4SL, ClL, NH3NL, ColourL, TurdidL, ECW, TSW, SSW, DSW, ALKW, $NO_2$NW, $SO_4^{2-}$SW, respectively. Other correlation coefficients recorded were 0.132, 0.913, 0.421, 0.441 and 0.655, respectively were recorded for the correlations of SSL Vs $PO_4^{3-}$PW, ClW, NH3NW, ColourW and TurbidW as presented in Table 4.15.

The correlations of DSL Vs ECW, TSW, SSW, DSW, ALKW, NO2NW, SO4SW, PO4PW, ClW, NH3NW, ColourW, and TurbidW were 0.846, 0.913, 0.556, 1.000, 0.783, 0.757, 0.849, 0.461, 0.109, 0.723, 0.366, 0.586, and 0.770, respectively as presented in the Table.

Also, the correlation coefficients of 0.098, 0.238, 0.266, 1.0, 0.98 and 0.237 were recorded for the correlations of THL Vs ALKL, $NH_3$NL, TempW, THW, ALKW, THW, ALKW and $NH_3$NW across the sites as presented in the Table.

The correlation coefficients of 0.509, 0.822, 0.274, 0.744, 0.459, 0.548, 0.540, 0.803, 0.819, 0.475, 0.783, 0.098, 1.000, 0.509, 0.822, 0.274, 0.744, 0.459, 0.548, 0.540, respectively for the correlations of ALKL Vs $NO_2$NL, $NO_3$NL, $SO_4$SL, ClL, $NH_3$NL, ColourL, TurbidL, ECW, TSW, SSW, DSW, THW, ALKW, $NO_2$NW, NO3NW, $SO_4$SW, ClW, NH3NW, ColourW and TurbidW respectively as presented in Table 4.15.

Similarly, the correlation coefficients of 0.098, 0.238, 0.266, 1.000, 0.098 and 0.237 were recorded for the correlations of THL Vs ALKL, $NH_3$NL, TempW, THW, ALKW and $NH_3$NW respectively as presented in Table 4.15.

Also, the correlation coefficients of $NO_3$NL Vs $SO_4$SL, $PO_4$SL, CIL, $NH_3$NL, ColourL, TurbidL, ECW, TSW, SSW, DSW, THW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$-PW, ClW, $NH_3$NW ColourW and TurbidW were 0.686, 0.520, 0.289, 0.450, 0.603, 0.113 and 0.785, respectively as presented in Table 4.15.

The correlation coefficients of 0.405, 0.159, 0.932, 0.435, 0.396, 0.611, 0.982, 0.985, 0.600, 0.849, 0.822, 0.686, 1.00, 0.405, 0.159, 0.932, 0.437, 0.396 and 0.611, respectively were recorded for the correlations of $NO_3$NL vs $SO_4$SL, $PO_4$PL, ClL, $NH_3$NL,

ColourL, TurbidL, ECW, TSW, SSW, DSW, THW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, ClW, $PO_4$PW, $NH_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW and TurbidW as presented in Table 4.15.

The correlation coefficients of 0.272, 0.302, 0.192, 0.198, 0.044, 0.373, 0.455, 0.325, 0.461, 0.274, 0.520, 0.405, 1.00 and 0.272 were recorded for the correlations of $SO_4$SL vs ClL, $NH_4$-NL, ColourL, TurbidL, pHW, ECW, TSW, SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, and ClW, respectively, as presented in the Table 4.15.

Also as presented in the same Table, the correlation coefficients for ClL Vs $NH_3$NL, ColourL, TurbidL, ECW, TSW, SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW and TurbidW across the sites were 0.216, 0.186, 0.064, 0.110, 0.093, 0.131, 0.063, 0.109, 0.289, 0.159, 1.00, 0.216, 0.189, 0.064 and 0.111, as presented in Table 4.15.

The correlations coefficients of $PO_4$PL vs ClL, $NH_3$NL, ColourL, TurbidL, ECW, TSW, SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW, and TurbidW as presented in the Table were: 0.377, 0.425, 0.376, 0.916, 0.897, 0.535, 0.723, 0.744, 0.450, 0.932, 0.272, 0.216, 1.000, 0.379, 0.425 and 0.376, respectively.

Also, the correlation coefficients of $NH_3$NL vs colourL, TurbidL, ECW, TSW, SSW, DSW, THW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW, and TurbidW were : 0.052, 0.304, 0.283, 0.417, 0.244, 0.366, 0.238, 0.459, 0.603, 0.435, 0.302, 0.186, 0.377, 1.00, 0.052 and 0.305, respectively as presented in Table 4.15.

Similarly, the correlations of ColourL vs Turbidl, pHW, ECW, TSW, SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW and TurbidW were: 0.308, 0.203, 0.432, 0.474, 0.301, 0.586, 0.548, 0.113, 0.396, 0.192, 0.064, 0.425, 0.054, 1.000 and 0.308, respectively as presented in the Table 4.15.

Also, the correlation coefficients of 0.215, 0.610, 0.686, 0.433, 0.770, 0.540, 0.785, 0.611, 0.198, 0.110, 0.376, 0.308, and 1.00, respectively were recorded for the correlations of TurbidL Vs pHW, ECW, TSW, SSW, DSW, THW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW, and TurbidW respectively as presented in the Table.

The correlation coefficients of 0.334, 0.021, 0.044, 0.203, and 0.215 were recorded for the correlations of pHW Vs SSW, $NO_2$NW, $SO_4$SW, ColourW, and TurbidW, respectively. Also, the correlation coefficients of 0.334, 0.021, 0.044, 0.203, and 0.215 were recorded for pHW Vs SSW, $NO_2$NW, $SO_4$SW, ColourW, and TurbidW, respectively as presented in Table 4.15.

The correlation coefficients of 0.977, 0.599, 0.846, 0.803, 0.602, 0.982, 0.373, 0.093, 0.916, 0.286, 0.432, and 0.610, respectively were recorded for the correlations of ECW vs TSW, SSW, DSW, ALKW, $NO_2$NW, ColourW, and TurbidW as presented in Table 4.15.

Also, as presented in the same Table, the correlation coefficients of 0.615, 0.913, 0.819, 0.720, 0.985, 0.455, 0.131, 0.897, 0.418, 0.474, and 0.686 were recorded for the correlations of TSW vs SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW and TurbidW, respectively.

In addition, the correlation coefficients of 0.556, 0.475, 0.451, 0.600, 0.325, 0.063, 0.535, 0.248, 0.301, and 0.433 were recorded for the correlations of SSW Vs DSW, THW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW, AND TurbidW, respectively as presented in Table.

The correlations of ALKW vs $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW, and TurbidW, respectively were: 0.783, 0.757, 0.849, 0.461, 0.109, 0.723, 0.366, 0.986, ands 0.770 as presented in Table 4.15.

Also, the correlation coefficients of 0.098 and 0.237 were recorded for THW Vs ALKW, $NH_3$NW, respectively as presented in the Table 4.15. Also, the correlation coefficients of Alkw vs $NO_2$NW, $NO_3$NW, $SO_4$SW, ClW, $NH_3$NW, Colour AND TurbidW were: 0.509, 0.822, 0.274, 0.744, 0.459, 0.548, and 0.540, respectively, as presented in Table.

Similarly, correlation coefficients of $NO_2$NW vs $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW and TurbidW were: 0.686, 0.520, 0.289, 0.450, 0.602, 0.113 and 0.785, respectively, as presented in the same Table 4.15.

The correlation coefficients of 0.405, 0.159, 0.932, 0.437, 0.396 and 0.611, respectively were recorded for the correlations of $NO_3$NW vs $SO_4$SW, $PO_4$PW, ClW, $NH_3$NW, ColourW and TurbidW as presented in the Table.

Also, the correlation coefficients of 0.272, 0.300, 0.192 and 0.198 were recorded for the correlations of $SO_4$SW vs ClW, $NH_3$NW, ColourW and TurbidW, respectively as presented in Table 4.15. The correlation coefficients of $PO_4$PW Vs ClW, $NH_3$NW, ColourW and TurbidW were 0.216, 0.189, 0.064, and 0.111, respectively, as presented in

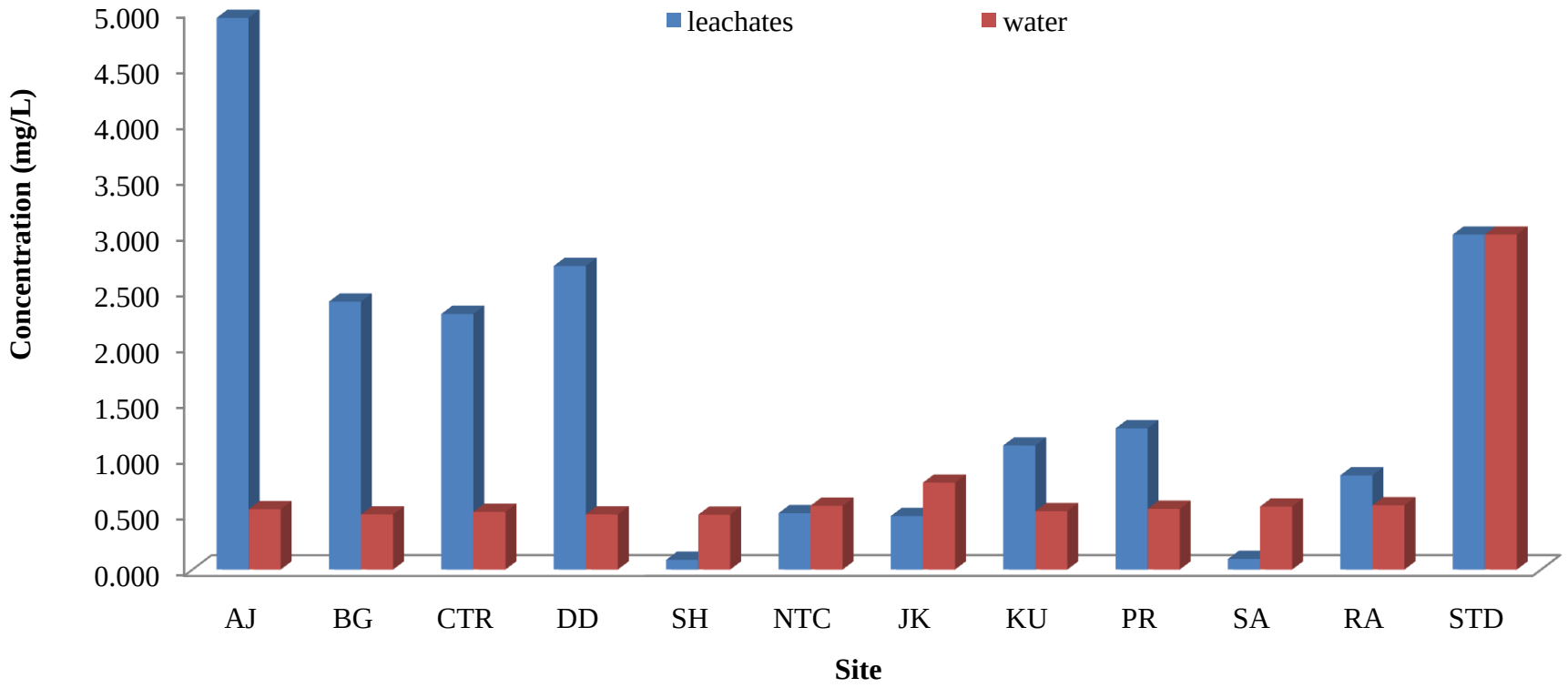


**Figure 4.31: Concentration of zinc in the dumpsite-leachates well waters**

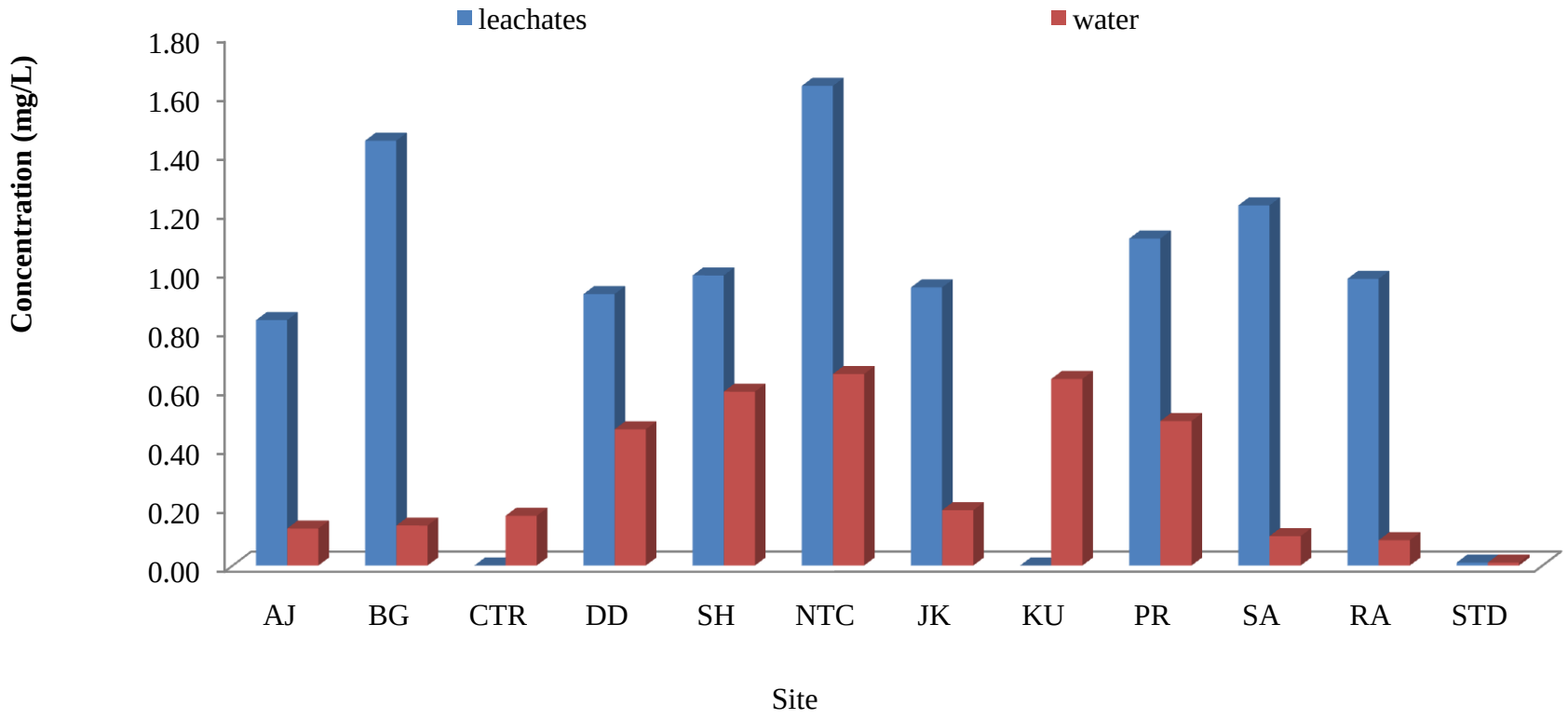


**Figure 4.32: Concentration of lead (Pb) in the dumpsite-leachates and well waters**

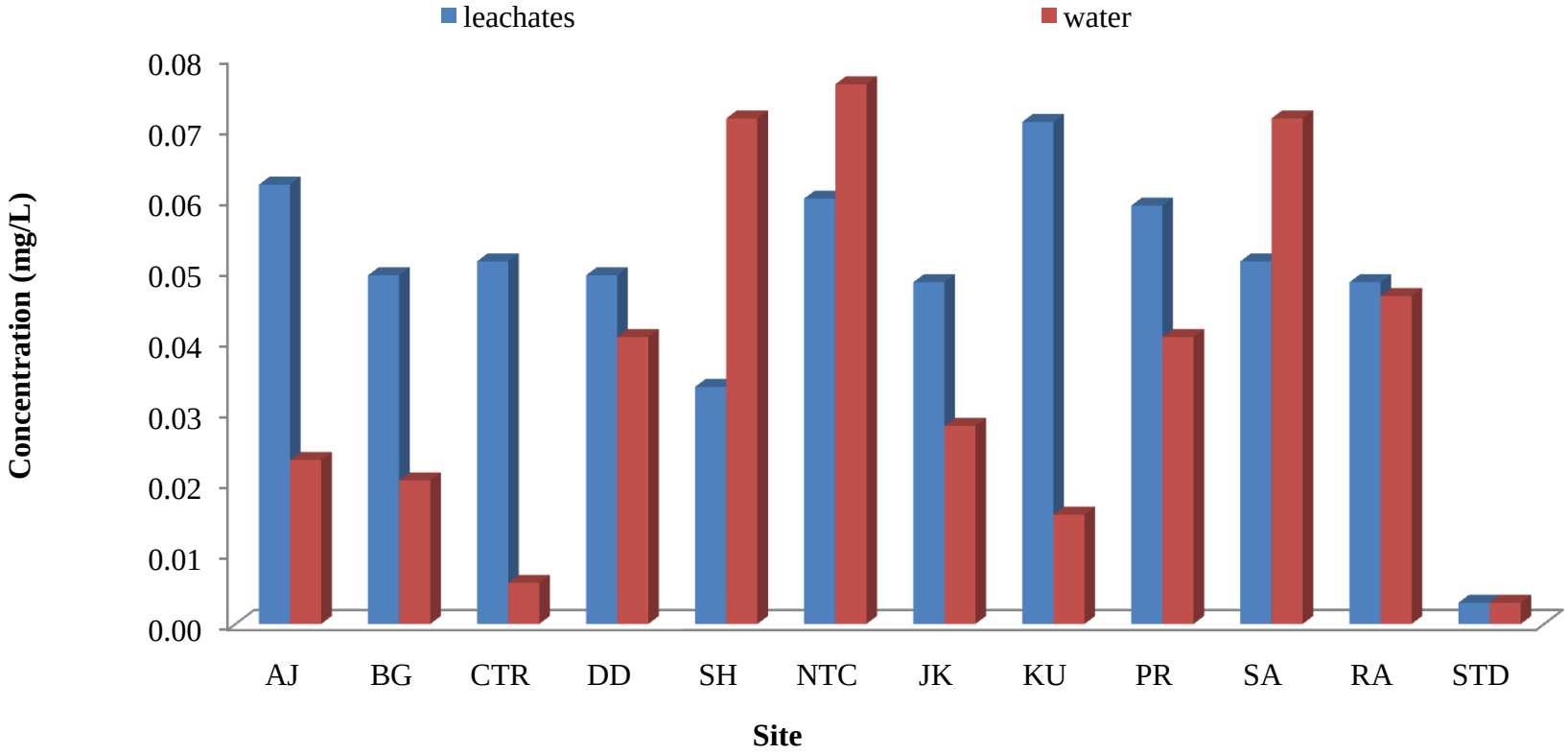


**Figure 4.33: Concentration of cadmium (Cd) in the dumpsite-leachates and wells waters**

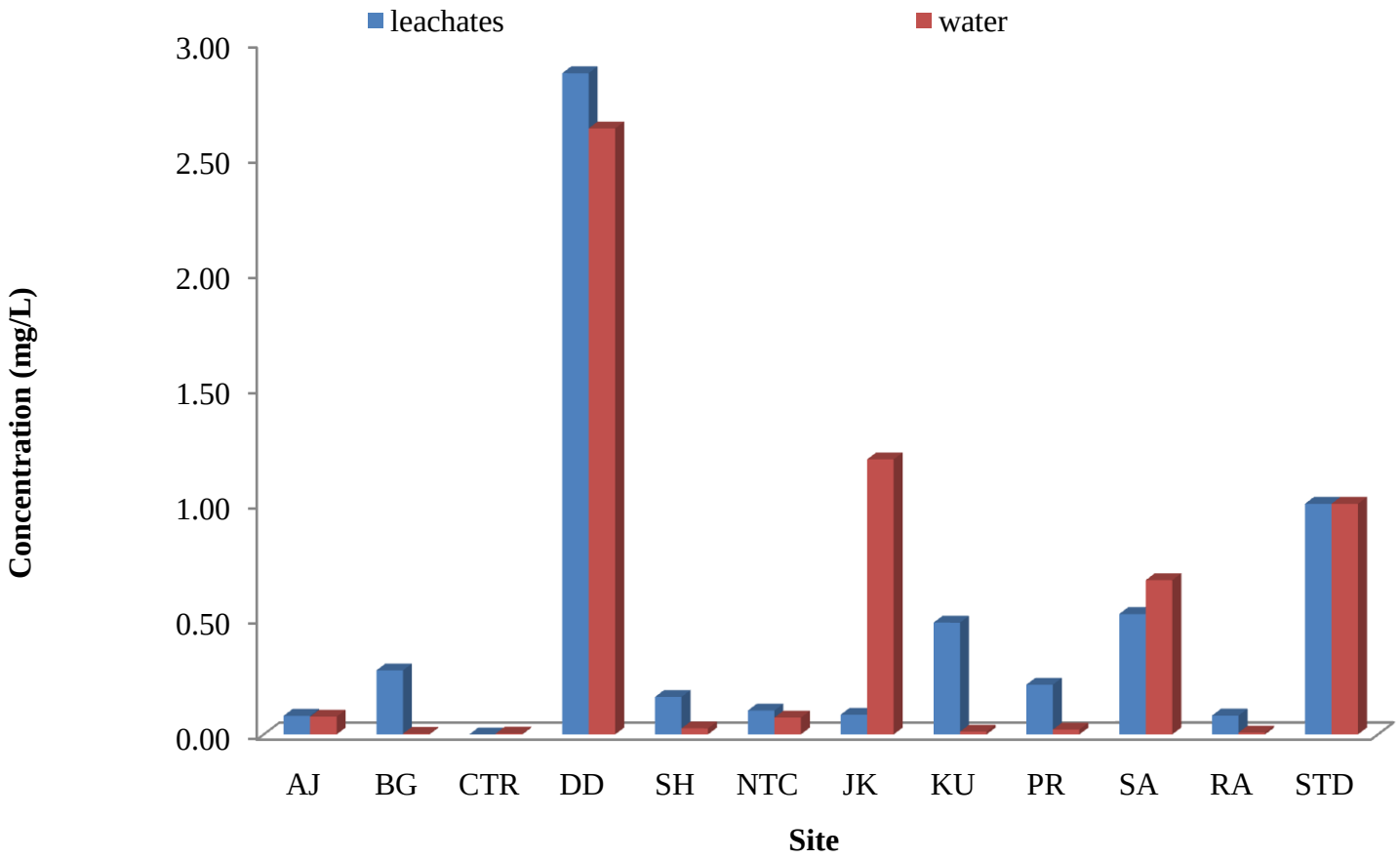


**Figure 4.34: Concentration of copper (Cu) in the dumpsite-leachates and well waters**

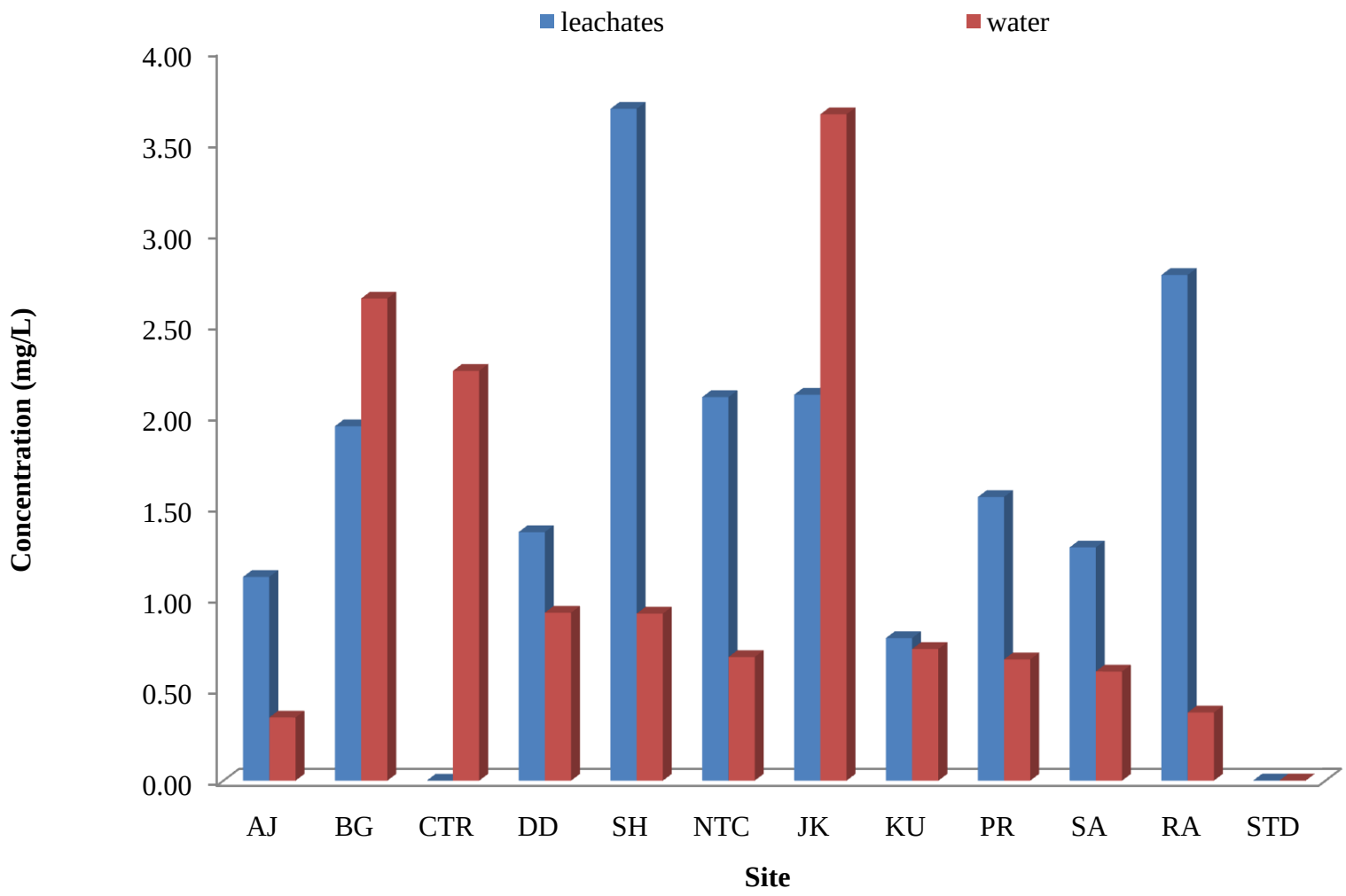


**Figure 4.35: Concentration of mercury in the leachates and well waters**

**TABLE 4.17 : Quality index assessment of the well waters for the dry season**

| Parameters | RANGE | MEAN | Si | wi | Qi | wiqi |
|---|---|---|---|---|---|---|
| Temp($^0$C) | 29.5-30.5 | 30.000 | 40.000 | 0.025 | 75.000 | 1.875 |
| pH | 6.75-7.95 | 7.350 | 7.550 | 0.132 | 97.351 | 12.894 |
| EC (µS/cm) | 4.23-2568.5 | 1286.365 | 1500.000 | 0.001 | 85.758 | 0.057 |
| Dissol.solids (mg/L) | 2.035-935.5 | 468.768 | 500.000 | 0.002 | 93.754 | 0.188 |
| Tot.hardness (mg/L) | 121.25-27272.5 | 13696.875 | 300.000 | 0.003 | 4565.625 | 15.219 |
| Alkalinity (mg/L) | 3.5-15.5 | 9.500 | 400.000 | 0.003 | 2.375 | 0.006 |
| nitrite-N (mg/L) | 67.5-126.5 | 97.000 | 45.000 | 0.022 | 215.556 | 4.790 |
| nitrate-N (mg/L) | BDL-115.5 | 57.750 | 45.000 | 0.022 | 128.333 | 2.852 |
| SO42—S v(mg/L) | 4.5-500.5 | 252.500 | 250.000 | 0.004 | 101.000 | 0.404 |
| phosphate-P (mg/L) | 1.05-2.85 | 1.950 | 0.700 | 1.429 | 278.571 | 397.959 |
| Chloride (mg/L) | 3.48-449.86 | 226.670 | 250.000 | 0.004 | 90.668 | 0.363 |
| Ammonia-N (mg/L) | 0.025-0.115 | 0.070 | 0.500 | 2.000 | 14.000 | 28.000 |
| Colour (TCU) | 4.5-14.5 | 9.500 | 7.000 | 0.143 | 135.714 | 19.388 |
| Turbidity (NTU) | 2.2-174.5 | 88.350 | 5.000 | 0.200 | 1767.000 | 353.400 |
| Zn (mg/L) | 0.092-0.826 | 0.4590 | 3 | 0.333 | 15.300 | 5.100 |
| Pb (mg/L) | 0.008-0.564 | 0.2875 | 0.010 | 100.000 | 2875.000 | 287500.000 |
| Cu(mg/L) | BDL-0.654 | 327.0000 | 1.000 | 1.000 | 32700.000 | 32700.000 |
| Cd (mg/L) | 0.0042-0.038 | 0.0211 | 0.030 | 33.333 | 70.333 | 2344.444 |
| Hg (mg/L) | 0.358-2.152 | 1.2550 | 0.001 | 1000.000 | 125500.000 | 125500000.000 |
| TOTAL | | | | 1138.656 | | 125823386.939 |
| ∑WQ/∑Wi | | | 110501.6201 | | | |

**Table 4.18: Quality index assessment of the well waters for the wet season**

| Parameter | Range | Mean | Si | Wi | Qi | Wiqi |
|---|---|---|---|---|---|---|
| Temp($^0$C) | 23-25.88 | 24.440 | 40.000 | 0.025 | 61.100 | 1.528 |
| pH | 4.6-5.16 | 4.884 | 7.550 | 0.132 | 64.682 | 8.567 |
| EC (µS/cm) | 54-9334.3 | 4694.150 | 1500.000 | 0.001 | 312.943 | 0.209 |
| dissolved solids (mg/L) | 127-1014.33 | 570.665 | 500.000 | 0.002 | 114.133 | 0.228 |
| total hardness (mg/L) | 159.67-6060.33 | 3110.000 | 300.000 | 0.003 | 1036.667 | 3.456 |
| Alkalinity (mg/L) | 133-1468 | 800.500 | 400.000 | 0.003 | 200.125 | 0.500 |
| nitrite-N (mg/L) | 1-52.33 | 26.665 | 45.000 | 0.022 | 59.256 | 1.317 |
| nitrate-N (mg/L) | 2.5-73.33 | 37.915 | 45.000 | 0.022 | 84.256 | 1.872 |
| $SO_4^{2-}$S (mg/L) | 9.67-666.3 | 337.985 | 250.000 | 0.004 | 135.194 | 0.541 |
| phosphate-P (mg/L) | 1.1-14.833 | 7.967 | 0.700 | 1.429 | 1138.071 | 1625.816 |
| Chloride (mg/L) | 5.32-1066 | 535.660 | 250.000 | 0.004 | 214.264 | 0.857 |
| Ammonia-N (mg/L) | 0.137-0.343 | 0.240 | 0.500 | 2.000 | 48.000 | 96.000 |
| Colour (TCU) | 9.67-47 | 28.335 | 7.000 | 0.143 | 404.786 | 57.827 |
| Turbidity (NTU) | 1.67-4.33 | 3.000 | 5.000 | 0.200 | 60.000 | 12.000 |
| Zn (mg/L) | 0.019-0.774 | 0.3965 | 3 | 0.333 | 13.217 | 4.406 |
| Pb (mg/L) | 0.068-0.6480 | 0.3580 | 0.010 | 100.000 | 3580.000 | 358000.000 |
| Cu (mg/L) | BDL-2.5887 | 1.2944 | 1.000 | 1.000 | 129.435 | 129.435 |
| Cd (mg/L) | 0.006-0.079 | 0.0425 | 0.030 | 33.333 | 141.667 | 4722.222 |
| Hg (mg/L) | 0.211-2.601 | 1.4060 | 0.001 | 1000.000 | 140600.000 | 140600000 |
| TOTAL | | | | 1138.656 | | 140964666 |
| ∑WQ/∑Wi | | | 123799.1159 | | | |

the Table. Also, the correlation coefficients of 0.054, 0.309 and 0.308 were recorded for $NH_3$NW vs Colourw and TurbidW and ColourW vs TurbidW, respectively as reflected in the Table.

## 4.9: Chemical Fractionation of Metals in Leachates and Well Waters

Chemical fractionation of the metals were carried out in soil, leachates and underground water samples so as to determine the bioavailable fractions of the metals in these samples.

### 4.9.1: Chemical fractionation of metals in dumpsite leachates

Figures 4.36 to 4.40 and appendices XV to XX showed the percentage bioavailable, residual and non-residual of metals in the extractable fractions across the sites.

(a) Zinc

Figure 4.36 and appendix XV showed the extractable fractions and the percentages of the bio-available fractions across the sites as presented in appendix XXII. The concentration of the total extractable fraction range from 0.338 (AJ) to 4.119 mg/L (KU) while the range of 53.387 (NTC) to 98.670 (CTR) was recorded in the bioavailable fractions across the sites.

(b) Lead

As presented in Appendix XVI and Figure 4.37, The concentrations of the extractable fractions of Pb range from BDL (CTR) to 0.388 mg/L (KU) with the range of BDL (CTR) to 97.215% (SH) for the bioavailable phases across the sites in the wet season.

(c) Cadmium

Appendix XVII and Figure 4.38 showed the trend of the bioavailable fractions of cadmium across the sites. The concentration of the total extractable fraction of Cd as presented in the Figure, range from BDL (AJ) to 0.074 mg/L while the bioavailable fractions range from 89.94 (SA) to 100 % (SH, RA, PR, NTC, KU and CTR) across the sites.

(d) Copper

The extractable fractions of copper in the analysed samples across the sites were presented in appendix XVIII and Figure 4.39. The concentration range of Cu in the total extractable fraction was BDL (CTR) to 1.598 mg/L (DD). Similarly, the range of 53.39% (PR) to 100% (SA) was recorded in the bioavailable phase across the sites.

(e) Mercury

Appendix XIX and Figure 4.40 showed the concentrations of mercury in the fractionated leachate samples across the sites, the range of 29.23 (CTR) to 100 % ( SH, SA, PR and DD) was recorded in the bioavailable phase while the total extratable fractions of Hg across the sites, range from BDL (DD) to 14.961 mg/L (KU).

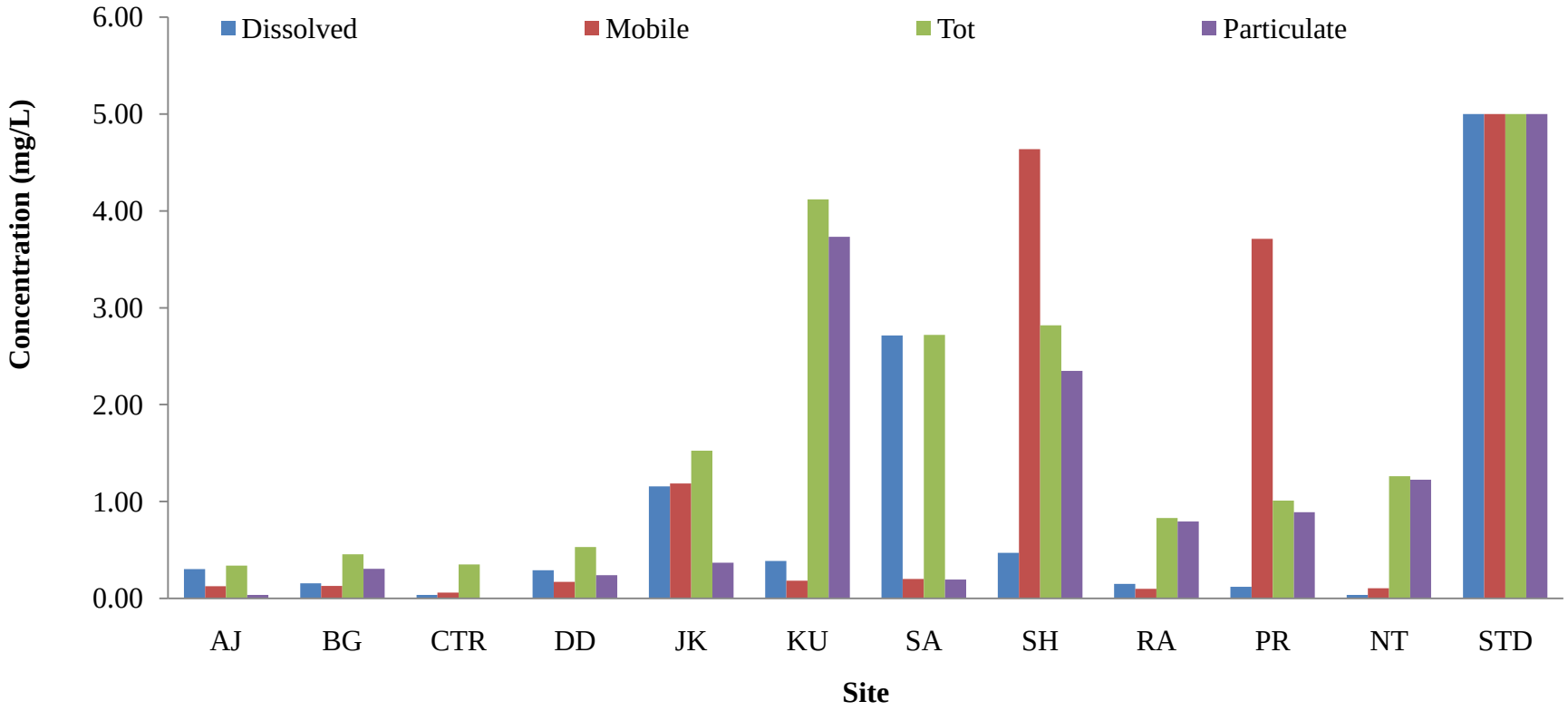


**Fig. 4.36: Concentrations of the fractionated zinc (Zn) in the dumpsite leachates samples**

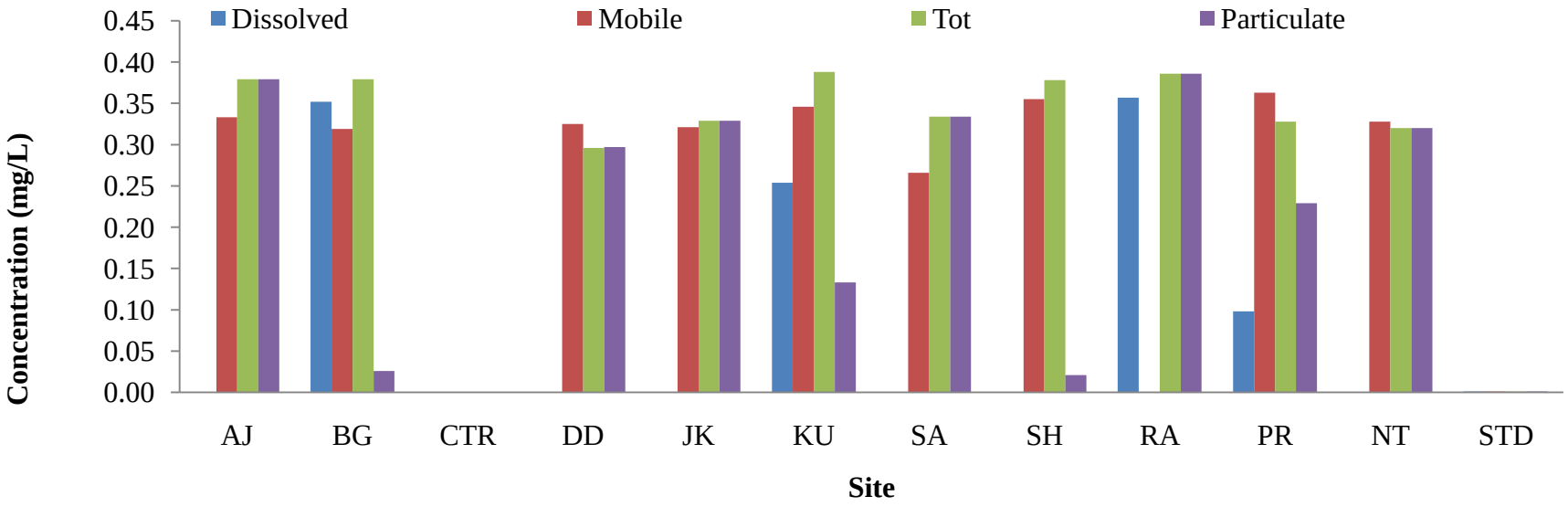


**Fig. 4.37: Concentrations of the fractionated lead (Pb) in the leachate samples**

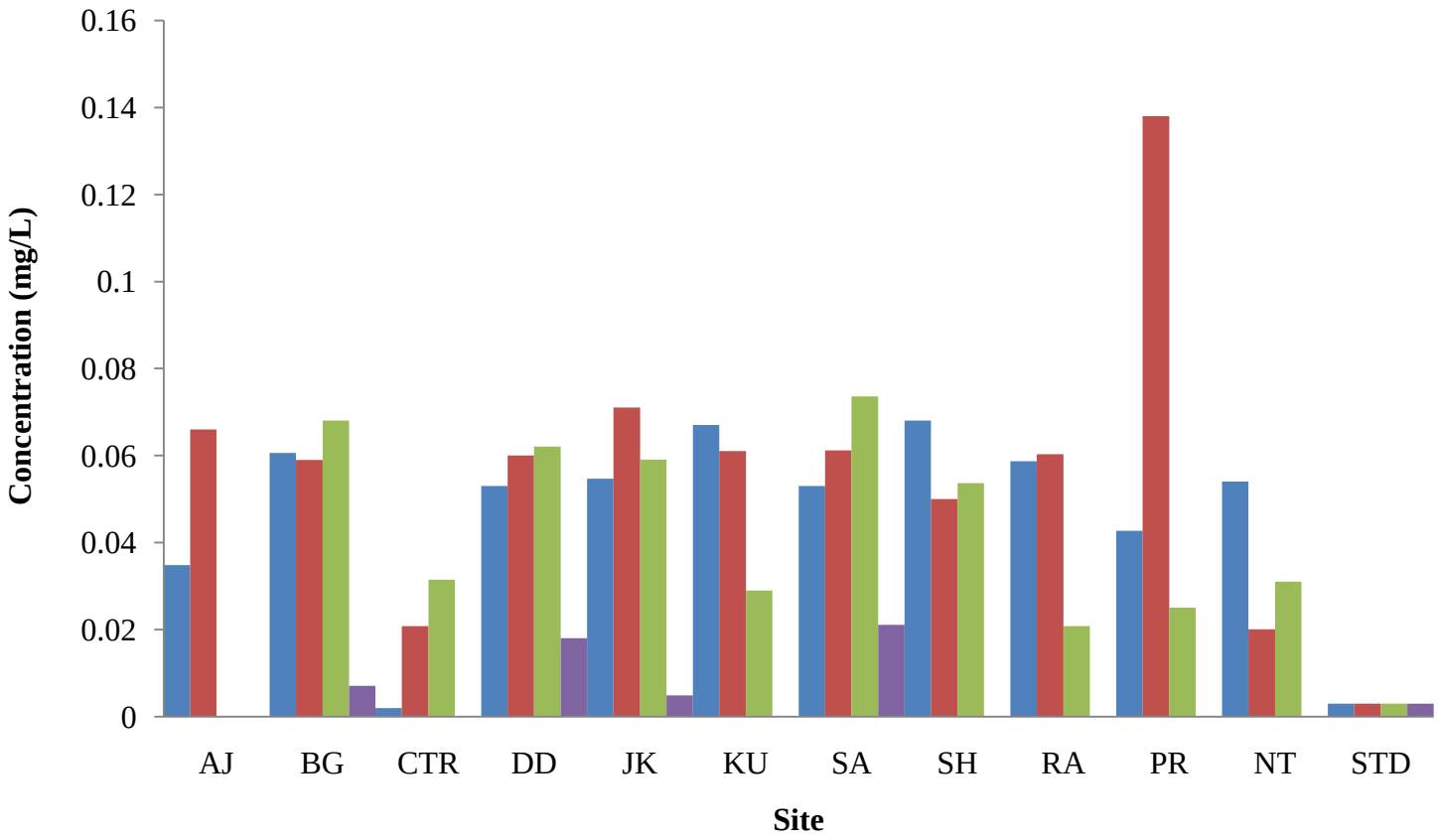


**Figure 4.38: Concentrations of cadmium (Cd) in the fractionated dumpsites leachates**

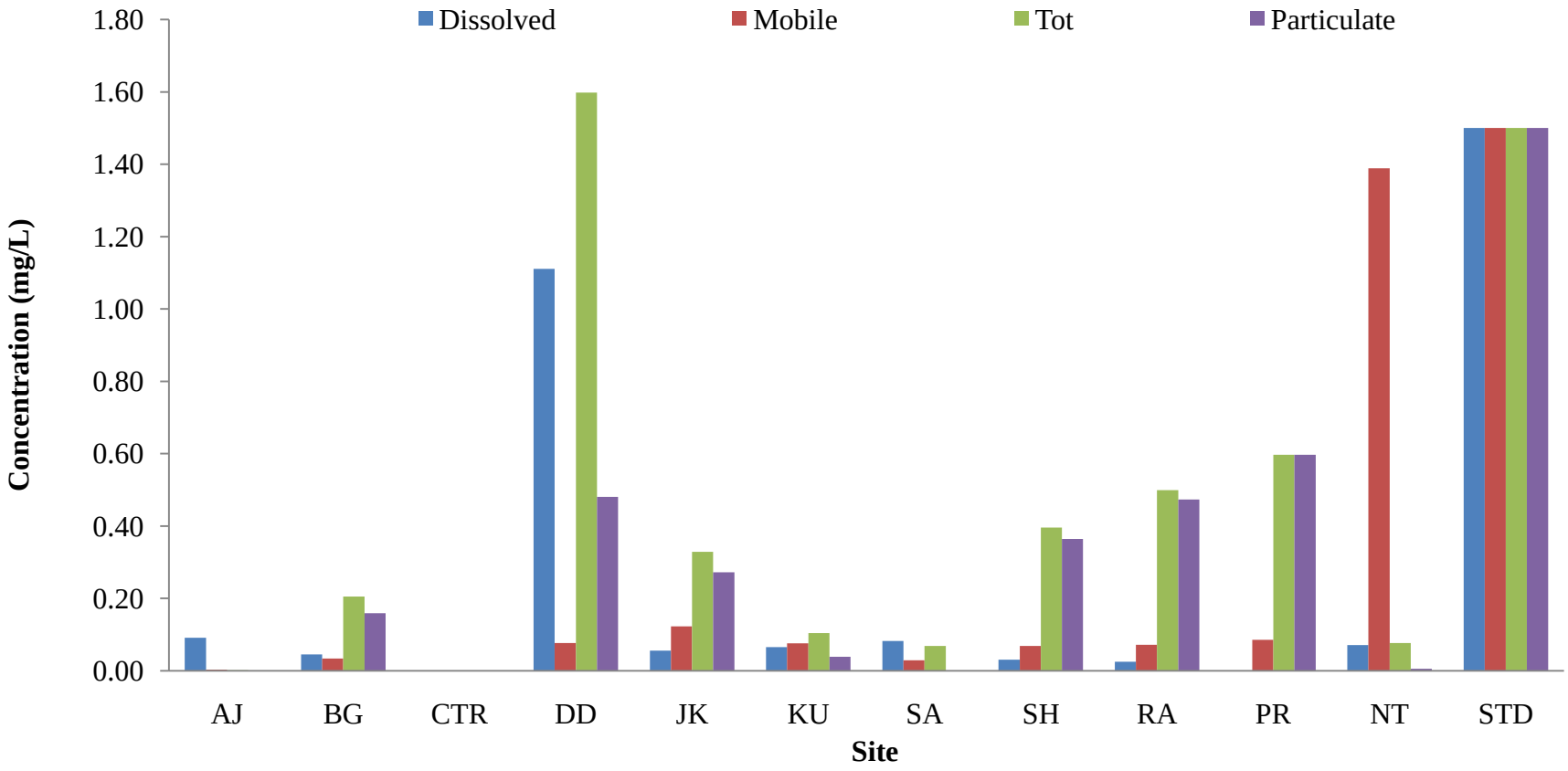


**Figure 4.39: Concentrations of copper (Cu) in the fractionated dumpsites leachates**

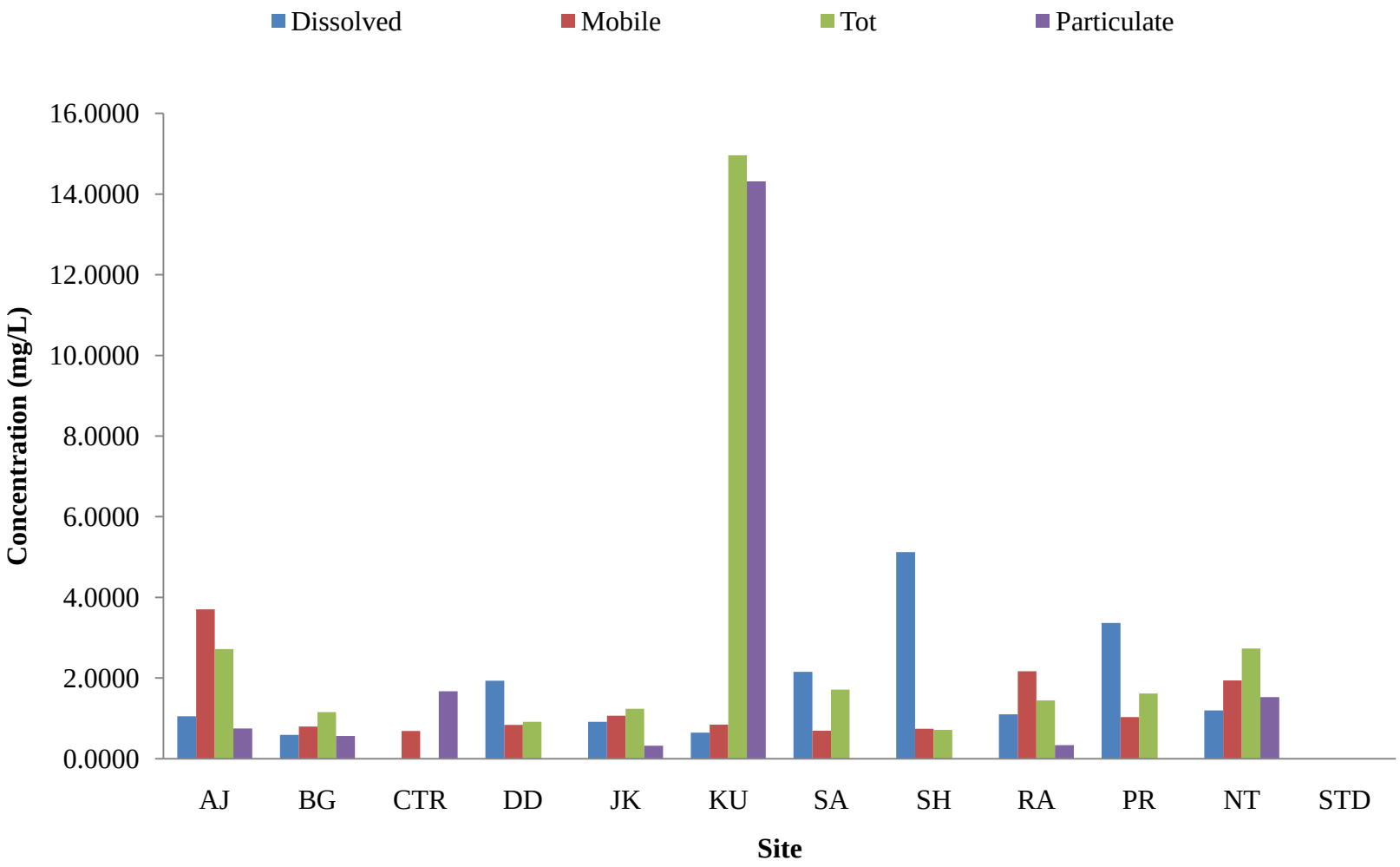


**Figure 4.40: Concentrations of mercury (Hg ) in the fractionated leachates**

### 4.9.2 Chemical fractionation of metals in the well waters

The summary of the concentrations of the fractionated hand-dug well water samples across the sites and seasons are presented in Figures 4.41 to 4.50 and appendices XXI to XXX

(a) Zinc

Figures 4.41 and 4.42 and appendices XXI and XXII showed the extractable fractions for zinc across the sites and seasons (wet and dry). The concentration of the total extractable fraction of Zn in the wet season across the sites range from 0.085 (PR) to 2.364mg/L mg/L (RA) while bioavailable fraction range from 31.567 % ( NTC) to 99.513 % (AJ). The range of the bioavailable fractions of Zn across the sites for the dry season range from 31.499 (CTR) to 99.513% (DD SA BG). However, the range of BDL (BG, CTR, DD, SA) to 0.373 mg/kg was recorded for the total extractable fraction.

(b) Lead

The concentrations of the extractable fractions of lead in the underground water are shown in appendices XXIII and XXIV and Figures 4.43 to 4.44, respectively. The concentration of the total extractable fraction of Pb in the wet season across the sites range from BDL (BG, CTR, SA ) to 1.877 mg/L (RA) while the range of 7.73 (CTR) to 100% (NTC, SA, JK, DD, CTR and BG) was recorded in the bioavailable phase. Similarly, the bioavailable fraction of Pb across the sites for dry season range from BDL (CTR) to 100% (SA DD and BG) while the total extractable fraction range from BDL (BG, CTR, and SA) to 2.816mg/L) (RA) respectively. Also, the range of BDL (CTR) to 100% (SA, DD and BG) was recorded in the bioavailable fractions of Pb across the sites.

(c) Cadmium

Appendices XXV and XXVI revealed the concentrations of the extractable fractions of the cadmium which were also presented in Figures 4.25 and 4.26, respectively. The concentration range of the total extractable fraction of Cd across the sites during the wet season range from BDL (CTR, DD, JK) to 0.134 mg/L (AJ) while range of the bioavailable fraction across the sites was 72.272 (PR) to 100% (BG, CTR, JK, DD, NTC). Also, the range of the total extractable fraction of Cd recorded during the dry season was BDL (CTR) to 0.089mg/L (AJ) with the range of 67.88% (PR) to 100 % (BG DD, JK, KU, SA and RA) in the bioavailable fraction as presented in the appendix XXX.

(d) Copper

The results of copper concentrations in the analysed samples of water at the vicinity of dumpsites are presented in Figures 4.27 to 4.28 and appendices XXVII and XXVIII, respectively. The concentration of the total extractable fraction of Cu across the sites for the wet season range from BDL (CTR, DD, JK) to 96.666 mg/L while the bioavailable fractions across the sites was between BDL (CTR)–100 % ( RA JK and DD). The levels of total extractable fraction of Cu recorded in the water during the dry season range from BDL (CTR, DD, JK, KU, SA and RA) to 73.23 mg/L (SA). The bioavailable fraction of Cu during the dry season across the sites range from BDL (CTR) to 100% (RA) as presented in the appendices.

(e) Mercury

The results of the sequential extraction of mercury in the water samples are also presented in appendices XXIX and XXXV and Figures 4.29 to 4.30 across the seasons.

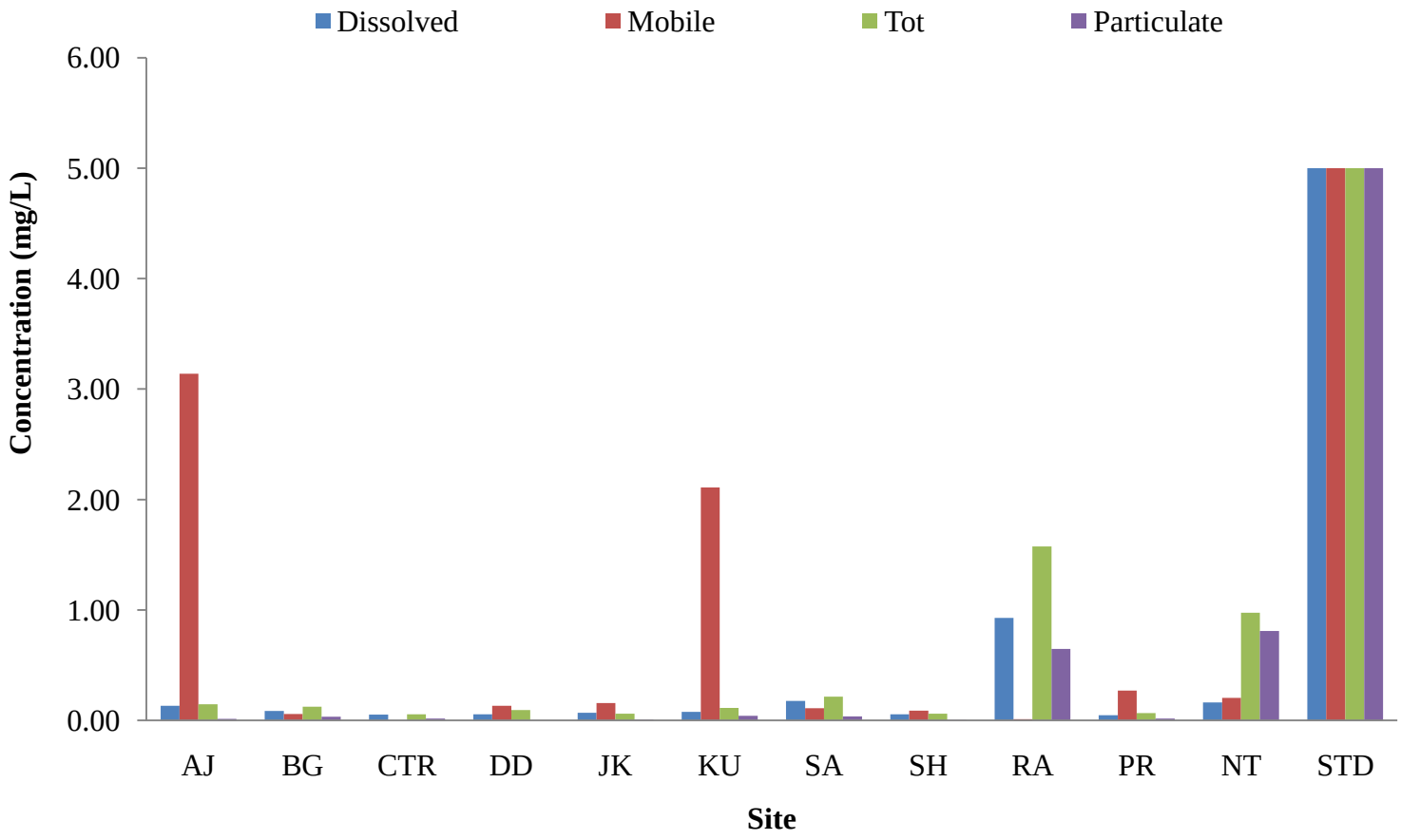


**Figure 4.41: Mean concentration of zinc (Zn) in well water for dry season**

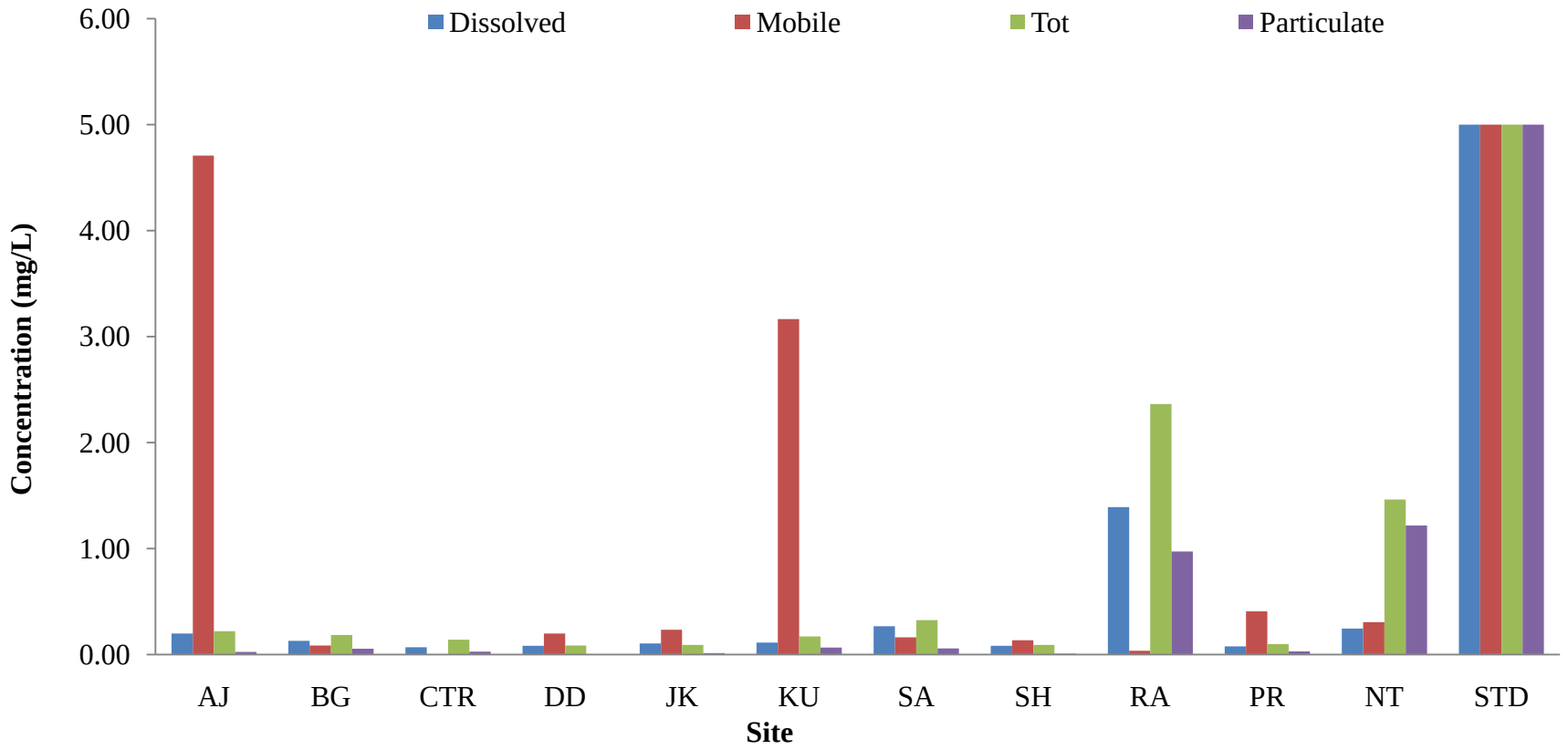


**Figure 4.42: Mean concentration of zinc (Zn) in well water for wet season**

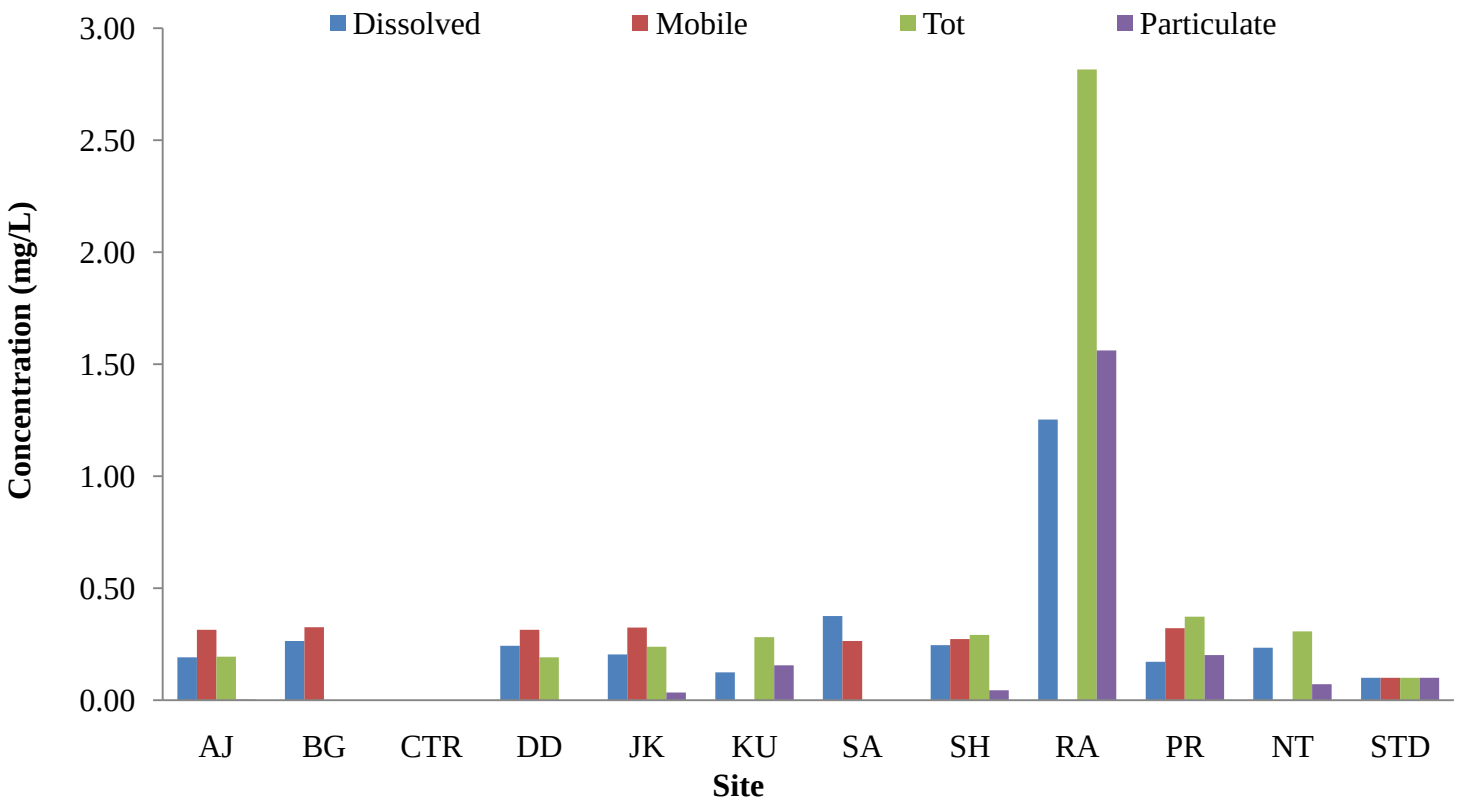


**Figure 4.43: Mean Concentration of lead (Pb) in the well water for dry seas**

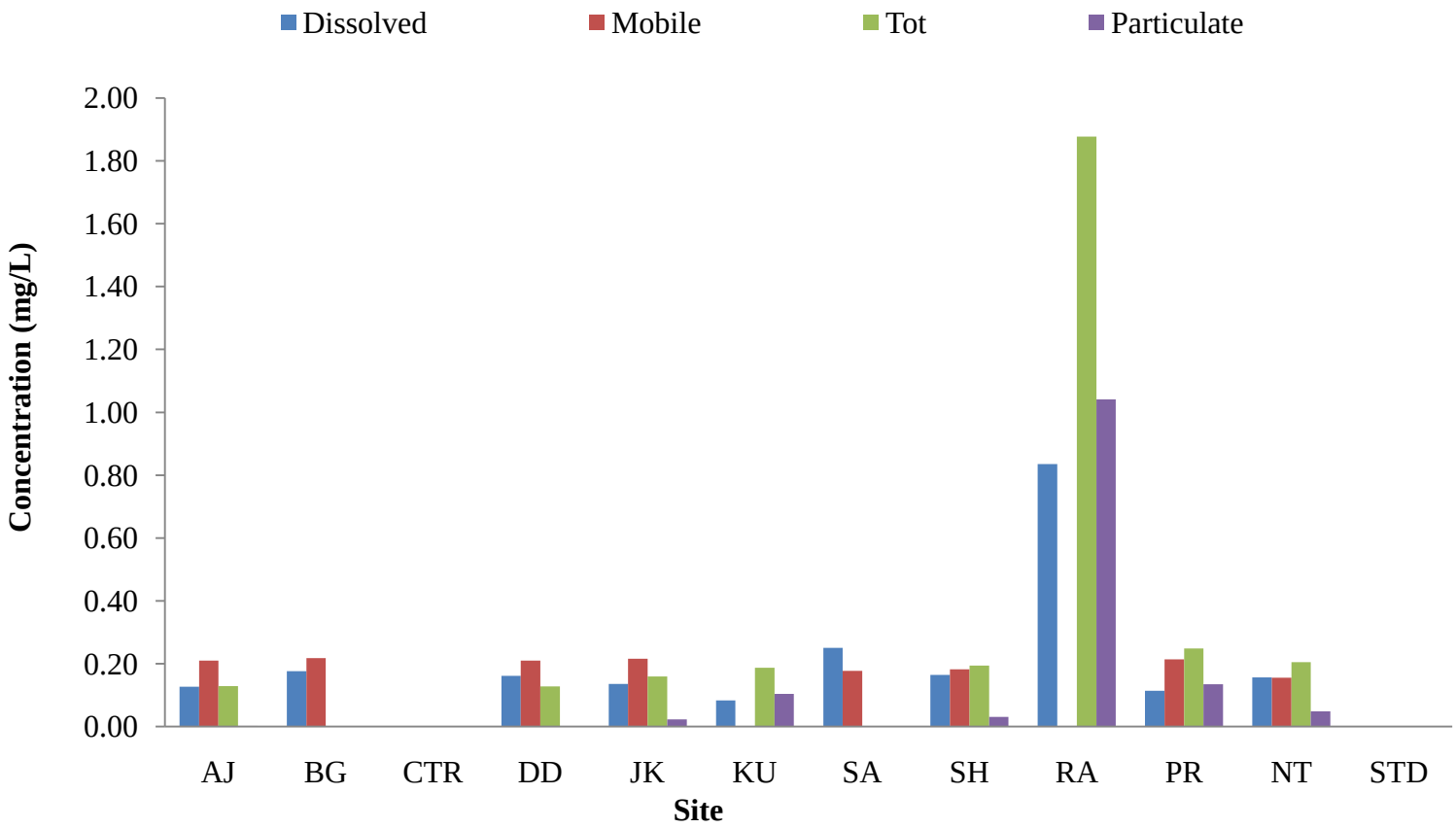


**Figure 4.44: Mean concentration of lead (Pb) in wells at the vicinity of dumpsites for wet season**

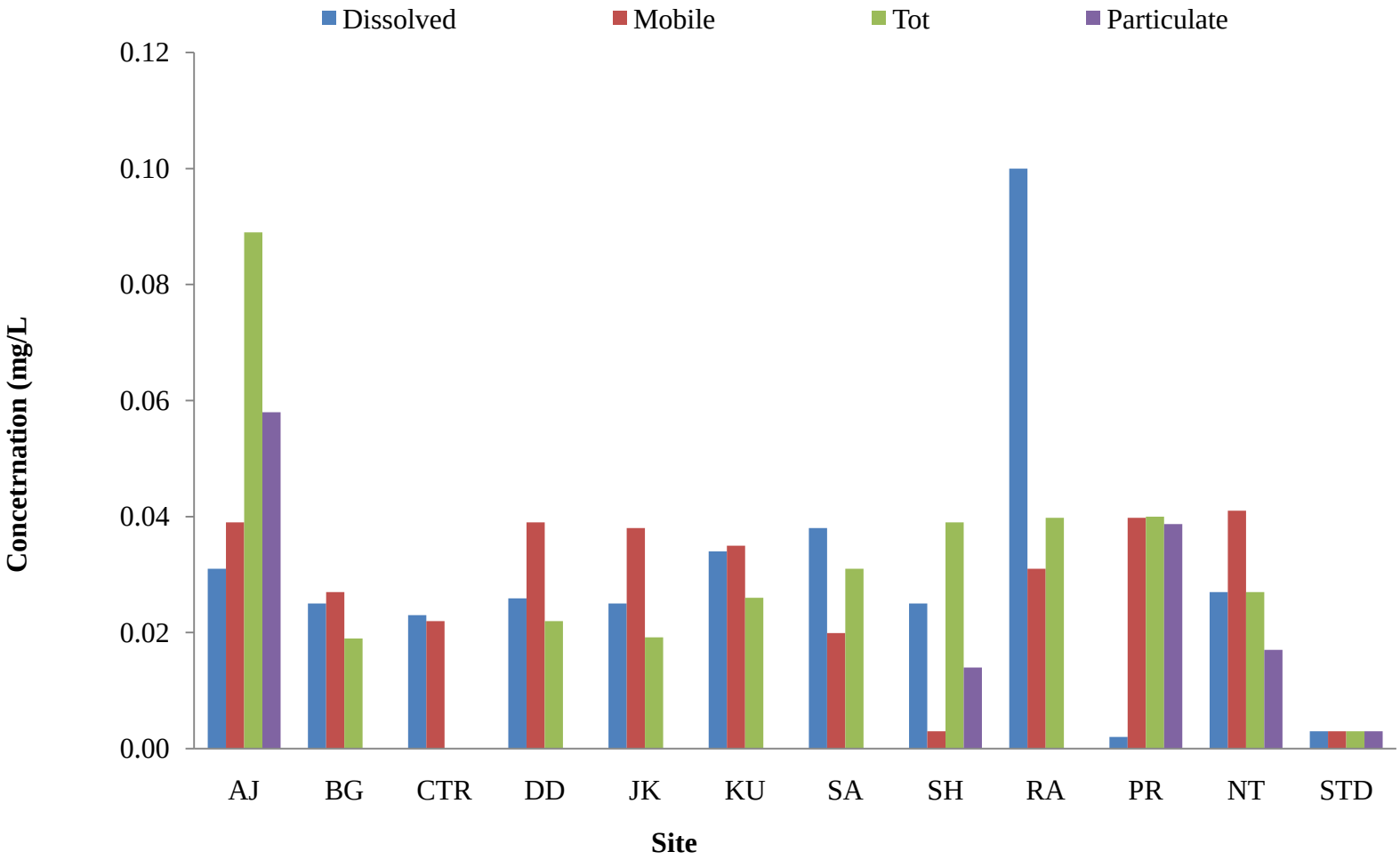


**Figure 4.45: Mean concentration of cadmium (Cd) in well water near the dumpsites for dry season**

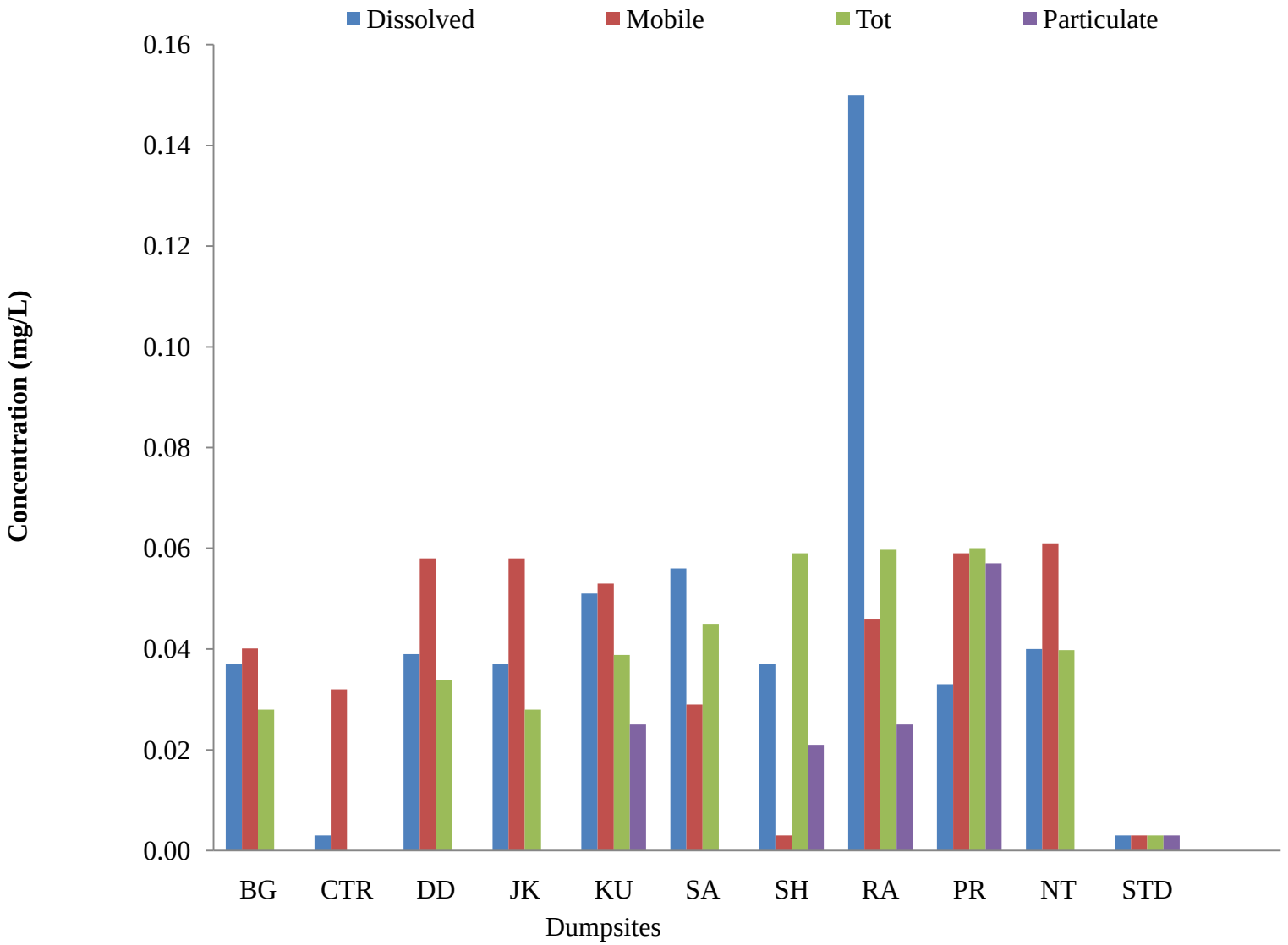


**Figure 4.46: Mean concentration of cadmium (Cd) in well water at the vicinity of dumpsites for wet season**

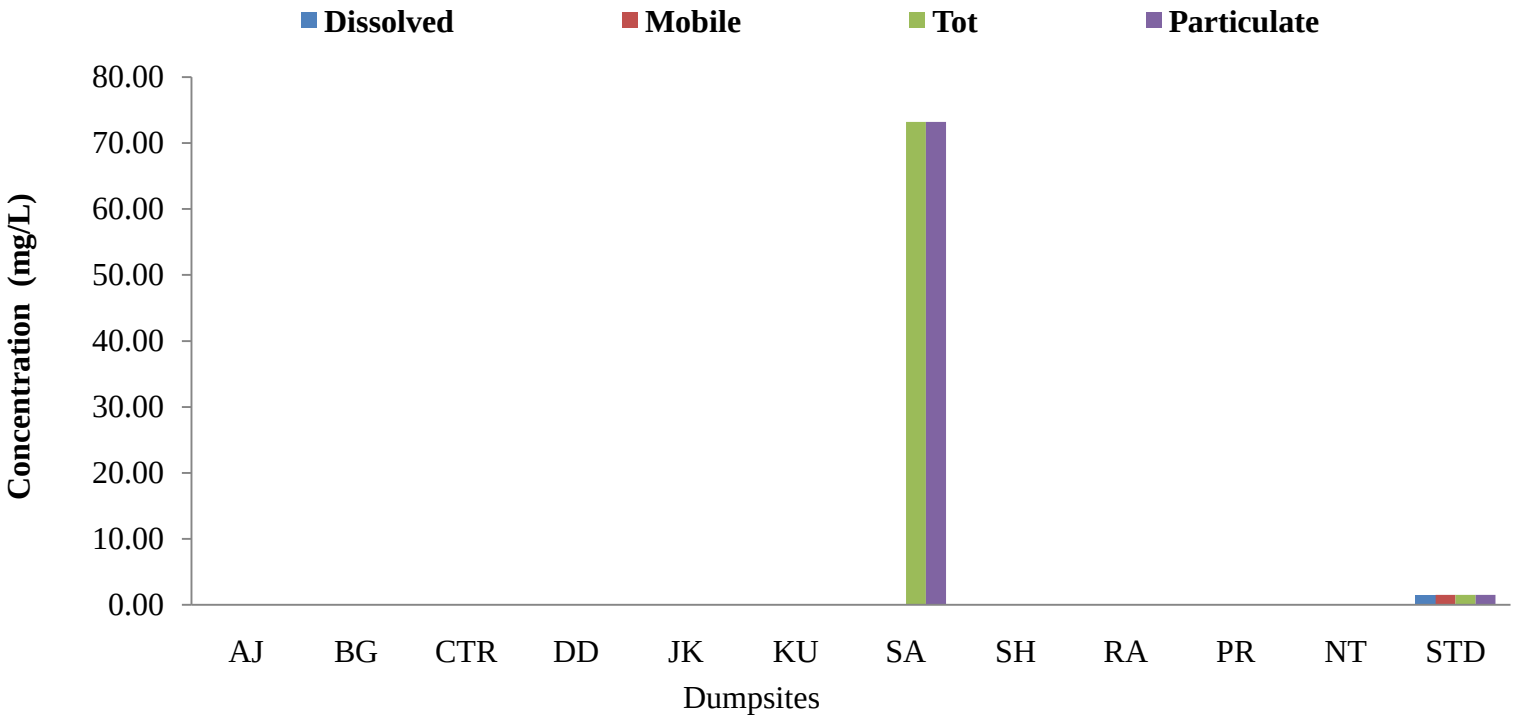


**Fig. 4.47: Mean concentration of copper (Cu) in well water at the vicinity of dumpsites for dry season**

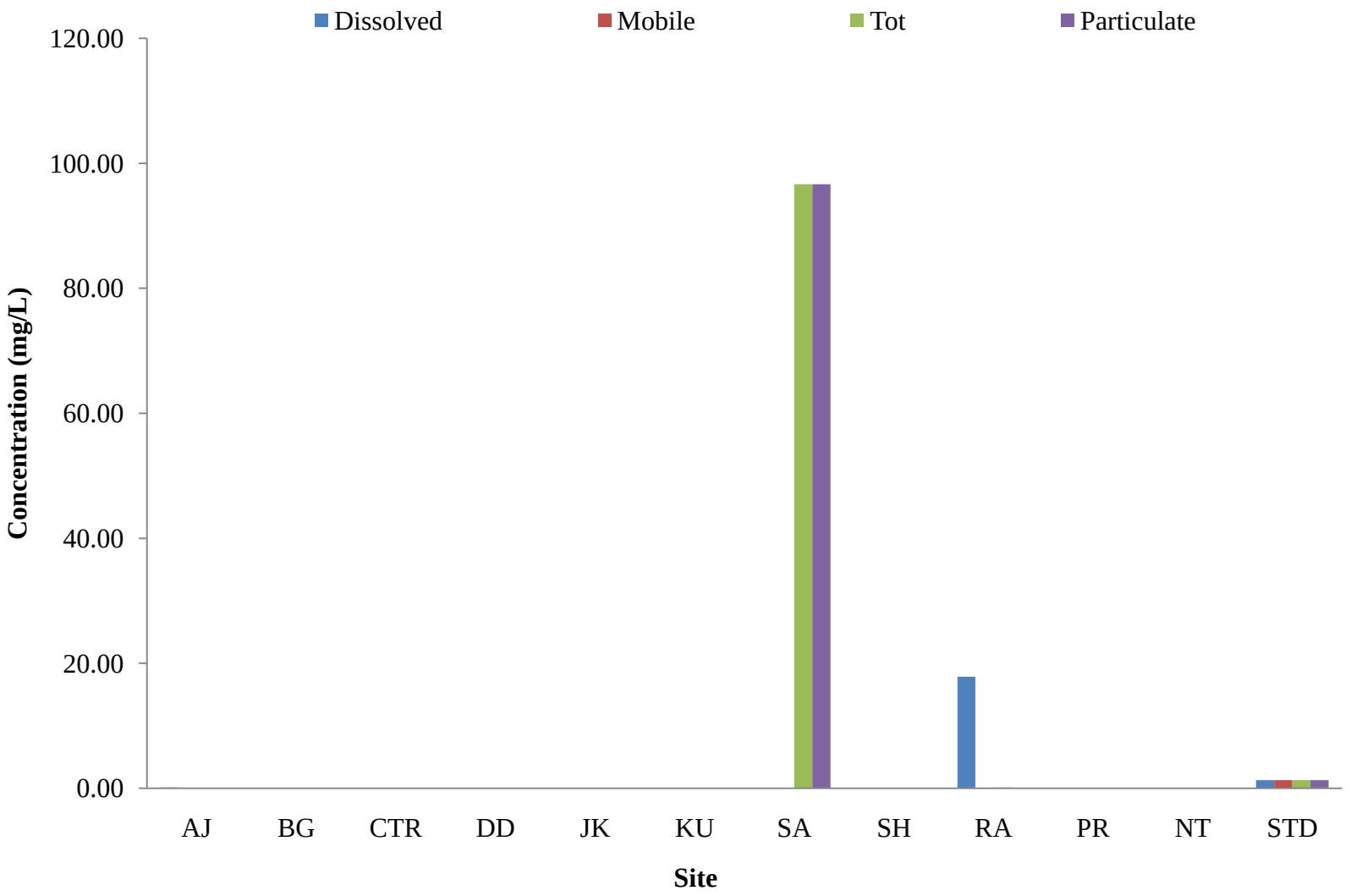


**Fig. 4.48: Mean concentration of copper (Cu) in wells at the vicinity of dumpsites for rainy season**

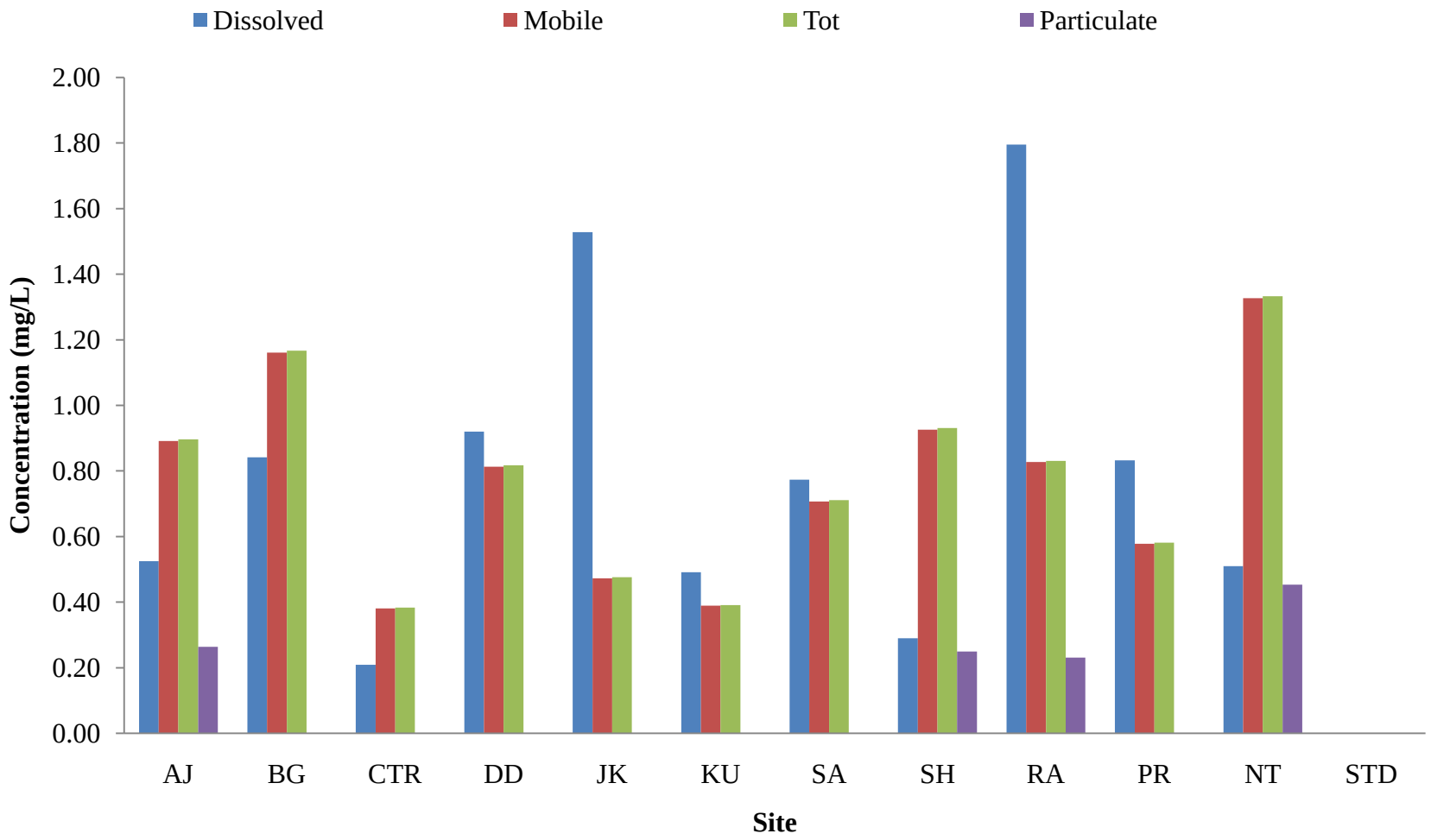


**Fig. 4.49: Mean concentration of mercury (Hg) in wells at the vicinity of dumpsites for dry season**

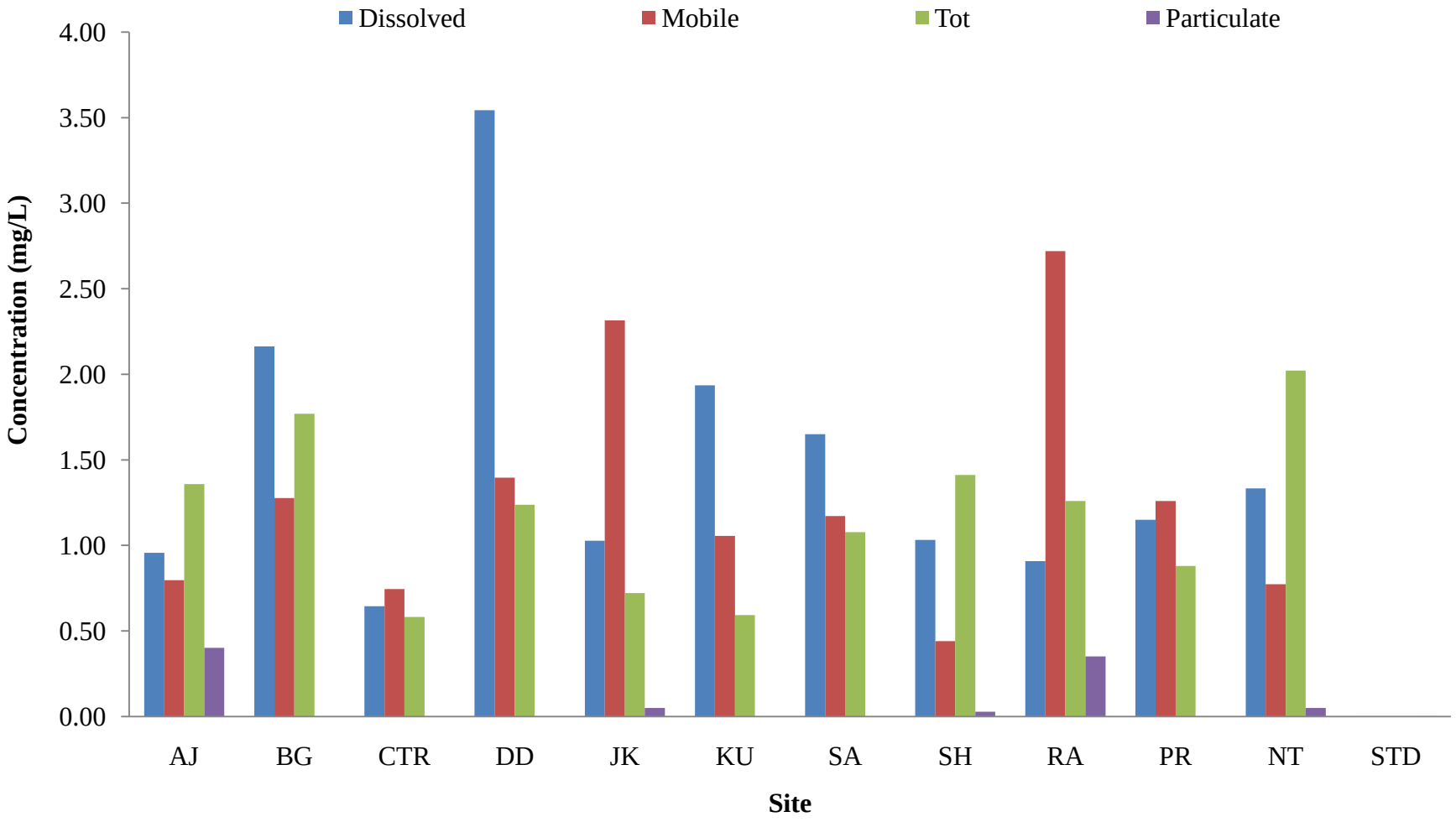


**Figure 4.50: Mean concentration of mercury (Hg) in well waters for wet season**

The concentration ranges of the extractable fractions of Hg in the wet season across the sites range from 0.581 (CTR) to 2.021 mg/L (NTC), while the bioavailable fractions across the sites range from 85.73(NTC) –100% (PR, SA, KU, DD, CTR and BG wells). The concentration range recorded for the total extractable fraction of Hg during the dry season was 0.383 (CTR) to 1.333 mg/kg (NTC) while the range recorded in the bioavailable fraction was 87.50 (NTC) to 100 % (BG, CTR, DD, KU, SA and PR), respectively.

### 4.10: Heavy Metals in Chicken Samples

4.10.1 Concentration of zinc in chicken samples

The results in Tables 19 to 28 summarize the mean (± SD) concentrations of heavy metals in different samples of chickens fed with dumpsite wastes in dry and wet seasons, respectively. The range of Zn observed in the samples were: BDL (CTR) to 4.27 mg/kg and BDL (CTR) to 5.77 mg/kg (KU) for oesophagus for samples of the contaminated chickens across the sites.

Similarly, the concentration ranges of Zn in the lungs of the chicken samples across the seasons (wet and dry) were: BDL (AJ, BG, CTR, DD, JK, SA, SH, PR) to 2.90 mg/kg (SA) and BDL (AJ, BG, CTR, DD, JK, SA, SH, PR) to 3.91 mg/kg (SA), respectively, as presented in Tables 4.16 and 4.17. Furthermore, as presented in Tables, the concentrations of zinc recorded in the bones of the contaminated chicken samples across the sites and seasons were: BDL (AJ, BG, CTR, DD, JK, SA, SH and PR) to 3.89 mg/kg (RA) and BDL (AJ, BG, CTR, DD, JK, SA, SH and PR) to 5.25 mg/kg (RA). The concentration ranges of Zn recorded in the kidneys of the chickens across the sites range from BDL (CTR) to 1.324 and BDL (CTR) to 1.787 mg/kg (DD) as presented in Table 4.19 and 4.20, respectively. Moreover, the concentration ranges of Zn in the intestine of the contaminated chicken

**Table 4.19: Concentrations (mg/kg) of Zinc in the contaminated chickens organs for the wet season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT | STD |
| OER | 0.756± 0.005 | 0.781± 0.006 | BDL | 4.134± 0.029 | 1.064± 0.008 | 4.271± 0.030 | 2.760± 0.020 | 0.776± 0.006 | 0.103± 0.001 | 0.529± 0.004 | 0.154± 0.001 | 5.000 |
| LUR | BDL | BDL | BDL | 2.013± 0.014 | 1.241± 0.009 | 0.098± 0.001 | 2.89± 0.021 | BDL | BDL | BDL | 1.449± 0.010 | 5.000 |
| BOR | BDL | BDL | BDL | BDL | BDL | 1.051± 0.007 | BDL | BDL | 3.892± 0.028 | BDL | 1.639± 0.012 | 5.000 |
| KIR | 0.755± 0.747 | 0.967± 0.957 | BDL | 1.324± 1.311 | 0.986± 0.976 | 1.004± 0.994 | 0.751± 0.743 | 0.856± 0.847 | 0.494± 0.489 | 1.093± 1.082 | 0.852± 0.843 | 5.000 |
| INTR | 0.972± 0.007 | 1.388± 0.010 | 0.185± 0.001 | 0.721± 0.005 | 0.997± 0.007 | 1.210± 0.009 | 1.109± 0.008 | 1.146± 0.008 | 3.334± 0.024 | 0.166± 0.001 | 3.159± 0.022 | 5.000 |
| HR | 0.946± 0.007 | 1.051± 0.007 | BDL | 2.992± 0.021 | 1.063± 0.008 | 1.189± 0.008 | 1.694± 0.012 | 0.496± 0.004 | 0.117± 0.001 | 0.133± 0.001 | 3.214± 0.023 | 5.000 |
| GIR | 1.372± 0.010 | 1.303± 0.009 | BDL | 0.412± 0.003 | 2.373± 0.017 | 1.312± 0.009 | 2.696± 0.019 | 1.918± 0.014 | 0.147± 0.001 | 0.907± 0.006 | 1.960± 0.014 | 5.000 |
| FER | 2.529± 0.018 | 1.657± 0.012 | BDL | 0.420± 0.003 | 2.415± 0.017 | 2.988± 0.021 | 0.468± 0.003 | 1.912± 0.014 | 0.131± 0.001 | 0.89± 0.006 | 0.349± 0.002 | 5.000 |
| WR | 1.156± 0.008 | 0.631± 0.004 | BDL | BDL | BDL | 0.347± 0.002 | BDL | 1.205± 0.009 | BDL | BDL | BDL | 5.000 |
| SKIR | 0.916± 0.007 | 0.999± 0.007 | 0.144± 0.001 | 0.629± 0.004 | 4.806± 0.034 | 0.830± 0.006 | 1.995± 0.014 | 1.224± 0.009 | 4.553± 0.032 | 0.497± 0.004 | 0.889± 0.006 | 5.000 |
| HER | BDL | BDL | BDL | 2.236± 0.016 | BDL | 0.551± 0.004 | 1.919± 0.014 | 1.973± 0.014 | 2.560± 0.018 | BDL | 4.445± 0.032 | 5.000 |
| MUR | 0.672± 0.005 | 0.119± 0.001 | BDL | 0.822± 0.006 | 6.551± 0.047 | 0.507± 0.004 | 1.662± 0.012 | 0.434± 0.003 | 3.634± 0.026 | 2.726± 0.019 | 0.130± 0.001 | 5.000 |
| LER | 1.821± 0.013 | 0.569± 0.004 | 0.445± 0.003 | 0.664± 0.005 | 2.816± 0.020 | 2.573± 0.018 | 1.473± 0.010 | 3.002± 0.021 | 1.236± 0.009 | 2.314± 0.016 | 1.311± 0.009 | 5.000 |
| LIR | 0.751± 0.005 | 1.046± 0.007 | BDL | 0.175± 0.001 | 0.123± 0.001 | 1.232± 0.009 | 0.492± 0.003 | 1.910± 0.014 | 1.540± 0.011 | 1.449± 0.010 | 0.209± 0.001 | 5.000 |
| BRR | BDL | BDL | BDL | BDL | BDL | BDL | 2.429± | BDL | BDL | BDL | 4.622 | 5.000 |

**Table 4.20: Concentrations of zinc in chicken samples for dry season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT | STD |
| OED | 1.021± 0.007 | 1.054± 0.007 | BDL | 5.581± 0.040 | 1.437± 0.010 | 5.767± 0.041 | 3.726± 0.026 | 1.048± 0.007 | 0.139± 0.001 | 0.715± 0.005 | 0.208± 0.001 | 5.000 |
| LUD | BDL | BDL | BDL | 2.717± 0.019 | 1.675± 0.012 | 0.131± 0.001 | 3.913± 0.028 | BDL | BDL | BDL | 1.957± 0.014 | 5.000 |
| BOD | BDL | BDL | BDL | BDL | BDL | 1.418± 0.010 | BDL 0.000 | BDL 0.000 | 5.254± 0.037 | BDL 0.000 | 2.214± 0.016 | 5.000 |
| KID | 1.019± 1.009 | 1.305± 1.292 | BDL 0.000 | 1.787± 1.770 | 1.331± 1.318 | 1.355± 1.342 | 1.014± 1.004 | 1.155± 1.144 | 0.666± 0.660 | 1.475± 1.461 | 1.150± 1.139 | 5.000 |
| INTD | 1.312± 0.009 | 1.874± 0.013 | 0.249± 0.002 | 0.974± 0.007 | 1.348± 0.010 | 1.635± 0.012 | 1.498± 0.011 | 1.547± 0.011 | 4.501± 0.032 | 0.224± 0.002 | 4.265± 0.030 | 5.000 |
| HD | 1.277± 0.009 | 1.418± 0.010 | BDL | 4.040± 0.029 | 1.436± 0.010 | 1.605± 0.011 | 2.287± 0.016 | 0.670± 0.005 | 0.159± 0.001 | 0.179± 0.001 | 4.338± 0.031 | 5.000 |
| GID | 1.852± 0.013 | 1.759± 0.013 | BDL | 0.557± 0.004 | 3.204± 0.023 | 1.771± 0.013 | 3.639± 0.026 | 2.589± 0.018 | 0.198± 0.001 | 1.225± 0.009 | 2.646± 0.019 | 5.000 |
| FED | 3.415± 0.024 | 2.237± 0.016 | BDL | 0.568± 0.004 | 3.261± 0.023 | 4.035± 0.029 | 0.633± 0.004 | 2.582± 0.018 | 0.177± 0.001 | 1.203± 0.009 | 0.471± 0.003 | 5.000 |
| WD | 1.561± 0.011 | 0.852± 0.006 | BDL | BDL | BDL | 0.468± 0.003 | BDL | 1.628± 0.012 | BDL | BDL | BDL | 5.000 |
| SKID | 1.237± 0.009 | 1.349± 0.010 | 0.194± 0.001 | 0.850± 0.006 | 6.489± 0.046 | 1.122± 0.008 | 2.693± 0.019 | 1.652± 0.012 | 6.146± 0.044 | 0.671± 0.005 | 1.201± 0.009 | 5.000 |
| HED | BDL | BDL | BDL | 3.019± 0.021 | BDL | 0.744± 0.005 | 2.591± 0.018 | 2.663± 0.019 | 3.456± 0.025 | BDL | 6.002± 0.043 | 5.000 |
| MUD | 0.908± 0.006 | 0.161± 0.001 | BDL | 1.111± 0.008 | 8.844± 0.063 | 0.685± 0.005 | 2.244± 0.016 | 0.585± 0.004 | 4.907± 0.035 | 3.681± 0.026 | 0.176± 0.001 | 5.000 |
| LED | 2.458± 0.017 | 0.768± 0.005 | 0.602± 0.004 | 0.896± 0.006 | 3.803± 0.027 | 3.474± 0.025 | 1.988± 0.014 | 4.053± 0.029 | 1.668± 0.012 | 3.124± 0.022 | 1.770± 0.013 | 5.000 |
| LID | 1.014± 0.007 BDL | 1.412± 0.010 | BDL | 0.236± 0.002 | 0.167± 0.001 | 1.662± 0.012 | 0.663± 0.005 | 2.579± 0.018 | 2.079± 0.015 | 1.957± 0.014 | 0.283± 0.002 | 5.000 |
| BRD | | BDL | BDL | BDL | BDL | BDL | 3.280± 0.023 | BDL | BDL | BDL | 6.239± 0.044 | 5.000 |

samples both across the sites and seasons were: 0.166 mg/kg (PR) to 3.334 mg/kg and 0.224 mg/kg(PR) to 4.501 mg/kg (RA), respectively.

The concentration ranges of Zn in the head samples of the contaminated chicken were BDL (CTR) to 3.214 mg/kg and BDL (CTR) to 4.339 mg/kg (NTC), respectively as Tables. Furthermore, the concentrations recorded in gizzard of the chicken samples across the sites and seasons were: BDL (CTR) to 2.70 mg/kg (SA) and BDL (CTR) to 3.64 mg/kg(SA) as presented in Tables 4.19 and 4.20. The concentration ranges of Zn across the sites and seasons in feather of the contaminated chicken samples were BDL (CTR) to 2.989 (KU) mg/kg and BDL (CTR) to 3.261 mg/kg (KU), respectively as presented in Tables The mean concentrations of Zn in the wattles of the chicken samples both across the sites and seasons were BDL (CTR, DD, JK, SA, RA, PR and NTC) to 1.206 mg/kg (SH) and BDL(CTR, DD, JK, SA, RA, PR and NTC) to 1.628 mg/kg respectively. The concentrations reported in this study in the skin of the contaminated chicken samples across the sites and seasons were 0.144 mg/kg(CTR) to 4.807 mg/kg(JK) and 0.195 mg/kg (CTR) to 6.489 mg/kg(JK) respectively as presented in the Tables 4.19 and 4.20.

The concentration ranges across the sites of and seasons of Zn in the heart of the contaminated chicken samples across the sites and seasons were BDL (AJ, BG, CTR, JK and PR) to 4.446 mg/kg (NT) and BDL (AJ, BG, CTR, JK and PR) to 6.002 mg/kg(NT) respectively as shown in Figure 4.63. The muscles of the contaminated chicken samples exhibit the following concentration ranges of Zn both across the sites and seasons: BDL (CTR) to 6.551 mg/kg and BDL(CTR) to 8.844 mg/kg (JK), respectively as presented in Tables 4.19 and 4.20, respectively. Furthermore, Zn concentrations in the leg samples of the contaminated chickens across the sites and seasons were 0.446 (CTR) to 3.002 mg/kg

and 0.602 (CTR) to 4.053 mg/kg (SH), respectively as presented in the Tables 4.19 and 4.20.

The Tables 4.19 and 4.20 show the mean concentrations of Zn in the liver of the contaminated chicken samples across the sites and seasons. The concentrations ranges of this metal both across the sites and seasons were BDL (CTR) to 1.910 mg/kg (SH) and BDL(CTR) to 2.579 mg/kg, respectively.

Moreover, the concentration of zinc in the brain samples of the contaminated chicken samples were analysed for zinc contents across the sites and seasons and zinc was not detected across the sites and seasons with the exception of two sites were concentrations of 2.430 (SH) to 4.622 mg/kg (NTC) and 3.280 (SA) to 6.240 mg/kg (NTC) were recorded as presented in the Tables 4.19 to 4.20.

4.10.2 Concentration of Pb in chicken samples

Tables 4.21 and 4.22 show the mean concentrations of lead in chicken samples across the sites and wet and dry. The concentration ranges of lead in the oesophagus samples during the wet and dry seasons were BDL (NTC, PR, RA, JK, SA and CTR) to 0.457 mg/kg (KU) and BDL (NTC, PR, RA, JK, SA and CTR) to 0.639 mg/kg (KU) as presented in Tables 4.18 and 4.19, respectively. The concentrations of lead in the lung, head, and bone samples were below the detection limit across the seasons were all below the detection limit (BDL) as presented in Tables 4.18 and 4.19, respectively. However, the levels recorded in the kidney samples were BDL (CTR, SA, RA, PR and NTC) to 0.338 mg/kg (BG) and BDL (CTR, SA, RA, PR and NTC) to 0.539 mg/kg (BG) as presented in Tables 4.21 and 4.22, respectively. The concentration ranges of lead recorded in the intestine of the contaminated chicken across the sites and seasons were BDL (CTR, JK, SA,

RA, PR, NT) to 0.557 ± 0.004mg/kg (NTC) to BDL(CTR, JK, SA, RA, PR, NTC) to 0.752 ± 0.005 mg/kg (NTC) as shown in the table.

Furthermore, the concentration recorded in the head of the contaminated chicken were below the detection limit across the sites as shown in The Tables. The concentration ranges recorded across the sites and seasons for lead in feather of the contaminated chickens were: BDL (AJ, SA, RA, CTR and PR) to 0.338 mg/kg (BG) and BDL (AJ, CTR, SA, RA and PR) to 0.457 mg/kg (BG) as presented in Tables.

The concentration ranges of lead recorded in gizzard of the contaminated chicken across the sites and seasons (wet and dry ) were: BDL ( CTR, DD, JK, SA, PR and NTC) to 0.379 ± 0.003 (RA) and BDL ( CTR, DD, JK, SA, PR and NTC) to 0.550 (RA), respectively as presented in the Tables 4.21 to 4.22, respectively. Similarly, the concentration ranges of lead recorded across the sites and seasons in the local chicken wattle samples were in the following ranges: BDL (AJ, DD, JK, SA, RA, PR, NTC and CTR) to 0.408 mg/kg (BG) and (JK, SA, RA, PR, NTC and CTR) to 0.551 mg/kg ( BG), respectively, as presented in Tables 4.21 and 4.22. Furthermore, the levels recorded in the skin samples across the sites and seasons were BDL (RA, SH, CTR) to 0.826 mg/kg (PR) and BDL (CTR, RA, SH) to 1.115 mg/kg, respectively, as presented in Tables 4.21 and 4.22, respectively. The concentration ranges for lead across the sites in the heart of the analysed chicken samples were BDL (CTR, DD , RA, PR) to 0.670 mg/kg (SH) and BDL (CTR, DD, RA, PR) to 0.904 (SH), respectively, as presented in appendices XL and XLI.

Similarly, as presented in the tables 4.18 and 4.19 below, the concentration ranges of lead in the samples of chicken legs were : BDL (CTR, DD, JK, SA, RA, PR and NTC) to 0.292 mg/kg (KU) and BDL (CTR, DD, JK, SA, RA, NT) to 0.394 mg/kg (KU) across the

**Table 4.21: Concentrations of lead in chicken organs for wet season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **AJ** | **BG** | **CTR** | **DD** | **JK** | **KU** | **SA** | **SH** | **RA** | **PR** | **NT** | **STD** |
| OER | 0.268± 0.002 | 0.245± 0.002 | | 0.473± 0.003 | BDL | 0.456± 0.003 | BDL | 0.247± 0.002 | BDL | BDL | BDL | 0.010 |
| LUR | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| BOR | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| KIR | 0.157± 0.001 | 0.330± 0.002 | BDL | 0.124± 0.001 | 0.110± 0.001 | 0.355± 0.003 | | 0.296± 0.0021 | BDL | BDL | BDL | 0.010 |
| INTR | 0.243± 0.002 | 0.203± 0.001 | BDL | 0.449± 0.003 | BDL | 0.259± 0.0018 | BDL | 0.215± 0.002 | BDL | BDL | 0.557± 0.0040 | 0.010 |
| HR | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| GIR | 0.308± 0.002 | 0.159± 0.001 | BDL | BDL | BDL | 0.253± 0.0018 | BDL | 0.379± 0.003 | 0.407± 0.0029 | BDL | BDL | 0.010 |
| FER | BDL | 0.338± 0.002 | BDL | 0.019± 0.001 | 0.132± 0.001 | 0.434± 0.0031 | BDL | 0.298± 0.002 | BDL | BDL | 0.065± 0.001 | 0.010 |
| WR | BDL | 0.407± 0.003 | BDL | BDL | BDL | 0.246± 0.0018 | BDL | 0.238± 0.0017 | BDL | BDL | BDL | 0.010 |
| SKIR | 0.320± 0.002 | 0.316± 0.002 | BDL | 0.367± 0.003 | 0.307± 0.002 | 0.131± 0.001 | 0.578± 0.004 | BDL | BDL | 0.825± 0.0059 | 0.820± 0.006 | 0.010 |
| HER | 0.337± 0.002 | 0.135± 0.001 | BDL | BDL | 0.048± 0.001 | 0.335± 0.002 | 0.005± 0.001 | 0.669± 0.005 | BDL | BDL | 0.084± 0.001 | 0.010 |
| MUR | 0.314± 0.002 | 0.344± 0.002 | BDL | 0.558± 0.004 | BDL | BDL | 0.428± 0.003 | 0.198± 0.001 | 0.817± 0.0058 | BDL | BDL | 0.010 |
| LER | 0.254± 0.002 | 0.163± 0.001 | BDL | BDL | BDL | 0.291± 0.002 | BDL | 0.199± 0.001 | BDL | BDL | BDL | 0.010 |
| LIR | 0.187± 0.001 | 0.283± 0.002 | BDL | BDL | BDL | 0.434± 0.003 | BDL | 0.415± 0.003 | BDL | BDL | BDL | 0.010 |
| BRR | BDL | 2.111± 0.015 | 2.213± 0.016 | 0.807± 0.006 | 1.501± 0.011 | BDL | 0.478± 0.003 | BDL | BDL | 1.925± 0.014 | 0.807± 0.0057 | 0.010 |

**Table 4.22: Concentrations of lead in chicken organs for dry season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **AJ** | **BG** | **CTR** | **DD** | **JK** | **KU** | **SA** | **SH** | **RA** | **PR** | **NT** | **STD** |
| OED | 0.362± 0.003 | 0.331± 0.002 | BDL | 0.639± 0.005 | BDL | 0.616± 0.004 | BDL | 0.334± 0.002 | BDL | BDL | BDL | 0.010 |
| LUD | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| BOD | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| KID | 0.250± 0.053 | 0.539± 0.114 | BDL | 0.198± 0.042 | 0.176± 0.037 | 0.566± 0.119 | BDL | 0.472± 0.100 | BDL | BDL | BDL | 0.010 |
| INTD | 0.329± 0.002 | 0.275± 0.002 | BDL | 0.607± 0.004 | BDL | 0.350± 0.003 | BDL | 0.291± 0.002 | BDL | BDL | 0.752± 0.005 | 0.010 |
| HD | BDL | BDL | BDL | BDL | BDL | 0.001 0.003 | BDL | BDL | BDL | BDL | BDL | 0.010 |
| GID | 0.416± 0.003 | 0.214± 0.002 | BDL | BDL | BDL | 0.342± 0.002 | BDL | 0.511± 0.004 | 0.550± 0.0039 | BDL | BDL | 0.010 |
| FED | 0.400± | 0.456± 0.003 | BDL | 0.026± 0.001 | 0.178± 0.001 | 0.587± 0.004 | BDL | 0.402± 0.003 | BDL | BDL | 0.087± 0.001 | 0.010 |
| WD | BDL | 0.550± 0.004 | BDL | BDL | BDL | 0.333± 0.002 | BDL | 0.322± 0.002 | BDL | BDL | BDL | 0.010 |
| SKID | 0.432± 0.003 | 0.427± 0.003 | BDL | 0.494± 0.004 | 0.415± 0.003 | 0.177± 0.001 | 0.780± 0.006 | BDL | BDL | 1.114± 0.008 | 1.108± 0.008 | 0.010 |
| HED | 0.455± 0.003 | 0.182± 0.001 | BDL | BDL | 0.064± 0.001 | 0.452± 0.003 | 0.006± | 0.904± 0.006 | BDL | BDL | 0.112± 0.001 | 0.010 |
| MUD | 0.424± 0.003 | 0.464± 0.003 | BDL | 0.753± 0.005 | BDL | BDL | 0.578± 0.004 | 0.267± 0.002 | 1.104± 0.0078 | BDL | BDL | 0.010 |
| LED | 0.343± 0.002 | 0.220± 0.002 | BDL | BDL | BDL | 0.393± 0.003 | BDL | 0.268± 0.002 | BDL | BDL | BDL | 0.010 |
| LID | 0.252± 0.002 | 0.382± 0.003 | BDL | BDL | BDL | 0.587± 0.0042 | BDL | 0.561± 0.004 | BDL | BDL | BDL | 0.010 |
| BRD | BDL | 2.850± 0.020 | 2.988± 0.021 | 1.090± 0.008 | 2.026± 0.014 | BDL | 0.646± 0.005 | BDL | BDL | 2.599± 0.019 | 1.091± 0.008 | 0.010 |

sites and seasons (wet and dry), respectively. The concentration ranges recorded in the chicken-liver samples across the seasons were BDL(CTR, DD, JK, SA, RA, PR and NTC) 0.43mg/kg (KU) and BDL (CTR, DD, JK, SA, RA, PR and NT) to 0.587 mg/kg (KU), respectively, as presented in Tables 4.21 and 4.22, respectively. Furthermore, the enhanced level of lead recorded in the brain of the contaminated chicken samples across the sites and seasons were BDL (AJ, KU, SH, RA) to 2.111 mg/kg (SH) and BDL (AJ, KU, SH, RA) to 2.850 mg/kg (BG) as presented in the Tables.

4.10.3 Concentration of Cd in chicken samples

Tables 4.23 and 4.24 show the mean concentrations of cadmium in the chicken samples across the sites and seasons. The concentrations of cadmium in the oesophagus of the contaminated chicken samples across the sites and seasons were presented in Tables The ranges of these concentrations were BDL (CTR) to 0.086 mg/kg (RA) and BDL (CTR) to 0.082 (BG and JK) for the wet and dry seasons, respectively. Similarly, the concentration ranges recorded for cadmium in the lung samples of the contaminated chicken samples were BDL (CTR) to 0.090 mg/kg (NTC) and BDL (CTR) to 0.121 mg/kg (NTC) respectively, as presented in the Tables 4.23 and 4.24. Furthermore, the concentrations of cadmium recorded in the bones samples of the contaminated chicken samples across the sites and seasons were BDL (AJ, BG, CTR, DD, KU, SH and PR) and BDL (AJ, BG, CTR, DD, KU, SH and PR) for the wet and dry seasons, respectively as presented in Tables 4.25 and 4.26. Moreover, the concentration ranges of cadmium in the kidney of the contaminated chicken samples across the sites and seasons were 0.020 (CTR) to 0.075 mg/kg (RA) and 0.027 mg/kg (CTR) to 0.101 mg/kg (RA), respectively, for the wet and dry seasons as presented in the Tables 4.23 and 4.24.

The concentrations of cadmium in the intestine of the contaminated chicken samples for the wet and dry were 0.002 (CTR) to 0.082 mg/kg (RA) and 0.003 (CTR) to 0.110 mg/kg (RA) respectively as presented in the Tables. Futhermore, the concentrations of Cd in the head samples of the contaminated chicken samples across the sites and seasons were in the ranges of BDL (CTR) to 0.063 mg/kg (AJ) and BDL (CTR) to 0.081 mg/kg (AJ), respectively. The levels of cadmium recorde in the gizzard of the contaminated chicken samples were 0.021 (CTR) to 0.071 mg/kg (SH) and 0.028 (CTR) to 0.095 mg/kg (JK), respectively, as shown in Table. The highest concentrations were recorded at sites JK and SH. Moreover, the concentrations of cadmium in feather of the contaminated chicken samples both across the sites and seasons were BDL (CTR) to 0.065 mg/kg and BDL (CTR) to 0.088 mg/kg (BG) as presented in the Tables 4.23 and 4.24, respectively.

The concentrations of cadmium recorded in the wattle samples of the contaminated chicken samples across the sites and seasons were presented in Figure 4.91. The following ranges were recorded in the wet and dry seasons: BDL (CTR, DD, JK, SA, SH, RA, PR and NTC) to 0.074 mg/kg (AJ) and BDL (CTR, DD, JK, SA, SH, RA, PR, and NTC) to 0.099 mg/kg (AJ) for the wet and dry seasons respectively as presented in Figure 4.92. Similarly, as presented in Figure 4.92, the concentrations of cadmium in the skin of the contaminated chicken samples were 0.021 (CTR) to 0.066 mg/kg (RA) and 0.028 (CTR) to 0.089 mg/kg during the wet and dry seasons, respectively.

**Table 4.23: Concentrations of cadmium in chicken samples for the wet season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT | STD |
| OER | 0.067± 0.0005 | 0.061± 0.0004 | BDL | 0.042± 0.0003 | 0.061± 0.0004 | 0.054± 0.0004 | 0.051± 0.0004 | 0.054± 0.0004 | 0.086± 0.0006 | 0.042± 0.0003 | 0.051± 0.0004 | 0.05 |
| LUR | 0.045± 0.0003 | 0.046± 0.0003 | BDL | 0.056± 0.0004 | 0.047± 0.0003 | 0.075± 0.0005 | 0.079± 0.0006 | 0.061± 0.0004 | 0.084± 0.0006 | 0.074± 0.0005 | 0.089± 0.0006 | 0.05 |
| BOR | BDL | BDL | BDL | BDL | BDL | BDL | 0.0716± 0.0005 | BDL | 0.081± 0.0006 | BDL | 0.048± 0.0003 | 0.05 |
| KIR | 0.055± 0.0004 | 0.066± 0.0005 | 0.019± 0.0001 | 0.049± 0.0004 | 0.041± 0.0003 | 0.059± 0.0004 | 0.051± 0.0004 | 0.062± 0.0004 | 0.075± 0.0005 | 0.044± 0.0003 | 0.054± 0.0004 | 0.05 |
| INTR | 0.061± 0.0004 | 0.048± 0.0003 | 0.002± 0.001 | 0.051± 0.0004 | 0.049± 0.0003 | 0.049± 0.0004 | 0.069± 0.0005 | 0.049± 0.0004 | 0.082± 0.0006 | 0.042± 0.0003 | 0.061± 0.0004 | 0.05 |
| HR | 0.062± 0.0004 | 0.046± 0.0003 | BDL | 0.059± 0.0004 | 0.052± 0.0004 | 0.055± 0.0004 | 0.039± 0.0003 | 0.056± 0.0004 | 0.019± 0.0001 | 0.043± 0.0003 | 0.053± 0.0004 | 0.05 |
| GIR | 0.059± 0.0004 | 0.041± 0.0003 | 0.021± 0.0001 | 0.047± 0.0003 | 0.071± 0.0005 | 0.040± 0.0003 | 0.069± 0.0005 | 0.071± 0.0005 | 0.058± 0.0004 | 0.039± 0.0003 | 0.062± 0.0004 | 0.05 |
| FER | 0.045± 0.0016 | 0.065± 0.0024 | BDL | 0.042± 0.0015 | 0.051± 0.0018 | 0.072± 0.0026 | 0.047± 0.0017 | 0.055± 0.0020 | 0.039± 0.0014 | 0.045± 0.0016 | 0.047± 0.0017 | 0.05 |
| WR | 0.073± 0.0005 | 0.065± 0.0005 | BDL | BDL | BDL | 0.068± 0.0005 | BDL | BDL | BDL | BDL | BDL | 0.05 |
| SKIR | 0.063± 0.0004 | 0.059± 0.0004 | 0.021± 0.0001 | 0.039± 0.0003 | 0.062± 0.0004 | 0.041± 0.0003 | 0.046± 0.0003 | 0.053± 0.0004 | 0.066± 0.0005 | 0.049± 0.0003 | 0.057± 0.0004 | 0.05 |
| HER | BDL | BDL | BDL | 0.061± 0.0004 | 0.036± 0.0003 | BDL | 0.079± 0.0006 | BDL | 0.071± 0.0005 | BDL | 0.076± 0.0005 | 0.05 |
| MUR | 0.063± 0.0047 | 0.073 0.0054 | 0.002± 0.0001 | 0.056± 0.0042 | 0.055± 0.0041 | 0.065± 0.0048 | 0.048± 0.0036 | 0.049± 0.0037 | 0.084± 0.0062 | 0.047± 0.0035 | 0.079± 0.0059 | 0.05 |
| LER | 0.061± 0.0045 | 0.065± 0.0048 | BDL | 0.039± 0.0029 | 0.051± 0.0038 | 0.061± 0.0045 | 0.041± 0.0030 | 0.059± 0.0045 | 0.064± 0.0047 | 0.064± 0.0047 | 0.050± 0.0037 | 0.05 |
| LIR | 0.044± 0.0033 | 0.055± 0.0041 | BDL | 0.041± 0.0030 | 0.042± 0.0031 | 0.054± 0.0040 | 0.053± 0.0040 | 0.067± 0.0049 | BDL | 0.047± 0.0035 | 0.045± 0.0033 | 0.05 |
| BRR | BDL | BDL | BDL | 0.001 | 0.055± | BDL | 0.058± | BDL | BDL | 0.062± | 0.000 | 0.05 |

**Table 4.24a: Concentrations (mg/l) of cadmium in chickens organs dry season**

| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT | STD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| OED | 0.089± 0.001 | 0.082± 0.001 | BDL | 0.056± 0.001 | 0.082± 0.001 | 0.073± 0.001 | 0.069± 0.001 | 0.073± 0.001 | 0.116± 0.001 | 0.056± 0.001 | 0.068± 0.001 | 0.05 |
| LUD | 0.060± 0.001 | 0.062± 0.001 | BDL | 0.075± 0.001 | 0.063± 0.001 | 0.101± 0.001 | 0.106± 0.001 | 0.082± 0.001 | 0.113± 0.001 | 0.099± 0.001 | 0.121± 0.001 | 0.05 |
| BOD | BDL | BDL | BDL | BDL | BDL | BDL | 0.097± 0.0007 | BDL | 0.109± 0.0008 | BDL 0.0000 | 0.066± 0.0005 | 0.05 |
| KID | 0.074± 0.001 | 0.089± 0.001 | 0.027± 0.001 | 0.067± 0.001 | 0.056± 0.001 | 0.081± 0.001 | 0.069± 0.001 | 0.083± 0.001 | 0.1007± 0.001 | 0.059± 0.001 | 0.073± 0.001 | 0.05 |
| INTD | 0.082± 0.0006 | 0.064± 0.0005 | 0.003± 0.001 | 0.069± 0.0005 | 0.066± 0.0005 | 0.067± 0.0005 | 0.094± 0.0007 | 0.067± 0.0005 | 0.110± 0.0008 | 0.056± 0.0004 | 0.082± 0.0006 | 0.05 |
| HD | 0.085± 0.0006 | 0.062± 0.0004 | BDL | 0.079± 0.0006 | 0.069± 0.0005 | 0.074± 0.0005 | 0.052± 0.0004 | 0.075± 0.0005 | 0.027± 0.0002 | 0.0578± 0.0004 | 0.0712± 0.0005 | 0.05 |
| GID | 0.080± 0.0006 | 0.055± 0.0004 | 0.028± 0.0002 | 0.063± 0.0004 | 0.095± 0.0007 | 0.054± 0.0004 | 0.094± 0.0007 | 0.095± 0.0007 | 0.078± 0.0006 | 0.052± 0.0004 | 0.083± 0.0006 | 0.05 |
| FED | 0.060± 0.002 | 0.088± 0.003 | BDL | 0.057± 0.002 | 0.068± 0.003 | 0.097± 0.004 | 0.063± 0.002 | 0.074± 0.003 | 0.054± 0.002 | 0.061± 0.002 | 0.063± 0.002 | 0.05 |
| WD | 0.099± 0.001 | 0.087± 0.001 | BDL | BDL | BDL | 0.091± 0.006 | BDL | BDL | BDL | BDL | BDL | 0.05 |
| SKID | 0.085± 0.001 | 0.081± 0.001 | 0.028± 0.002 | 0.052± 0.002 | 0.083± 0.001 | 0.055± 0.002 | 0.062± 0.006 | 0.071± 0.001 | 0.088± 0.001 | 0.066± 0.003 | 0.077± 0.001 | 0.05 |
| HED | BDL | BDL | BDL | 0.082± 0.0006 | 0.048± 0.0003 | BDL | 0.106± 0.0008 | BDL | 0.095± 0.0007 | BDL | 0.102± 0.0007 | 0.05 |
| MUD | 0.085± 0.006 | 0.099± 0.007 | 0.003± 0.001 | 0.076± 0.006 | 0.074± 0.006 | 0.087± 0.007 | 0.065± 0.005 | 0.067± 0.005 | 0.113± 0.008 | 0.063± 0.005 | 0.107± 0.008 | 0.01 |
| LED | 0.082± 0.006 | 0.087± 0.007 | BDL | 0.053± 0.004 | 0.069± 0.005 | 0.082± 0.006 | 0.055± 0.004 | 0.081± 0.006 | 0.086± 0.006 | 0.086± 0.006 | 0.068± 0.005 | 0.05 |
| LID | 0.059 | 0.074± | BDL | 0.055± | 0.056± | 0.073± | 0.072± | 0.089± | BDL | 0.063± | 0.060± | 0.05 |

| Sample | | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT | STD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.0055 | | 0.0041 | 0.0042 | 0.0054 | 0.0053 | 0.0067 | | 0.0047 | 0.0045 | |
| BRD | BDL | BDL | BDL | BDL | 0.074± 0.055 | BDL | 0.078± 0.0058 | BDL | BDL | 0.083± 0.0062 | BDL | 0.05 |

The concentrations of cadmium recorded in the heart samples of the contaminated chicken samples across the sites and seasons were presented in the Tables 4.23 and 4.24, respectively. The concentration ranges recorded for the wet and dry seasons were BDL (AJ, BG, CTR, KU, SH, PR) to 0.079 mg/kg (SA) and BDL (AJ, BG, CTR, KU, SH, PR) to 0.106 mg/kg (SA), respectively. Tables 4.23 and 4.24 show the concentrations of cadmium in the muscles of the contaminated chicken samples across the sites and seasons (wet and dry sesons). The ranges of the concentration of Cd in the samples were 0.002 (CTR) to 0.084 mg/kg (RA) and 0.003 (CTR) to 0.113 mg/kg (RA). The concentration ranges recorded in the leg samples of the contaminated chicken during the wet and dry seasons were: BDL (CTR) to 0.065 mg/kg (BG) and BDL (CTR) to 0.087 mg/kg (BG).

The levels of cadmium in the liver of the contaminated chicken samples acrosss the sites and seasons were presented in the Tables. The ranges across the sites and seasons were: BDL (CTR, RA) to 0.067 mg/kg (SH) and BDL (CTR, RA) to 0.090 mg/kg (SH) for the wet and dry seasons respectively. Similarly, the concentrations recorded in the brain samples across the sites and seasons were in the following ranges: BDL (AJ, BG, CTR, DD, KU, SH, RA, NTC) to 0.062 mg/kg (PR) and BDL (AJ, BG, CTR, DD, KU, SH, RA, NTC) to 0.083 mg/kg (PR) for the wet and dry seasons as presented in Tables 4.23 and 4.24, respectively.

4.10.4 Concentration of Cu in chicken samples

The mean concentration ranges for copper in the analysed chicken samples across the sites and seasons (wet and dry) were presented in Tables 4.25 and 4.26, respectively.The concentration ranges of copper recorded in oesophagus of the contaminated chicken across the sites and seasons (wet and dry) were: BDL (CTR, PR) – 30.746 (NTC) and BDL (CTR, PR)–41.506 mg/kg (NTC), as presented in the Tables. Furthermore, the concentration ranges of copper recorded in the lungs of the contaminated chicken range from BDL (CTR, KU) to 0.438 (SH) and BDL(CTR, KU) to 0.591 mg/kg (SH), respectively as presented in the Tables 4.25 and 4.26, respectively. The concentration ranges of copper recorded in bones of the contaminated chicken across the sites and seasons (wet and dry) were BDL (CTR, DD, JK, KU) to 0.300 (AJ, SH) and BDL (CTR, DD, JK) to 0.406 mg/kg (SH, AJ) as presented in the Tables. Moreover, the concentration ranges recorded for copper in the kidney across the sites and seasons (wet and dry) as presented in the Tables were BDL (CTR, DD, JK) to 1.432 (PR) and BDL (CTR, DD, JK) to 1.933 mg/kg (NTC), respectively.

The results of the concentration ranges of copper in the intestine of the contaminated chicken as presented in the Tables were BDL ( CTR) to 6.255 (NTC) and BDL (CTR) to 8.443 mg/kg (NTC) respectively. The concentration ranges of copper in the head of the contaminated chicken samples as presented in Figure 4.103 across the sites were BDL ( CTR) to 66.148 0.4701 (NTC) and BDL (CTR) to 89.299 (NTC), respectively.

**Table 4.25: Concentrations of copper in chicken samples for wet season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **AJ** | **BG** | **CTR** | **DD** | **JK** | **KU** | **SA** | **SH** | **RA** | **PR** | **NT** | **STD** |
| OER | 0.049± 0.004 | 0.087± 0.0006 | BDL | 0.093± 0.0007 | 0.104± 0.0007 | 0.038± 0.0003 | 0.101± 0.0007 | 0.036± 0.0003 | 0.187± 0.0013 | BDL | 30.745± 0.2185 | 2.000 |
| LUR | 0.209± 0.002 | 0.126± 0.0009 | BDL | 0.258± 0.0018 | 0.134± 0.0010 | BDL | 0.109± 0.0008 | 0.438± 0.0031 | 0.126± 0.0009 | 0.142± 0.0010 | 0.107± 0.0008 | 2.000 |
| BOR | 0.300± 0.0021 | 0.221± 0.0016 | BDL | BDL | BDL | BDL | 0.063± 0.0004 | 0.300± 0.0021 | 0.269± 0.0019 | 0.221± 0.0016 | 0.128± 0.0009 | 2.000 |
| KIR | 0.026± 0.002 | 0.082± 0.0006 | BDL | BDL | BDL | 0.069± 0.0005 | 0.215± 0.0015 | 0.064± 0.0005 | 0.082± 0.0006 | 0.234± 0.0017 | 1.432± 0.0102 | 2.000 |
| INTR | 0.059± 0.004 | 0.031± 0.0002 | BDL | 0.195± 0.0014 | 0.325± 0.0023 | 0.068± 0.0005 | 0.209± 0.0015 | 0.059± 0.0004 | 0.097± 0.0007 | 0.214± 0.0015 | 6.255± 0.0444 | 2.000 |
| HR | 0.136± 0.001 | 0.147± 0.0010 | BDL | 0.246± 0.0017 | 0.0269± 0.0002 | 0.159± 0.0011 | 0.306± 0.0022 | 0.181± 0.0013 | 0.279± 0.0020 | 0.334± 0.0024 | 66.148± 0.4701 | 2.000 |
| GIR | 0.077± 0.005 | 0.028± 0.0002 | BDL | 0.143± 0.0010 | 0.174± 0.0012 | 0.033± 0.0002 | 0.143± 0.0010 | 0.084± 0.0006 | 0.0229± 0.0002 | 0.173± 0.0012 | 128.017± 0.9098 | 2.000 |
| FER | 0.074± 0.0005 | 0.085± 0.0006 | BDL | 0.3045± 0.0022 | 0.089± 0.0006 | 0.046± 0.0003 | 0.112± 0.0008 | 0.076± 0.0005 | BDL | 0.041± 0.0003 | | 2.000 |
| WR | BDL | BDL | BDL | BDL 0.0000 | BDL | BDL | BDL | 0.123± 0.0009 | BDL | BDL | BDL | 2.000 |
| SKIR | 0.059± 0.004 | 0.059± 0.004 | BDL | 0.703± 0.0050 | 0.183± 0.0013 | 0.002± | 0.052± 0.0004 | 0.024± 0.0002 | 0.071± 0.0005 | 0.068± 0.0005 | BDL | 2.000 |
| HER | BDL | BDL | BDL | 0.201± 0.0014 | BDL | BDL | 0.301± 0.0021 | 0.269± 0.0019 | 0.082± 0.0006 | BDL | 0.249± 0.0018 | 2.000 |
| MUR | 0.024± 0.002 | 0.173± 0.0012 | BDL | 0.027± 0.0002 | 0.10± 0.0007 | 0.019± 0.0001 | 0.296± 0.0021 | 0.019± 0.0001 | 0.045± 0.0003 | 1.259± 0.0089 | 7.217± 0.0513 | 2.000 |
| LER | 0.019± 0.004 | 0.0009± 0.0002 | BDL | 0.138± 0.0030 | 0.103± 0.0022 | 0.049± 0.0011 | 0.138± 0.0030 | 0.013± 0.0003 | 0.123± 0.0027 | 0.082± 0.0018 | 15.366± 0.3309 | 2.000 |
| LIR | 0.064± 0.001 | 0.148± 0.003 | BDL | 0.171± 0.0037 | 0.149± 0.0032 | 0.191± 0.0041 | 0.195± 0.0042 | 0.184± 0.0040 | BDL | 0.0029± 0.0001 | 319.378± 6.878 | 2.000 |
| BRR | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 2.000 |

**Table 4.26: Concentrations of copper in chicken samples for dry season**

| | Site | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **AJ** | **BG** | **CTR** | **DD** | **JK** | **KU** | **SA** | **SH** | **RA** | **PR** | **NT** | **STD** |
| OED | 0.0677± 0.0005 | 0.117± 0.0008 | BDL | 0.125± 0.0009 | 0.141± 0.0010 | 0.0523± 0.0004 | 0.137± 0.0010 | 0.048± 0.0003 | 0.253± 0.0018 | BDL | 41.506± 0.2950 | 2.000 |
| LUD | 0.283± 0.0020 | 0.171± 0.0012 | BDL | 0.349± 0.0025 | 0.181± 0.0013 | BDL | 0.148± 0.0011 | 0.591± 0.0042 | 0.171± 0.0012 | 0.191± 0.0014 | 0.145± 0.0010 | 2.000 |
| BOD | 0.406± 0.0029 | 0.298± 0.0021 | BDL | BDL | BDL | BDL | 0.085± 0.0006 | 0.406± 0.0029 | 0.364± 0.0026 | 0.298± 0.0021 | 0.173± 0.0012 | 2.000 |
| KID | 0.035± 0.0002 | 0.11± 0.0008 | BDL | BDL | BDL | 0.094± 0.0007 | 0.290± 0.0021 | 0.086± 0.0006 | 0.110± 0.0008 | 0.315± 0.0022 | 1.933± 0.0137 | 2.000 |
| INTD | 0.081± 0.0006 | 0.042± 0.0003 | BDL | 0.263± 0.0019 | 0.439± 0.0031 | 0.092± 0.0007 | 0.283± 0.0020 | 0.081± 0.0006 | 0.130± 0.0009 | 0.289± 0.0021 | 8.443± 0.0600 | 2.000 |
| HD | 0.184± 0.0013 | 0.199± 0.0014 | BDL | 0.332± 0.0024 | 0.036± 0.0003 | 0.214± 0.0015 | 0.414± 0.0029 | 0.244± 0.0017 | 0.377± 0.0027 | 0.451± 0.0032 | 89.299± 0.6346 | 2.000 |
| GID | 0.103± 0.0007 | 0.038± 0.0003 | BDL | 0.193± 0.0014 | 0.235± 0.0017 | 0.045± 0.0003 | 0.193± 0.0014 | 0.113± 0.0008 | 0.031± 0.0002 | 0.233± 0.0017 | 172.822± 1.2282 | 2.000 |
| FED | 0.099± 0.0007 | 0.114± 0.0008 | BDL | 0.411± 0.0029 | 0.119± 0.0008 | 0.062± 0.0004 | 0.152± 0.0011 | 0.102± 0.0007 | BDL | 0.055± 0.0004 | BDL | 2.000 |
| WD | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.167± 0.001 | BDL | BDL | BDL | 2.000 |
| SKID | 0.079± 0.0006 | 0.081± 0.0006 | BDL | 0.949± 0.0067 | 0.247± 0.0018 | 0.0027± 0.0000 | 0.069± 0.0005 | 0.032± 0.0002 | 0.095± 0.0007 | 0.091± 0.0006 | BDL | 2.000 |
| HED | BDL | BDL | BDL | 0.272± 0.0019 | BDL | BDL | 0.407± 0.0029 | 0.363± 0.0026 | 0.110± 0.0008 | BDL | 0.337± 0.0024 | 2.000 |
| MUD | 0.032± 0.0002 | 0.234± 0.0017 | BDL | 0.036± 0.0003 | 0.141± 0.0010 | 0.026± 0.0002 | 0.400± 0.0028 | 0.025± 0.0002 | 0.062± 0.0004 | 1.699± 0.0121 | 9.743± 0.0692 | 2.000 |
| LED | 0.030± 0.0005 | 0.001± 0.001 | BDL | 0.186± 0.0040 | 0.139± 0.0030 | 0.066± 0.0014 | 0.186± 0.0040 | 0.017± 0.0004 | 0.166± 0.0036 | 0.110± 0.0024 | 20.744± 0.4468 | 2.000 |
| LID | 0.086± 0.0019 | 0.199± 0.0043 | BDL | 0.231± 0.0050 | 0.201± 0.0043 | 0.257± 0.0056 | 0.263± 0.0057 | 0.248± 0.0054 | BDL | 0.004± 0.0001 | 431.158± 9.2855 | 2.000 |
| BRD | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 2.000 |

The concentration ranges of copper in gizzard of the contaminated chicken as presented in the Tables 4.25 and 4.26 across the sites and seasons (wet and dry) were BDL (CTR) to 128.017 (NTC) and BDL (CTR) to 172. 822 (NTC), respectively. The concentration ranges of copper recorded in feather of the contaminated chicken samples across the seasons and sites were BDL ( CTR, RA, NTC) to 0.305 (DD) and BDL (CTR, RA, NTC) to 0.411mg/kg (DD), as presented in Tables 4.25 and 4.26, respectively. The concentrations recorded in the wattles of the contaminated chicken were all below the toxic limit across the sites and seasons with the exception of the SH–site where concentrations of 0.123 (SH) and 0.167 mg/kg (SH) were recorded, as presented in the Tables 4.25 and 4.26, respectively. The concentration ranges of copper recorded in the skin of the contaminated chicken samples across the sites and seasons (wet and dry) as presented in Tables 4.25 and 4.26 were BDL (CTR, NTC) to 0.703 (DD) and BDL (CTR, NTC) to 0.949 mg/kg (DD), respectively.

The concentration ranges of copper in the heart of the contaminated chicken were BDL (CTR,BG, CTR, JK, KU and PR) to 0.301 mg/kg (SA) and BDL (CTR,BG, CTR, JK, KU and PR) to 0.407 mg/kg (SA) as presented in the Tables 4.25 and 4.26, respectively. Moreover, the concentrations of copper were also investigated in muscles of the contaminated chicken samples across the sites and seasons. The concentration ranges recorded were BDL (CTR) to 7.217 (NTC) and BDL (CTR) to 9.743 mg/kg (NTC) as presented in the Tables 4.25 and 4.26, respectively. Furthermore, concentration ranges of copper investigated in the leg of the contaminated chicken across the sites and seasons were BDL (CTR) to 15.366 mg/kg (NTC) and BDL (CTR) to 20.744 mg/kg (NTC) as presented in Tables 4.25 and 4.26, respectively. The results of copper contamination in liver of the contaminated chickens across the sites and seasons were presented in the Tables. The

concentration ranges recorded in both the dry and wet seasons were BDL (CTR) to 319.378 (NTC) to BDL (CTR) to 431.158 mg/kg (NTC) as presented in the Tables. Conversely, the concentrations of copper recorded in the brain of the contaminated chicken samples were below the detection limit and it was not detected across the sites as presented in the Tables 4.25 an. 4.26, respectively.

4.10.5 Concentration of Hg in chicken samples

The concentration ranges of mercury recorded in the oesophagus across the sites and seasons (wet and dry) were 1.029 (CTR) to 4.968 mg/kg (RA) and 1.389 (CTR) to 6.707 mg/kg (RA) as presented in Tables 4.27 and 4.28, respectively. Furthermore, the concentration ranges of mercury in the lungs of the chicken sample across the sites and seasons (wet and dry season) were BDL (CTR) to 4.171 mg/kg (JK) and BDL (CTR) to 5.631 mg/kg (JK) as reflected in the Tables 4.27 and 4.28. The concentration ranges of mercury in bones of the contaminated chicken across the sites and seasons (wet and seasons), as presented in Tables 4.27 and 4.28 were BDL ( AJ, BG, CTR, DD, JK, KU) to 2.126 mg/kg (SA) and BDL (AJ, BG, CTR, DD, JK, KU ) to 2.866 (SA), respectively. The concentration ranges of mercury recorded in the kidney of the contaminated chicken across the sites and seasons (wet and dry ) were BDL (CTR) to 12.236 mg/kg (RA) and BDL (CTR) to 16.518 mg/kg (RA), as presented in Tables 4.27 and 4.28, respectively. The levels of mercury recorded in the intestine of the contaminated chicken across the sites were BDL (CTR) to 6.87 mg/kg (RA) and BDL (CTR) to 9.282 ± 0.120 mg/kg (RA), respectively. These concentrations were above the tolerable limit of 0.010 mg/kg across the sites and seasons. Furthermore, the concentrations of mercury recorded in the head of the contaminated chicken across the sites and seasons was presented in the Tables. The ranges

**Table 4.27: Mercury contents in chicken samples for wet season**

| SAMPLE | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT | STD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **OER** | 1.403± 0.030 | 1.135± 0.024 | 1.029± 0.022 | 2.134± 0.046 | 1.929± 0.041 | 2.614± 0.056 | 1.577± 0.034 | 4.232± 0.091 | 4.968± 0.107 | 4.377± 0.094 | 1.542± 0.033 | 0.010 |
| LUR | 0.944± 0.020 | 0.983± 0.021 | BDL | 1.502± 0.032 | 4.171± 0.089 | 1.283± 0.028 | BDL | BDL | BDL | BDL | 1.399± 0.030 | 0.010 |
| BOR | BDL | BDL | BDL | BDL | BDL | BDL | 2.126± 0.046 | 2.036± 0.044 | 1.508± 0.033 | 1.663± 0.035 | 1.319± 0.028 | 0.010 |
| KIR | 2.287± 0.049 | 1.682± 0.036 | BDL | 0.779± 0.017 | 8.147± 0.176 | 1.352± 0.029 | 3.864± 0.083 | 1.319± 0.028 | 12.236± 0.264 | 2.159± 0.047 | 2.429± 0.052 | 0.010 |
| INTR | 2.603± 0.056 | 1.853± 0.040 | BDL | 1.666± 0.036 | 0.989± 0.021 | 2.269± 0.049 | 1.981± 0.043 | 1.641± 0.035 | 6.875± 0.148 | 3.672± 0.079 | 1.332± 0.029 | 0.010 |
| HR | 4.153± 0.0894 | 2.332± 0.050 | BDL | 3.054± 0.066 | 2.335± 0.050 | 3.323± 0.072 | 2.967± 0.064 | 2.421± 0.052 | 53.508± 1.152 | 2.351± 0.051 | 0.945± 0.020 | 0.010 |
| GIR | 9.139± 0.197 | 1.579± 0.034 | BDL | 0.982± 0.021 | 1.416± 0.031 | 3.438± 0.074 | 0.601± 0.013 | 1.634± 0.035 | 0.966± 0.021 | 2.185± 0.0471 | 0.424± 0.009 | 0.010 |
| FER | 1.571± 0.034 | 1.521± 0.033 | 0.774± 0.017 | 2.689± 0.058 | 35.425± 0.763 | 1.919± 0.041 | 1.176± 0.0253 | 1.440± 0.031 | 35.425± 0.763 | 1.595± 0.034 | 5.351± 0.115 | 0.010 |
| WR | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| SKIR | 1.342± 0.029 | 1.525± 0.033 | BDL | 1.837± 0.040 | 1.669± 0.036 | 1.527± 0.033 | 1.180± 0.025 | 2.211± 0.048 | 2.354± 0.051 | 1.102± 0.024 | 1.451± 0.031 | 0.010 |
| HER | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| MUR | 1.579± 0.034 | 2.085± 0.045 | 0.527± 0.011 | 3.498± 0.075 | 2.174± 0.047 | 0.865± 0.019 | 5.749± 0.124 | 3.215± 0.069 | 1.533± 0.033 | 1.065± 0.023 | 1.269± 0.027 | 0.010 |
| LER | 1.205± 0.026 | 1.731± 0.037 | BDL | 61.572± 1.326 | 11.937± 0.257 | 1.302± 0.028 | 0.842± 0.018 | 1.172± 0.025 | 10.097± 0.218 | 0.792± 0.017 | 0.866± 0.019 | 0.010 |
| LIR | 1.222± 0.026 | 2.354± 0.051 | BDL | 6.041± 0.130 | 0.524± 0.011 | 2.554± 0.055 | 1.020± 0.022 | 1.407± 0.030 | 6.041± 0.130 | 2.145± 0.046 | 1.257± 0.027 | 0.010 |
| BRR | BDL | BDL | BDL | BDL | BDL | BDL | 1.019± | BDL | BDL | BDL | BDL | 0.010 |

**Table 4.28: Mercury contents in chickens organs dry season**

| SAMPLE | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT | STD |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **OER** | 1.532 0.033 | 1.389± 0.030 | 2.882± 0.062 | 2.605± 0.056 | 3.529± 0.076 | 2.130± 0.046 | 5.713± 0.123 | 6.707± 0.144 | 5.909± 0.127 | 2.081± 0.045 | 0.010 |
| LUR | 1.327± 0.029 | BDL | 2.028± 0.044 | 5.631± 0.121 | 1.733± 0.037 | BDL | BDL | BDL | BDL | 1.889± 0.041 | 0.010 |
| BOR | BDL | BDL | BDL | BDL | BDL | 2.866± 0.062 | 2.748± 0.059 | 2.035± 0.044 | 2.245± 0.048 | 1.781± 0.038 | 0.010 |
| KIR | 2.270± 0.049 | BDL | 1.052± 0.023 | 10.998± 0.237 | 1.826± 0.039 | 5.217± 0.112 | 1.782± 0.038 | 16.518± 0.356 | 2.915± 0.063 | 3.281± 0.071 | 0.010 |
| INTR | 2.501± 0.054 | BDL | 2.249± 0.048 | 1.336± 0.029 | 3.063± 0.066 | 2.674± 0.058 | 2.215± 0.048 | 9.282± 0.200 | 4.957± 0.107 | 1.798± 0.039 | 0.010 |
| HR | 3.149± 0.068 | BDL | 4.122± 0.089 | 3.150± 0.068 | 4.487± 0.096 | 4.005± 0.086 | 3.269± 0.070 | 72.236± 1.556 | 3.174± 0.068 | 1.275± 0.028 | 0.010 |
| GIR | 2.132± 0.046 | BDL | 1.326± 0.029 | 1.912± 0.041 | 4.641± 0.100 | 0.811± 0.018 | 2.206± 0.048 | 1.304± 0.028 | 2.949± 0.064 | 0.572± 0.012 | 0.010 |
| FER | 2.05± 0.044 | 1.045± 0.023 | 3.630± 0.078 | 47.823± 1.030 | 2.592± 0.056 | 1.588± 0.034 | 1.944± 0.042 | 47.823± 1.030 | 2.153± 0.046 | 7.223± 0.156 | 0.010 |
| WR | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| SKIR | 2.058± 0.044 | BDL | 2.479± 0.053 | 2.253± 0.049 | 2.061± 0.044 | 1.593± 0.034 | 2.985± 0.064 | 3.178± 0.068 | 1.487± 0.032 | 1.958± 0.042 | 0.010 |
| HER | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.010 |
| MUR | 2.82± 0.061 | 0.711± 0.015 | 4.722± 0.102 | 2.935± 0.063 | 1.167± 0.025 | 7.762± 0.167 | 4.340± 0.094 | 2.069± 0.045 | 1.437± 0.031 | 1.714± 0.037 | 0.010 |
| LER | 2.34± 0.050 | BDL | 83.122± 1.790 | 16.115± 0.347 | 1.758± 0.038 | 1.137± 0.025 | 1.582± 0.034 | 13.631± 0.294 | 1.070± 0.023 | 1.169± 0.025 | 0.010 |
| LIR | 3.18± 0.068 | BDL | 8.155± 0.176 | 0.707± 0.015 | 3.448± 0.074 | 1.378± 0.030 | 1.899± 0.041 | 8.155± 0.177 | 2.896± 0.062 | 1.697± 0.037 | 0.010 |
| BRR | BDL | BDL | BDL | BDL | BDL | 1.376± 0.030 | BDL | BDL | BDL | BDL | 0.010 |

of these concentrations were BDL (CTR) to 53.508 mg/kg (RA) and BDL (CTR) to 72.236 mg/kg (RA), respectively.

The concentration ranges of mercury recorded in gizzard across the sites and seasons (wet and dry) were BDL (CTR) to 9.139 ± 0.197 mg/kg (AJ) and BDL (CTR) to 12.337 mg/kg (AJ) as presented in the Tables 4.27 to 4.28, respectively. Moreover, the concentration ranges of mercury recorded in feather of the contaminated chickens across the sites and seasons (wet and dry) were 1.045 (CTR) to 47.823 mg/kg (RA) and 0.774 ± 0.017 (CTR) to 35.425 mg/kg (RA) as presented in the Tables 4.27 and 4.28, respectively. Mercury was not detected across the sites and seasons all the concentrations recorded were below the detection limit as presented in the Tables. Similarly, the concentration ranges of mercury recorded in the skin of the contaminated chicken across the sites and seasons were BDL (CTR) to 2.354 mg/kg (RA) and BDL (CTR) to 3.178 mg/kg (RA) as presented in Tables 4.27 and 4.28, respectively. The concentration ranges of mercury recorded in the heart of the investigated chicken samples across the sites were all below the detection limit and were not detected across the sites and seasons as reflected in Tables 4.27 and 4.28.

The concentration ranges of mercury recorded in muscles of the contaminated chicken samples across the sites for the wet and dry seasons were 0.527 (CTR) to 5.749 (SH) and 0.711 mg/kg (CTR) to 7.762 mg/kg (SA), respectively as reflected in the Tables 4.27 and 4.28. The concentration ranges of mercury in the leg of the investigated chicken samples were BDL (CTR) to 61.572 mg/kg (DD) and BDL (CTR) to 83.122 mg/kg (DD), as presented in Tables 4.27 and 4.28, respectively. Moreover, the concentrations of mercury were also investigated in the liver of the contaminated chickens acrosss the sites and the ranges recorded across the seasons wet and dry were BDL (CTR)

to 6.041 mg/kg (DD) and BDL (CTR) to 8.155 mg/kg (DD, RA) as presented in the Tables 4.27 and 4.28, respectively. Finally, the levels of mercury recorded in brain samples of the contaminated chicken samples across the sites and seasons were BDL (AJ, BG, CTR, DD, JK, KU, SH, RA, NTC, PR) to 1.019 mg/kg (SA) and BDL (AJ, BG, CTR, DD, JK, KU, SH, RA, NTC, PR) to 1.376 BDL (AJ, BG, CTR, DD, JK, KU, SH, RA, NTC, PR) mg/kg (SA) as presented in the Tables 4.27 and 4.28.

### 4.10.6 Bioaccumulation factor (BAF) of Zn in chicken samples

The bioaccumulation factor (BAF) of Zn in chicken samples during the wet season are presented in Table 4.29. The BAFs ranges of 0.000(RA) to 0.340(DD) and 0.000(AJ, BG, CTR, JK, SA, SH, PR) to 0.017(DD) were recorded in OER and LUR samples. Also the BAFs ranges for Zn in the KIR, INTR, HR, GIR, and FER samples as presented in Table 4.29 were 0.000(AJ, BG, CTR, DD, SA, SH, PR) to 0.017, 0.000(CTR) to 0.008(PR), 0.001 (PR) to 0.025(DD), 0.00(CTR) to 0.010(SH), and 0.000(CTR) to 0.015(AJ), respectively. Similarly, the ranges of BAFs recorded for Zn in WR, SKIR, HER, MUR, LER, LIR, and BRR, as presented in the Table 4.29 were 0.000(CTR, DD, JK, SA, RA, PR, NTC) to 0.018(DD), 0.000(CTR) TO 0.031 (JK), 0.003(BG, SA) to 0.017(PR), 0.000(CTR) to 0.011(PR) and 0.000(AJ, BG, CTR, DD, JK, KU, SH, RA, PR) to 0.012 (NTC), respectively.

Similarly, the BAFs recorded for Zn in the chicken samples during the dry season are presented in Table 4.30. The BAFs of Zn recorded in OED, LUD and BOD samples were 0.000 (CTR, RA, NTC) to 0.022 (DD), 0.000 (across the sites), 0.000 (AJ, BG, CTR, KU, SH, RA, PR) to 0.011(DD). The BAFs ranges for Zn in KID, INTD, HD

**Table 4.29 BAFs of zinc for wet season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NTC |
| OER | 0.004 | 0.005 | 0.000 | 0.034 | 0.005 | 0.009 | 0.005 | 0.004 | 0.000 | 0.004 | 0.000 |
| LUR | 0.000 | 0.000 | 0.000 | 0.017 | 0.006 | 0.000 | 0.005 | 0.000 | 0.000 | 0.000 | 0.004 |
| BOR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.000 | 0.000 | 0.017 | 0.000 | 0.004 |
| KIR | 0.004 | 0.006 | 0.000 | 0.011 | 0.005 | 0.002 | 0.001 | 0.004 | 0.002 | 0.008 | 0.002 |
| INTR | 0.006 | 0.009 | 0.002 | 0.006 | 0.005 | 0.003 | 0.002 | 0.006 | 0.015 | 0.001 | 0.009 |
| HR | 0.006 | 0.006 | 0.000 | 0.025 | 0.005 | 0.003 | 0.003 | 0.003 | 0.001 | 0.001 | 0.009 |
| GIR | 0.008 | 0.008 | 0.000 | 0.003 | 0.011 | 0.003 | 0.005 | 0.010 | 0.001 | 0.007 | 0.005 |
| FER | 0.015 | 0.010 | 0.000 | 0.003 | 0.012 | 0.007 | 0.001 | 0.010 | 0.001 | 0.007 | 0.001 |
| WR | 0.007 | 0.004 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.006 | 0.000 | 0.000 | 0.000 |
| SKIR | 0.005 | 0.006 | 0.001 | 0.005 | 0.023 | 0.002 | 0.004 | 0.006 | 0.020 | 0.004 | 0.002 |
| HER | 0.000 | 0.000 | 0.000 | 0.018 | 0.000 | 0.001 | 0.003 | 0.010 | 0.011 | 0.000 | 0.012 |
| MUR | 0.004 | 0.001 | 0.000 | 0.007 | 0.031 | 0.001 | 0.003 | 0.002 | 0.016 | 0.020 | 0.000 |
| LER | 0.011 | 0.003 | 0.004 | 0.005 | 0.013 | 0.006 | 0.003 | 0.016 | 0.005 | 0.017 | 0.004 |
| LIR | 0.004 | 0.006 | 0.000 | 0.001 | 0.001 | 0.003 | 0.001 | 0.010 | 0.007 | 0.011 | 0.001 |
| BRR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.004 | 0.000 | 0.000 | 0.000 | 0.012 |

BAFs= Bioaccumulation factors

**Table 4.30 BAFs of zinc for dry season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NTC |
| OED | 0.003 | 0.003 | 0.000 | 0.022 | 0.003 | 0.006 | 0.003 | 0.003 | 0.000 | 0.003 | 0.000 |
| LUD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| BOD | 0.000 | 0.000 | 0.000 | 0.011 | 0.004 | 0.000 | 0.003 | 0.000 | 0.000 | 0.000 | 0.003 |
| KID | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| INTD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.000 | 0.000 | 0.011 | 0.000 | 0.003 |
| HD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| GID | 0.003 | 0.004 | 0.000 | 0.007 | 0.003 | 0.001 | 0.001 | 0.003 | 0.001 | 0.005 | 0.002 |
| FED | 0.003 | 0.004 | 0.000 | 0.007 | 0.003 | 0.001 | 0.001 | 0.003 | 0.001 | 0.005 | 0.001 |
| WD | 0.004 | 0.006 | 0.001 | 0.004 | 0.003 | 0.002 | 0.001 | 0.004 | 0.010 | 0.001 | 0.006 |
| SKID | 0.004 | 0.004 | 0.000 | 0.016 | 0.003 | 0.002 | 0.002 | 0.002 | 0.000 | 0.001 | 0.006 |
| HED | 0.005 | 0.005 | 0.000 | 0.002 | 0.007 | 0.002 | 0.003 | 0.007 | 0.000 | 0.004 | 0.003 |
| MUD | 0.010 | 0.007 | 0.000 | 0.002 | 0.008 | 0.004 | 0.001 | 0.007 | 0.000 | 0.004 | 0.001 |
| LED | 0.004 | 0.003 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.004 | 0.000 | 0.000 | 0.000 |
| LID | 0.004 | 0.004 | 0.001 | 0.003 | 0.015 | 0.001 | 0.002 | 0.004 | 0.013 | 0.002 | 0.002 |
| BRD | 0.000 | 0.000 | 0.000 | 0.012 | 0.000 | 0.001 | 0.002 | 0.007 | 0.007 | 0.000 | 0.008 |

and GID samples were 0.000 (across the sites), 0.000 (AJ, BG, CTR, DD, JK, SA, SH, PR) to 0.003 (NTC), 0.000 (AJ, BG, CTR, JK, SA, SH and PR) to 0.011 (RA), 0.000 (across the sites) and 0.000(CTR) to 0.007 (DD) as presented in the Table. Other BAFs of Zn recorded in the samples of FED, WD, SKID, HED, MUD, LED, LID, and BRR were 0.000 (CTR) to 0.007 (DD), 0.001 (CTR, SA) to 0.006 (BG, NTC) , 0.000 (CTR, RA) to 0.016 (DD), 0.000 (CTR) to 0.007 (JK, SH), 0.000 (CTR, DD, JK, SA, RA, PR and NTC) to 0.004 (AJ, SH), 0.001 (CTR, KU) to 0.015 (JK) and 0.000 (AJ, BG, CTR, JK and PR) to 0.012 (DD), respectively.

4.10.7 Bioaccumulation factor (BAF) of Pb in chicken samples

The BAFs of Pb recorded in the contaminated samples of chicken across the sites and seasons (wet and dry) are presented in Tables 4.31 and 4.32, respectively. The BAFs ranges of Pb recorded in the samples of OER, LUR, BOR, KIR and INTR during the wet season were 0.000 (JK, SA, RA, PR, and NTC) to 0.229 (AJ), 0.000 (across the sites), 0.000 (across the sites), 0.000 (CTR, SA, RA, PR) to 0.276 (AJ), 0.000 (CTR, SA, PR, RA) to 0.413 (NTC), respectively. Other BAF for Pb were 0.000 (across the sites), 0.000 (CTR, DD, JK, SA, PR and NTC) to 0.282 (BG), 0.000 (AJ, CTR, SA, RA, PR) to 0.282 (BG) and 0.000 (AJ, CTR, DD, JK, SA, RA and PR) to 0.340 (BG) for HR, GIR, FER, and WR, respectively. Similarly, the BAF ranges recorded for Pb in SKIR, HER, MUR, LER, LIR, and BRR samples during the wet season were 0.000 (CTR, SH, RA) to 0.607(NTC), 0.000 (CTR, DD, RA, PR) to 0.343 (SH), 0.000 (CTR, JK, PR, NTC) to 0.335 (RA), 0.000 (CTR, DD, JK, SA, RA, PR and NTC) to 0.236 (BG) and 0.000 (AJ and BG), respectively.

The ranges of BAFs recorded for Pb in OED, LUD, BOD, KID, INTD across the sites during the dry season were (CTR, JK, SA, RA, PR, NTC) to 0.034 (KU),

**Table 4.31 BAFs of lead for wet season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NTC |
| OER | 0.229 | 0.205 | 0.000 | 0.207 | 0.000 | 0.097 | 0.000 | 0.127 | 0.000 | 0.000 | 0.000 |
| LUR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| BOR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| KIR | 0.134 | 0.276 | 0.000 | 0.054 | 0.032 | 0.075 | 0.000 | 0.152 | 0.000 | 0.000 | 0.000 |
| INTR | 0.207 | 0.170 | 0.000 | 0.196 | 0.000 | 0.055 | 0.000 | 0.110 | 0.000 | 0.000 | 0.413 |
| HR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| GIR | 0.263 | 0.133 | 0.000 | 0.000 | 0.000 | 0.054 | 0.000 | 0.194 | 0.167 | 0.000 | 0.000 |
| FER | 0.000 | 0.282 | 0.000 | 0.008 | 0.039 | 0.092 | 0.000 | 0.153 | 0.000 | 0.000 | 0.048 |
| WR | 0.000 | 0.340 | 0.000 | 0.000 | 0.000 | 0.052 | 0.000 | 0.122 | 0.000 | 0.000 | 0.000 |
| SKIR | 0.273 | 0.264 | 0.000 | 0.160 | 0.090 | 0.028 | 0.401 | 0.000 | 0.000 | 0.277 | 0.607 |
| HER | 0.288 | 0.113 | 0.000 | 0.000 | 0.014 | 0.071 | 0.003 | 0.343 | 0.000 | 0.000 | 0.062 |
| MUR | 0.268 | 0.287 | 0.000 | 0.244 | 0.000 | 0.000 | 0.297 | 0.102 | 0.335 | 0.000 | 0.000 |
| LER | 0.217 | 0.136 | 0.000 | 0.000 | 0.000 | 0.062 | 0.000 | 0.102 | 0.000 | 0.000 | 0.000 |
| LIR | 0.160 | 0.236 | 0.000 | 0.000 | 0.000 | 0.092 | 0.000 | 0.213 | 0.000 | 0.000 | 0.000 |
| BRR | 0.000 | 1.764 | 0.431 | 0.352 | 0.441 | 0.000 | 0.331 | 0.000 | 0.000 | 0.647 | 0.598 |

**Table 4.32 BAFs of lead for dry season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT |
| OED | 0.016 | 0.023 | 0.000 | 0.024 | 0.000 | 0.034 | 0.000 | 0.016 | 0.000 | 0.000 | 0.000 |
| LUD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| BOD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| KID | 0.011 | 0.037 | 0.000 | 0.007 | 0.007 | 0.031 | 0.000 | 0.023 | 0.000 | 0.000 | 0.000 |
| INTD | 0.015 | 0.019 | 0.000 | 0.022 | 0.000 | 0.019 | 0.000 | 0.014 | 0.000 | 0.000 | 0.020 |
| HD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| GID | 0.019 | 0.015 | 0.000 | 0.000 | 0.000 | 0.019 | 0.000 | 0.025 | 0.007 | 0.000 | 0.000 |
| FED | 0.018 | 0.032 | 0.000 | 0.001 | 0.008 | 0.032 | 0.000 | 0.020 | 0.000 | 0.000 | 0.002 |
| WD | 0.000 | 0.038 | 0.000 | 0.000 | 0.000 | 0.018 | 0.000 | 0.016 | 0.000 | 0.000 | 0.000 |
| SKID | 0.020 | 0.030 | 0.000 | 0.018 | 0.018 | 0.010 | 0.029 | 0.000 | 0.000 | 0.054 | 0.029 |
| HED | 0.021 | 0.013 | 0.000 | 0.000 | 0.003 | 0.025 | 0.000 | 0.044 | 0.000 | 0.000 | 0.003 |
| MUD | 0.019 | 0.032 | 0.000 | 0.028 | 0.000 | 0.000 | 0.021 | 0.013 | 0.014 | 0.000 | 0.000 |
| LED | 0.016 | 0.015 | 0.000 | 0.000 | 0.000 | 0.022 | 0.000 | 0.013 | 0.000 | 0.000 | 0.000 |
| LID | 0.011 | 0.027 | 0.000 | 0.000 | 0.000 | 0.032 | 0.000 | 0.027 | 0.000 | 0.000 | 0.000 |
| BRD | 0.000 | 0.198 | 0.143 | 0.040 | 0.086 | 0.000 | 0.024 | 0.000 | 0.000 | 0.126 | 0.029 |

0.000 (across the sites), 0.000 (across the sites), 0.000 (CTR, SA, RA, PR and NTC) to 0.011 (AJ) and 0.000 (CTR, JK, SA, RA, PR) to 0.022 (DD), respectively during the dry season as presented in Table 4.31. Also, the BAF ranges for Pb recorded during the dry season were 0.000 (across the sites), 0.000 ( CTR, DD, JK, SA, PR and NTC) to 0.025 (SH), 0.000 (CTR, SA, RA, PR) to 0.032 (BG, KU), 0.000 (AJ, CTR, DD, JK, SA, RA, PR and NTC) to 0.038 (BG), 0.000 (CTR, SH, RA) to 0.054 (PR), 0.000 (CTR, DD, SA, RA, PR) to 0.054) for the samples of HD, GID, FED, WD, and SKID, respectively, as presented in Table 4.31.

Also, the BAF ranges recorded for Pb in the samples of HED, MUD, LED, LID, and BRR were: 0.000(CTR, DD, SA, RA, PR) to 0.044 (SH), 0.000(CTR, JK, KU, PR, NTC) to 0.032(BG), 0.000(CTR, DD, JK, RA, PR and NTC) to 0.022 (KU), 0.000(CTR, DD, JK, SA, RA, PR, NTC) to 0.032 (KU) and 0.000(AJ, KU, SH and RA) to 0.198 (BG), respectively as presented in the Table 4.31.

### 4.10.8 Bioaccumulation factor (BAF) of Cu in chicken samples

The BAFs of Cu in the samples of contaminated chickens across sites and seasons (wet and dry) are presented in Tables 4.33 and 4.34, respectively. The BAFs ranges recorded for Cu in the samples of OER, LUR, BOR, KIR, INTR and HR during the wet season were 0.000 (CTR, PR) to 0.668 (NTC), 0.000 (CTR, KU) to 0.355 (SH), 0.000 (CTR, DD, JK, KU) to 0.243 (SH), 0.000 (CTR, DD, JK) to 0.052 (SH), 0.000 (CTR) to 0.136 (NTC) and 0.000 (CTR, JK) to 0.147 (SH), as presented in Table 4.33. In the same way, the ranges of BAFs recorded for lead were 0.000 (CTR) to 2.783 (NTC), 0.000 (CTR, RA, NTC) to 0.062 (SH), 0.000(AJ, BG, CTR, DD, JK, KU, and NTC) to 0.100 (SH), 0.000 (CTR,KU,NTC) to 0.107 (DD), 0.000 (AJ, BG, CTR, JK, KU, PR) to 0.218 (SH),

0.000 (CTR) to 0.1567 (NTC), 0.000 (BG, CTR) to 0.334 (NTC) and 0.000 (across the sites), for the samples of GIR, WR, SKIR, HER, MUR, LER, LIR and BRR, respectively.

The BAFs ranges of Cu recorded in the samples during the dry season across the sites range from 0.000 (CTR, RA, PR) to 2.17(NTC), 0.000 (CTR, DD, JK, KU, and PR) to 0.153 (BG), 0.000 (CTR, DD, JK, KU, and RA), 0.000 (DD, CTR, JK, RA) to 0.101 (NTC), 0.000 (RA, CTR) to 0.442 (NTC) in the OED, LUD, BOD, KID, and INTD samples of the contaminated chicken samples, respectively. Other samples of the contaminated chickens investigated for risk assessment were HD, GID, FED, WD, SKID, HED, MUD, LED, LID and BRR revealing the BAFs ranges of 0.000 (CTR, RA) to 4.670 (NTC), 0.000 (CTR, RA, NTC) to 0.102 (BG), 0.000 (AJ, BG, CTR, DD, JK, SA, RA, PR , NTC) to 0.021 (SH), 0.000(CTR, RA, NTC) to 0.072 (BG), 0.000(AJ, BG, CTR, JK, KU, RA, PR) to 0.088 (SA), 0.000(CTR, RA) to 0.510 (NTC), 0.000 (CTR, RA) to 1.085 (NTC) , 0.000(CTR, RA, PR) to 22.55(NTC) and 0.000(across the sites), respectively.

4.10.9 Bioaccumulation factor (BAF) of Cd in chicken samples

The BAFs ranges of Cd in the samples of OER, LUR, BOR, KIR, INTR, HR, GIR, FER and WR were: 0.000 (CTR) to 0.047 (BG), 0.000 (CTR) to 0.064 (SH), 0.000(AJ, BG, CTR, DD, JK, KU, SH and PR) to 0.036 (RA), 0.019 (SA,AJ) to 0.065 (SH), 0.003 (CTR) to 0.051 (SH), 0.000 (CTR) to 0.058 (SH), 0.018 (PR) to 0.074 (SH), 0.000 (CTR) to 0.057 (SH), 0.000 (CTR, DD, JK, SA, SH, RA,PRNTC) to 0.050 (BG), respectively, as presented in Table 4.33 during the wet season. Other BAFs ranges recorded in the samples during the wet seasons across the sites were 0.017 (SA) to 0.055 (SH), 0.000 (AJ, BG, CTR,

**Table 4.33 BAFs of copper for wet season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT |
| OER | 0.005 | 0.015 | 0.000 | 0.014 | 0.002 | 0.001 | 0.003 | 0.029 | 0.013 | 0.000 | 0.668 |
| LUR | 0.021 | 0.021 | 0.000 | 0.039 | 0.002 | 0.000 | 0.003 | 0.355 | 0.008 | 0.009 | 0.002 |
| BOR | 0.031 | 0.037 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.243 | 0.018 | 0.014 | 0.003 |
| KIR | 0.003 | 0.014 | 0.000 | 0.000 | 0.000 | 0.002 | 0.006 | 0.052 | 0.006 | 0.015 | 0.031 |
| INTR | 0.006 | 0.005 | 0.000 | 0.030 | 0.005 | 0.002 | 0.006 | 0.048 | 0.007 | 0.014 | 0.136 |
| HR | 0.014 | 0.025 | 0.000 | 0.037 | 0.000 | 0.005 | 0.008 | 0.147 | 0.019 | 0.021 | 1.438 |
| GIR | 0.008 | 0.005 | 0.000 | 0.022 | 0.003 | 0.001 | 0.004 | 0.068 | 0.002 | 0.011 | 2.783 |
| FER | 0.008 | 0.014 | 0.000 | 0.046 | 0.001 | 0.001 | 0.003 | 0.062 | 0.000 | 0.003 | 0.000 |
| WR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.100 | 0.000 | 0.000 | 0.000 |
| SKIR | 0.006 | 0.010 | 0.000 | 0.107 | 0.003 | 0.000 | 0.001 | 0.019 | 0.005 | 0.004 | 0.000 |
| HER | 0.000 | 0.000 | 0.000 | 0.031 | 0.000 | 0.000 | 0.008 | 0.218 | 0.006 | 0.000 | 0.005 |
| MUR | 0.002 | 0.029 | 0.000 | 0.004 | 0.002 | 0.001 | 0.008 | 0.015 | 0.003 | 0.081 | 0.157 |
| LER | 0.002 | 0.000 | 0.000 | 0.021 | 0.002 | 0.001 | 0.004 | 0.011 | 0.008 | 0.005 | 0.334 |
| LIR | 0.007 | 0.025 | 0.000 | 0.026 | 0.002 | 0.006 | 0.005 | 0.149 | 0.000 | 0.000 | 6.943 |
| BRR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

**Table 4.34 BAFs of copper for dry season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT |
| OED | 0.019 | 0.104 | 0.000 | 0.007 | 0.011 | 0.012 | 0.030 | 0.006 | 0.000 | 0.000 | 2.171 |
| LUD | 0.080 | 0.153 | 0.000 | 0.020 | 0.014 | 0.000 | 0.032 | 0.074 | 0.000 | 0.022 | 0.008 |
| BOD | 0.115 | 0.266 | 0.000 | 0.000 | 0.000 | 0.000 | 0.018 | 0.051 | 0.000 | 0.034 | 0.009 |
| KID | 0.010 | 0.098 | 0.000 | 0.000 | 0.000 | 0.022 | 0.063 | 0.011 | 0.000 | 0.036 | 0.101 |
| INTD | 0.023 | 0.038 | 0.000 | 0.015 | 0.034 | 0.021 | 0.061 | 0.010 | 0.000 | 0.033 | 0.442 |
| HD | 0.052 | 0.178 | 0.000 | 0.019 | 0.003 | 0.050 | 0.090 | 0.031 | 0.000 | 0.051 | 4.670 |
| GID | 0.029 | 0.034 | 0.000 | 0.011 | 0.018 | 0.011 | 0.042 | 0.014 | 0.000 | 0.026 | 9.039 |
| FED | 0.028 | 0.102 | 0.000 | 0.024 | 0.009 | 0.014 | 0.033 | 0.013 | 0.000 | 0.006 | 0.000 |
| WD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.021 | 0.000 | 0.000 | 0.000 |
| SKID | 0.022 | 0.072 | 0.000 | 0.055 | 0.019 | 0.001 | 0.015 | 0.004 | 0.000 | 0.010 | 0.000 |
| HED | 0.000 | 0.000 | 0.000 | 0.016 | 0.000 | 0.000 | 0.088 | 0.045 | 0.000 | 0.000 | 0.018 |
| MUD | 0.009 | 0.209 | 0.000 | 0.002 | 0.011 | 0.006 | 0.087 | 0.003 | 0.000 | 0.193 | 0.510 |
| LED | 0.009 | 0.001 | 0.000 | 0.011 | 0.011 | 0.015 | 0.040 | 0.002 | 0.000 | 0.012 | 1.085 |
| LID | 0.024 | 0.178 | 0.000 | 0.013 | 0.015 | 0.060 | 0.057 | 0.031 | 0.000 | 0.000 | 22.550 |
| BRD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

**Table 4.35 BAFs of cadmium during the wet season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT |
| OER | 0.023 | 0.047 | 0.000 | 0.026 | 0.034 | 0.023 | 0.019 | 0.056 | 0.038 | 0.019 | 0.026 |
| LUR | 0.015 | 0.036 | 0.000 | 0.035 | 0.026 | 0.032 | 0.029 | 0.064 | 0.037 | 0.033 | 0.046 |
| BOR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.026 | 0.000 | 0.036 | 0.000 | 0.025 |
| KIR | 0.019 | 0.051 | 0.026 | 0.031 | 0.023 | 0.025 | 0.019 | 0.065 | 0.033 | 0.020 | 0.028 |
| INTR | 0.021 | 0.037 | 0.003 | 0.032 | 0.027 | 0.021 | 0.025 | 0.051 | 0.036 | 0.019 | 0.032 |
| HR | 0.021 | 0.036 | 0.000 | 0.037 | 0.029 | 0.024 | 0.014 | 0.058 | 0.008 | 0.019 | 0.027 |
| GIR | 0.020 | 0.032 | 0.029 | 0.030 | 0.040 | 0.017 | 0.025 | 0.074 | 0.025 | 0.018 | 0.032 |
| FER | 0.015 | 0.050 | 0.000 | 0.026 | 0.028 | 0.031 | 0.017 | 0.057 | 0.017 | 0.020 | 0.024 |
| WR | 0.025 | 0.050 | 0.000 | 0.000 | 0.000 | 0.029 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| SKIR | 0.021 | 0.046 | 0.029 | 0.025 | 0.035 | 0.018 | 0.017 | 0.055 | 0.029 | 0.022 | 0.030 |
| HER | 0.000 | 0.000 | 0.000 | 0.038 | 0.020 | 0.000 | 0.029 | 0.000 | 0.031 | 0.000 | 0.039 |
| MUR | 0.021 | 0.057 | 0.003 | 0.035 | 0.031 | 0.028 | 0.018 | 0.051 | 0.037 | 0.021 | 0.041 |
| LER | 0.021 | 0.050 | 0.000 | 0.025 | 0.028 | 0.026 | 0.015 | 0.061 | 0.028 | 0.029 | 0.026 |
| LIR | 0.015 | 0.043 | 0.000 | 0.026 | 0.023 | 0.023 | 0.019 | 0.070 | 0.000 | 0.021 | 0.023 |
| BRR | 0.000 | 0.000 | 0.000 | 0.001 | 0.031 | 0.000 | 0.021 | 0.000 | 0.000 | 0.028 | 0.000 |

**Table 4.36 BAFs of cadmium for dry season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NT |
| OED | 0.043 | 0.080 | 0.000 | 0.026 | 0.038 | 0.030 | 0.023 | 0.022 | 0.033 | 0.025 | 0.037 |
| LUD | 0.029 | 0.061 | 0.000 | 0.035 | 0.029 | 0.041 | 0.036 | 0.024 | 0.032 | 0.043 | 0.066 |
| BOD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.033 | 0.000 | 0.031 | 0.000 | 0.036 |
| KID | 0.036 | 0.087 | 0.015 | 0.031 | 0.026 | 0.033 | 0.023 | 0.025 | 0.029 | 0.026 | 0.040 |
| INTD | 0.040 | 0.063 | 0.002 | 0.032 | 0.030 | 0.027 | 0.032 | 0.020 | 0.032 | 0.025 | 0.045 |
| HD | 0.041 | 0.061 | 0.000 | 0.037 | 0.032 | 0.030 | 0.017 | 0.022 | 0.008 | 0.025 | 0.039 |
| GID | 0.039 | 0.054 | 0.016 | 0.029 | 0.044 | 0.022 | 0.032 | 0.028 | 0.022 | 0.023 | 0.045 |
| FED | 0.029 | 0.086 | 0.000 | 0.027 | 0.031 | 0.039 | 0.021 | 0.022 | 0.016 | 0.027 | 0.034 |
| WD | 0.048 | 0.085 | 0.000 | 0.000 | 0.000 | 0.037 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| SKID | 0.041 | 0.079 | 0.016 | 0.024 | 0.038 | 0.022 | 0.021 | 0.021 | 0.025 | 0.029 | 0.042 |
| HED | 0.000 | 0.000 | 0.000 | 0.038 | 0.022 | 0.000 | 0.036 | 0.000 | 0.027 | 0.000 | 0.056 |
| MUD | 0.041 | 0.097 | 0.002 | 0.036 | 0.034 | 0.035 | 0.022 | 0.020 | 0.032 | 0.028 | 0.058 |
| LED | 0.040 | 0.085 | 0.000 | 0.025 | 0.032 | 0.033 | 0.018 | 0.024 | 0.025 | 0.038 | 0.037 |
| LID | 0.029 | 0.073 | 0.000 | 0.026 | 0.026 | 0.030 | 0.024 | 0.026 | 0.000 | 0.028 | 0.033 |
| BRD | 0.000 | 0.000 | 0.000 | 0.000 | 0.034 | 0.000 | 0.026 | 0.000 | 0.000 | 0.036 | 0.000 |

KU, SH and PR) to 0.039 (NTC), 0.003 (CTR) to 0.057 (BG), 0.000 (CTR, RA) to 0.070 (SH), 0.000 (AJ, BG, CTR, KU, SH, RA and NTC) to 0.031(JK) in the samples of SKIR, HER, MUR, LER, and LIR, respectively, as presented in the Table during the wet season.

The ranges of BAFs for Cd recorded in the contaminated chiceken samples across the sites were 0.000 (CTR) to 0.080 (BG), 0.000 (CTR) to 0.066 (NTC), 0.000 (CTR, AJ, BG, DD, JK, KU, SH and PR) to 0.036 (NTC), 0.015 (CTR) to 0.087 (BG), 0.002 (CTR) to 0.063 (BG), 0.000 (CTR) to 0.061 (BG), 0.016 (CTR) to 0.054 (BG), 0.000 (CTR) to 0.086, 0.000 (CTR) to 0.085 (BG) and 0.021 (SA,SH) to 0.079 (BG) for OED, LUD, BOD, KID, INTD, HD, GID, FED,WD and SKID samples, respectively. Other BAFs ranges recorded for Cd in the HER, MUR, LER, LIR and BRR samples of the contaminated Chickens during the dry season across the sites were 0.000 (AJ, BG, CTR, KU and SH) to 0.056 (NTC), 0.002 (CTR) to 0.097 (BG), 0.000 (CTR) to 0.085 (BG), 0.000 (CTR) to 0.085 (BG), 0.000 (BG) to 0.073 (BG) and 0.000 (AJ, BG, CTR, DD, KU, SH, RA and NTC) to 0.036 (PR), respectively, as presented in Table 4.36.

### 4.10.10 Bioaccumulation factor (BAF) of Hg in chicken samples

The BAFs recorded for Hg in the contaminated chicken samples across the sites and seasons (wet and dry) are presented in Tables 4.37 and 4.38, respectively. The BAFs of Hg recorded across the sites during the wet season were 0.002 (AJ) to 0.026 (RA), 0.000 (CTR, SA, SH, RA, PR) to 0.025 (JK), 0.000 (AJ, BG, CTR, DD, JK, KU) to 0.010 (SA), 0.000 (AJ, BG,) to 0.064 (RA), 0.000 (CTR) to 0.036 (RA), 0.000 (CTR) to 0.278 (RA), 0.000 (CTR) to 0.013 (AJ, BG), 0.002 (AJ) to 0.209 (JK) and 0.000 (across the sites) for the samples of OER, LUR, BOR, KIR, INTR, HR, GIR, FER, and WR,

**Table 4.37 BAFs of mercury for wet season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Samples | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NTC |
| OER | 0.002 | 0.009 | 0.005 | 0.010 | 0.011 | 0.013 | 0.007 | 0.015 | 0.026 | 0.022 | 0.007 |
| LUR | 0.001 | 0.008 | 0.000 | 0.007 | 0.025 | 0.006 | 0.000 | 0.000 | 0.000 | 0.000 | 0.007 |
| BOR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.010 | 0.007 | 0.008 | 0.008 | 0.006 |
| KIR | 0.003 | 0.014 | 0.000 | 0.004 | 0.048 | 0.007 | 0.018 | 0.005 | 0.064 | 0.011 | 0.011 |
| INTR | 0.004 | 0.015 | 0.000 | 0.008 | 0.006 | 0.011 | 0.009 | 0.006 | 0.036 | 0.018 | 0.006 |
| HR | 0.006 | 0.019 | 0.000 | 0.014 | 0.014 | 0.016 | 0.014 | 0.009 | 0.278 | 0.012 | 0.004 |
| GIR | 0.013 | 0.013 | 0.000 | 0.005 | 0.008 | 0.017 | 0.003 | 0.006 | 0.005 | 0.011 | 0.002 |
| FER | 0.002 | 0.013 | 0.004 | 0.012 | 0.209 | 0.009 | 0.006 | 0.005 | 0.184 | 0.008 | 0.025 |
| WR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| SKIR | 0.002 | 0.013 | 0.000 | 0.008 | 0.010 | 0.007 | 0.006 | 0.008 | 0.012 | 0.005 | 0.007 |
| HER | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| MUR | 0.002 | 0.017 | 0.003 | 0.016 | 0.013 | 0.004 | 0.027 | 0.011 | 0.008 | 0.005 | 0.006 |
| LER | 0.002 | 0.014 | 0.000 | 0.284 | 0.070 | 0.006 | 0.004 | 0.004 | 0.052 | 0.004 | 0.004 |
| LIR | 0.002 | 0.020 | 0.000 | 0.028 | 0.003 | 0.012 | 0.005 | 0.005 | 0.031 | 0.011 | 0.006 |
| BRR | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.005 | 0.000 | 0.000 | 0.000 | 0.000 |

**Table 4.38 BAFs of mercury for dry season**

| | Site | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| samples | AJ | BG | CTR | DD | JK | KU | SA | SH | RA | PR | NTC |
| OED | 0.003 | 0.013 | 0.007 | 0.013 | 0.015 | 0.017 | 0.010 | 0.020 | 0.035 | 0.029 | 0.010 |
| LUD | 0.002 | 0.011 | 0.000 | 0.009 | 0.033 | 0.008 | 0.000 | 0.000 | 0.000 | 0.000 | 0.009 |
| BOD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.014 | 0.010 | 0.011 | 0.011 | 0.008 |
| KID | 0.004 | 0.019 | 0.000 | 0.005 | 0.065 | 0.009 | 0.025 | 0.006 | 0.086 | 0.014 | 0.015 |
| INTD | 0.005 | 0.021 | 0.000 | 0.010 | 0.008 | 0.015 | 0.013 | 0.008 | 0.048 | 0.024 | 0.008 |
| HD | 0.008 | 0.026 | 0.000 | 0.019 | 0.019 | 0.022 | 0.019 | 0.012 | 0.375 | 0.016 | 0.006 |
| GID | 0.017 | 0.018 | 0.000 | 0.006 | 0.011 | 0.022 | 0.004 | 0.008 | 0.007 | 0.015 | 0.003 |
| FED | 0.003 | 0.017 | 0.006 | 0.017 | 0.282 | 0.012 | 0.007 | 0.007 | 0.248 | 0.011 | 0.034 |
| WD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| SKID | 0.002 | 0.017 | 0.000 | 0.011 | 0.013 | 0.010 | 0.008 | 0.011 | 0.017 | 0.007 | 0.009 |
| HED | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| MUD | 0.003 | 0.023 | 0.004 | 0.022 | 0.017 | 0.006 | 0.037 | 0.015 | 0.011 | 0.007 | 0.008 |
| LED | 0.002 | 0.019 | 0.000 | 0.384 | 0.095 | 0.008 | 0.005 | 0.006 | 0.071 | 0.005 | 0.005 |
| LID | 0.002 | 0.026 | 0.000 | 0.038 | 0.004 | 0.017 | 0.006 | 0.007 | 0.042 | 0.014 | 0.008 |
| BRD | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.006 | 0.000 | 0.000 | 0.000 | 0.000 |

respectively as presented in Table 4.37. Other BAFs ranges of Hg recorded across the sites during the wet season were 0.000 (CTR) to 0.013(BG), 0.000 (across the sites), 0.003 (CTR) to 0.027 (SA), 0.027 (SA), 0.002 (AJ) to 0.284 (DD), 0.000 (CTR) to 0.031 (RA) and 0.000 (AJ, BG, CTR, DD, JK, KU, SH, RA, PR and NTC) to 0.005 (SA) for the samples of SKIR, HER, MUR, LER, LIR and BRR, respectively.

Similarly, as presented in Table 4.38, the BAFs of Hg recorded during the dry season were 0.003 (AJ) to 0.035 (RA), 0.000 (CTR, SA, SH, RA, PR) to 0.033 (JK), 0.000 (AJ, BG, CTR, DD, JK, KU) to 0.014 (SA), 0.000 (CTR) to 0.048 (RA), 0.000 (CTR) to 0.375 (RA), 0.000 (CTR) to 0.018 (BG), 0.003 (AJ) to 0.282 (JK), 0.000 (across the sites) and 0.000 (CTR) to 0.017 (RA,BG) in the OED, LUD, BOD, KID, INTD, HD, GID, FED, and SKID samples, respectively. Other BAFs recorded in the samples during the dry season in SKID, HED, MUD, LED, LID and BRD samples were 0.000 (across the sites), 0.000 (CTR) to 0.095 (JK), 0.000 (CTR) to 0.042 (RA) and 0.000 (SH, RA, PR, NTC, KU, JK, DD, CTR, BG, and AJ) to 0.006 (SA), respectively, as presented in Table 4.38.

## 4.11 Heavy Metals in Human Resident Tissues Near the Dumpsites

### 4.11.1 Heave metal contents in the tissues of the residents

Figures 4.51 to 4.60 and appendices XXXI to XL showed the concentrations of Zn, Pb, Cu, Cd and Hg in samples of urine, blood, nails and hair in both dry and wet seasons.

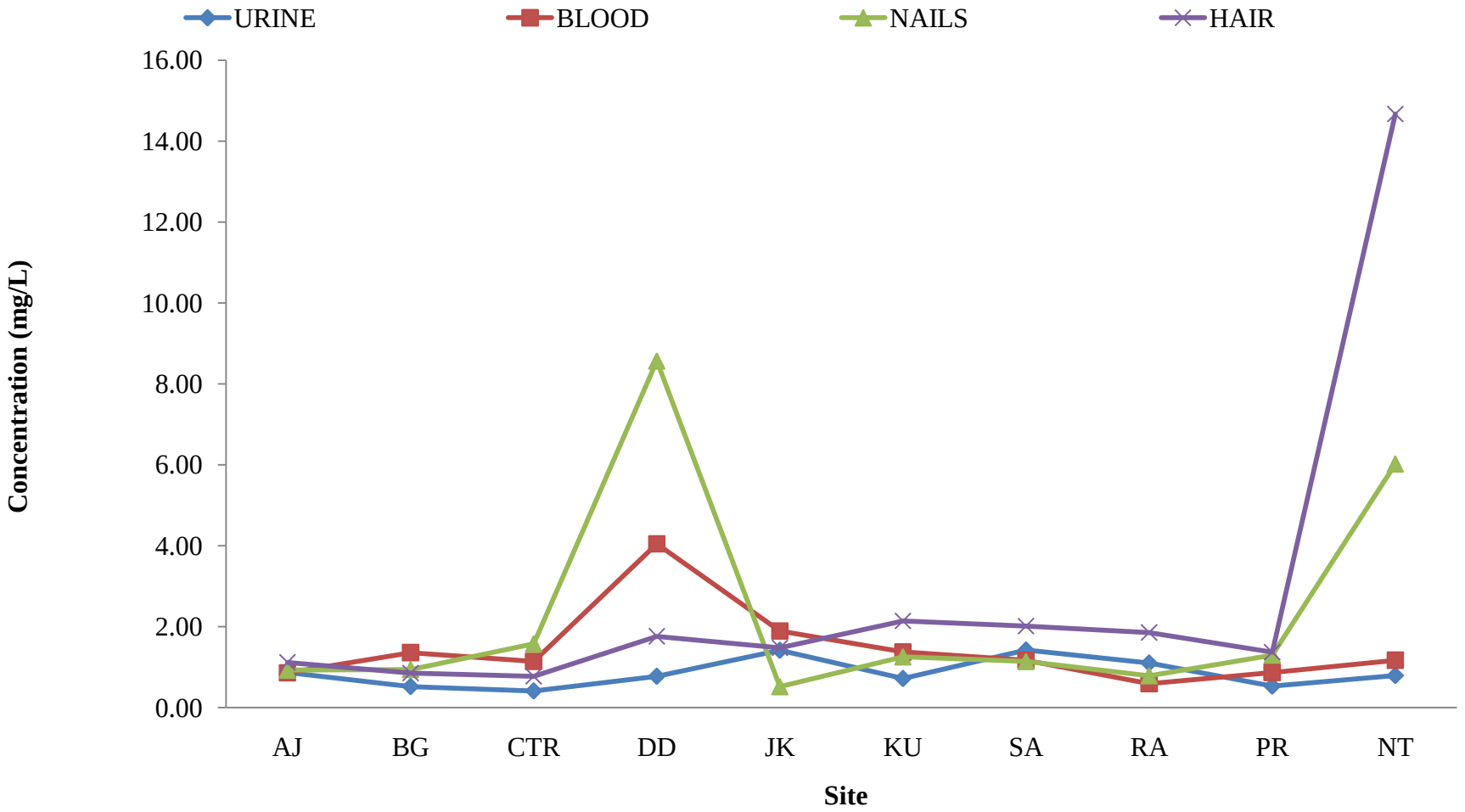


**Figure 4.51: Concentrations of zinc in the tissues and urine of human residents' samples near the dumpsite during the dry Season**

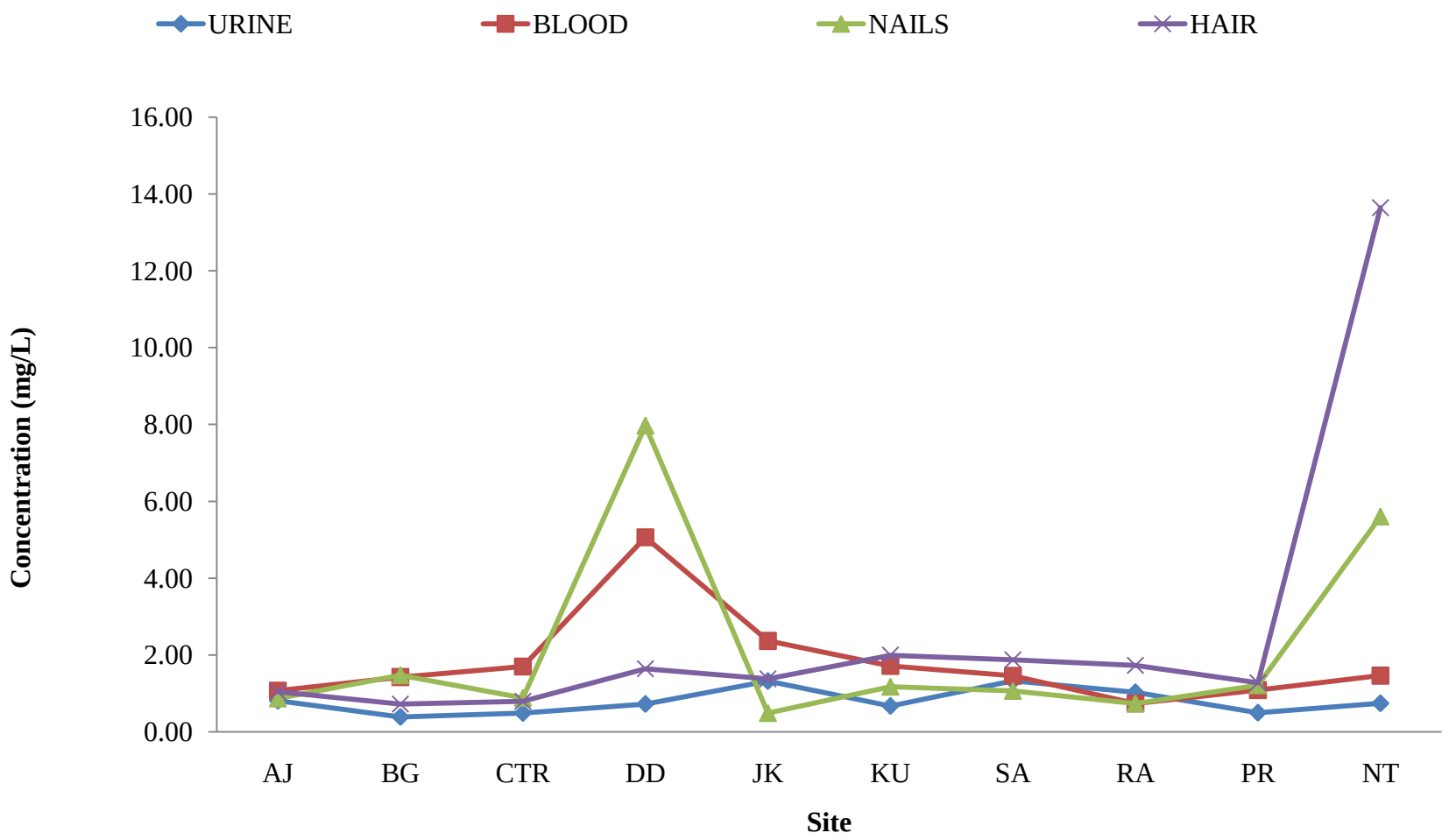


**Figure 4.52: Conentrations of zinc in the tissues and urine of human residents' samples near the dumpsites during the wet season**

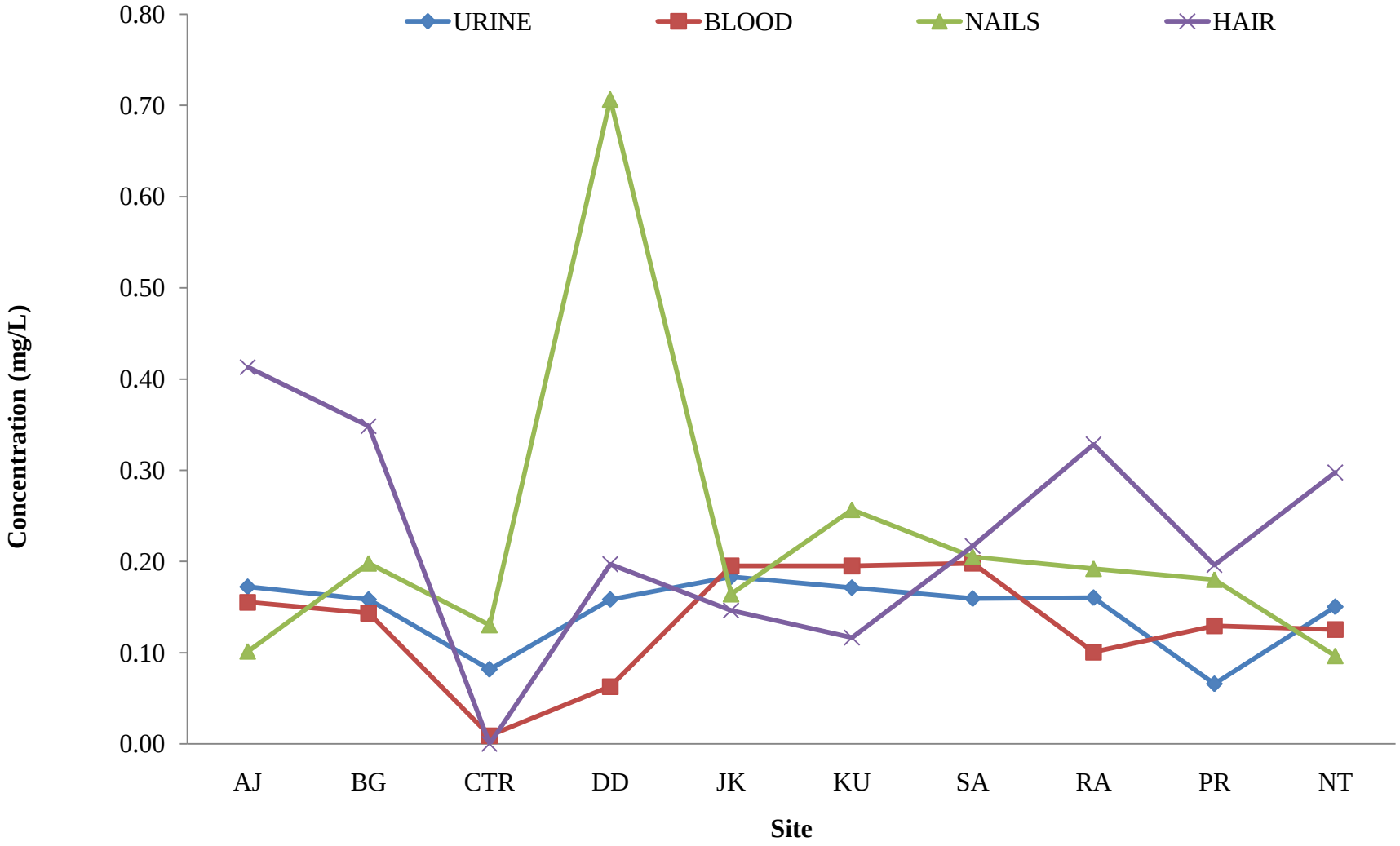


**Figure 4.53: Concentrations of lead in the tissues and urine of human residents' samples near the dumpsite duringthe dry season**

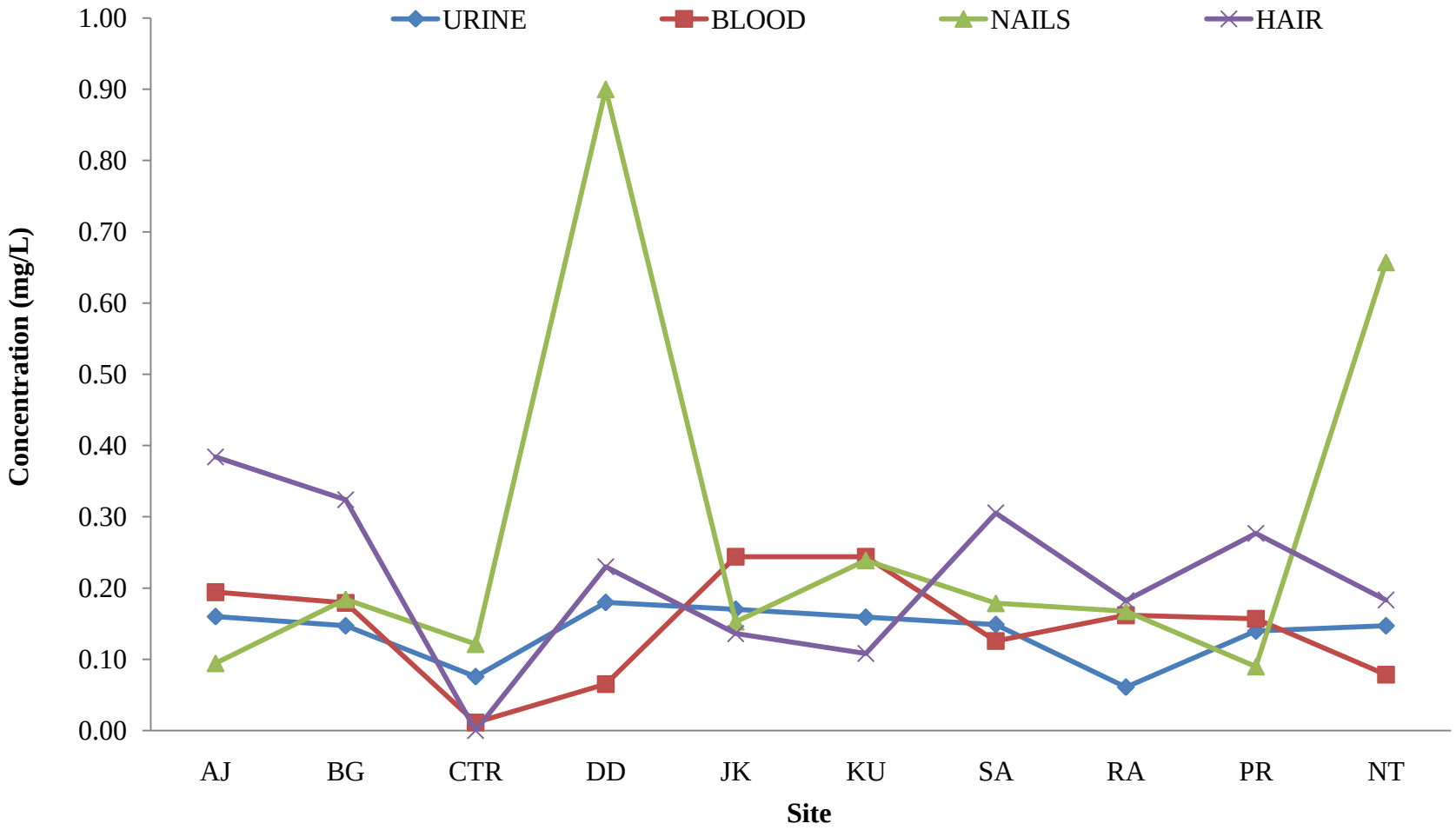


**Figure 4.54: Concentrations of lead in the tissues and urine of human residents' samples near the dumpsite during the wet Season**

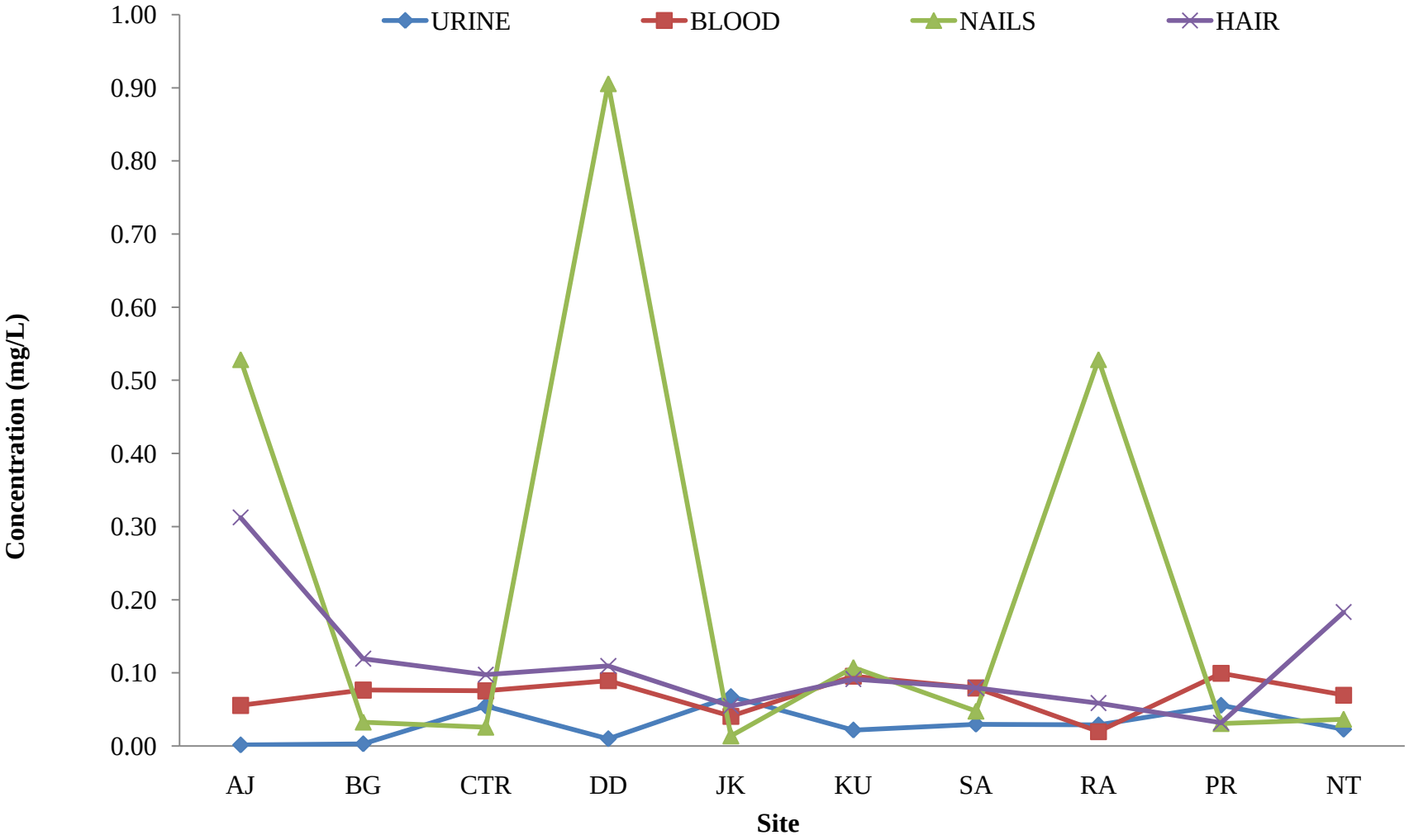


**Figure 4.55: Conentrations of copper in the tissues and urine of human residents' samples near the dumpsites duringthe dry season**

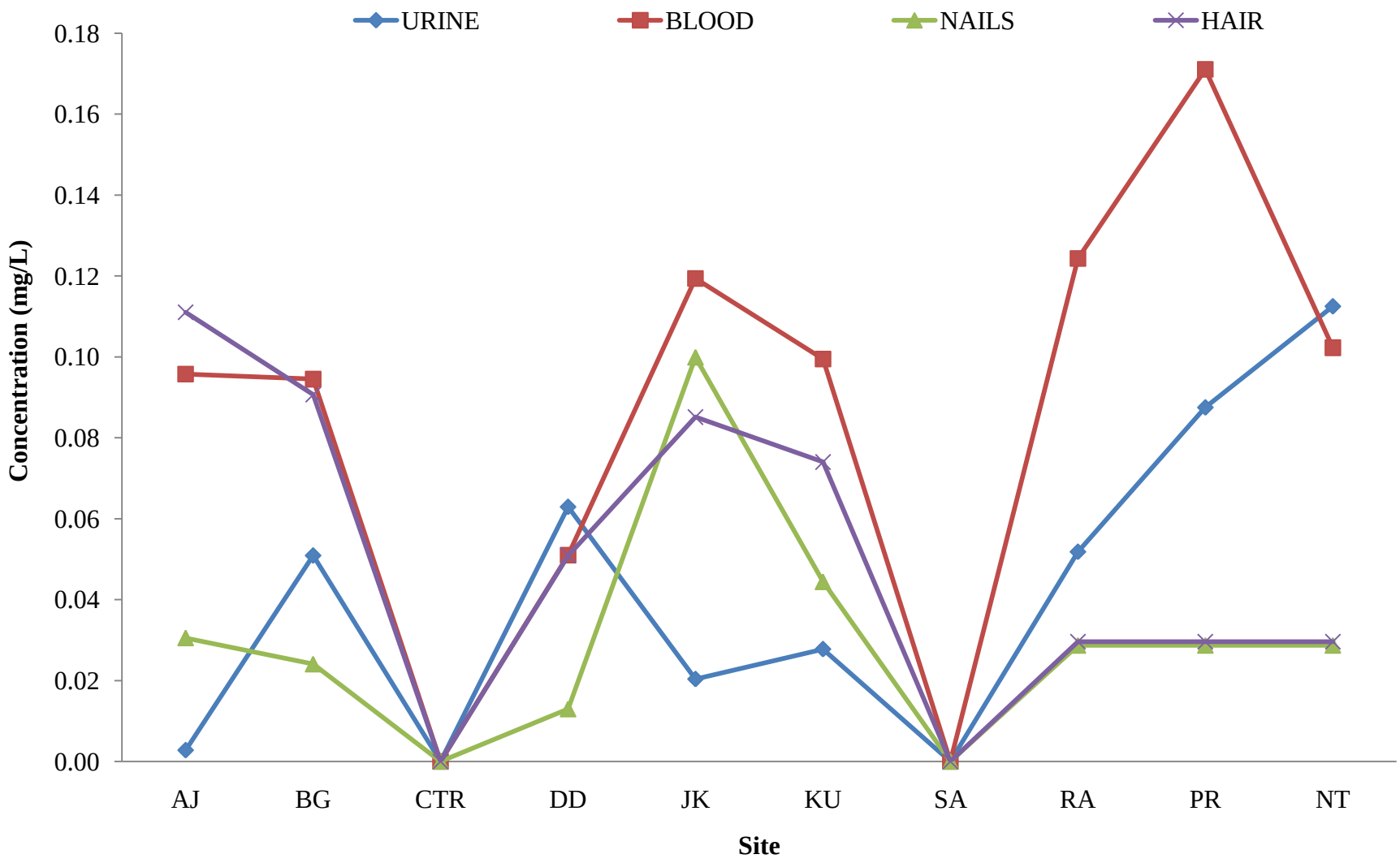


**Figure 4.56: Concentrations of copper in the tissues and urine of human residents' samples near the dumpsites during the wet Season**

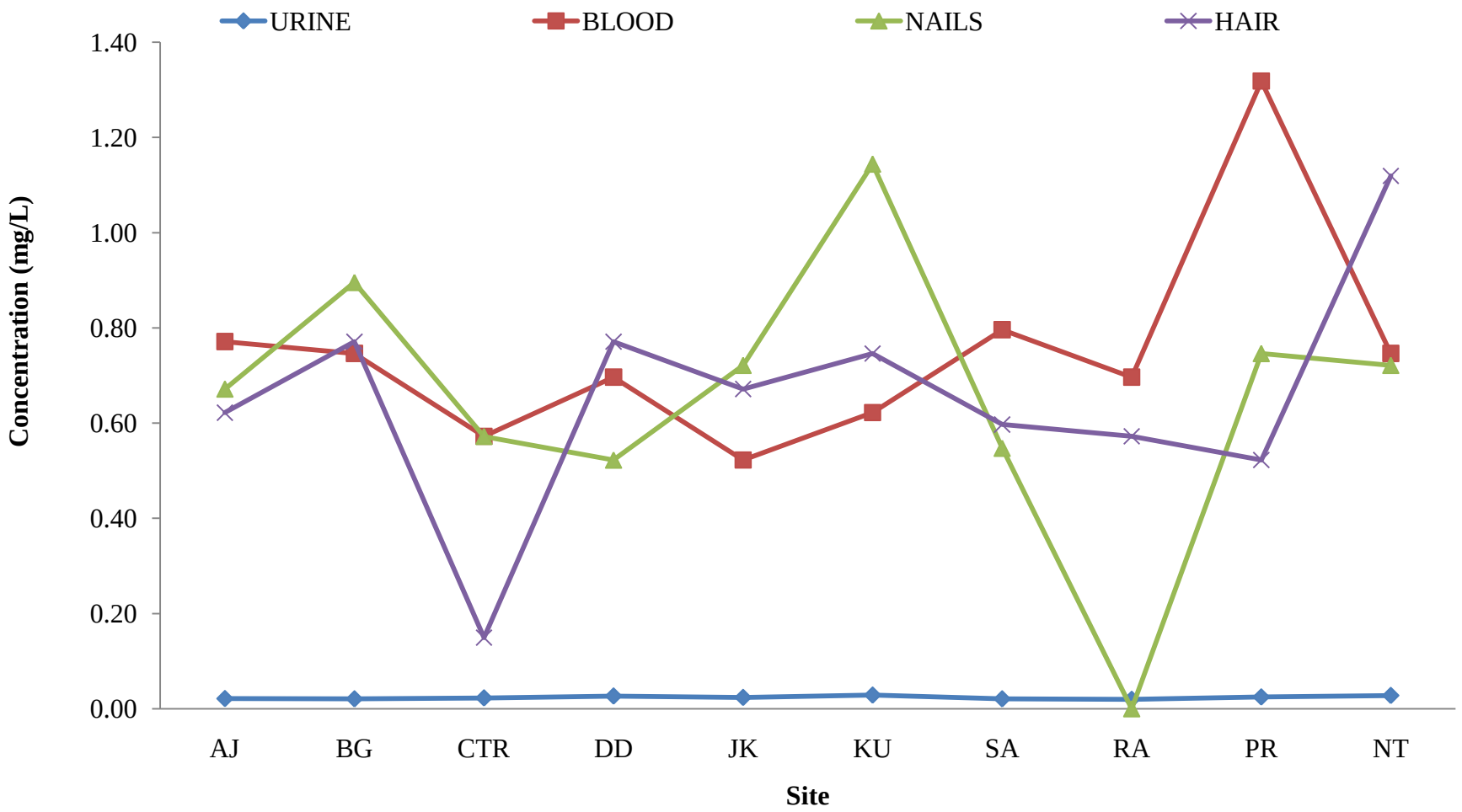


**Figure 4.57: Concentrations of cadmium in the tissues and urine of human residents' samples near the dumpsites duringthe dry season**

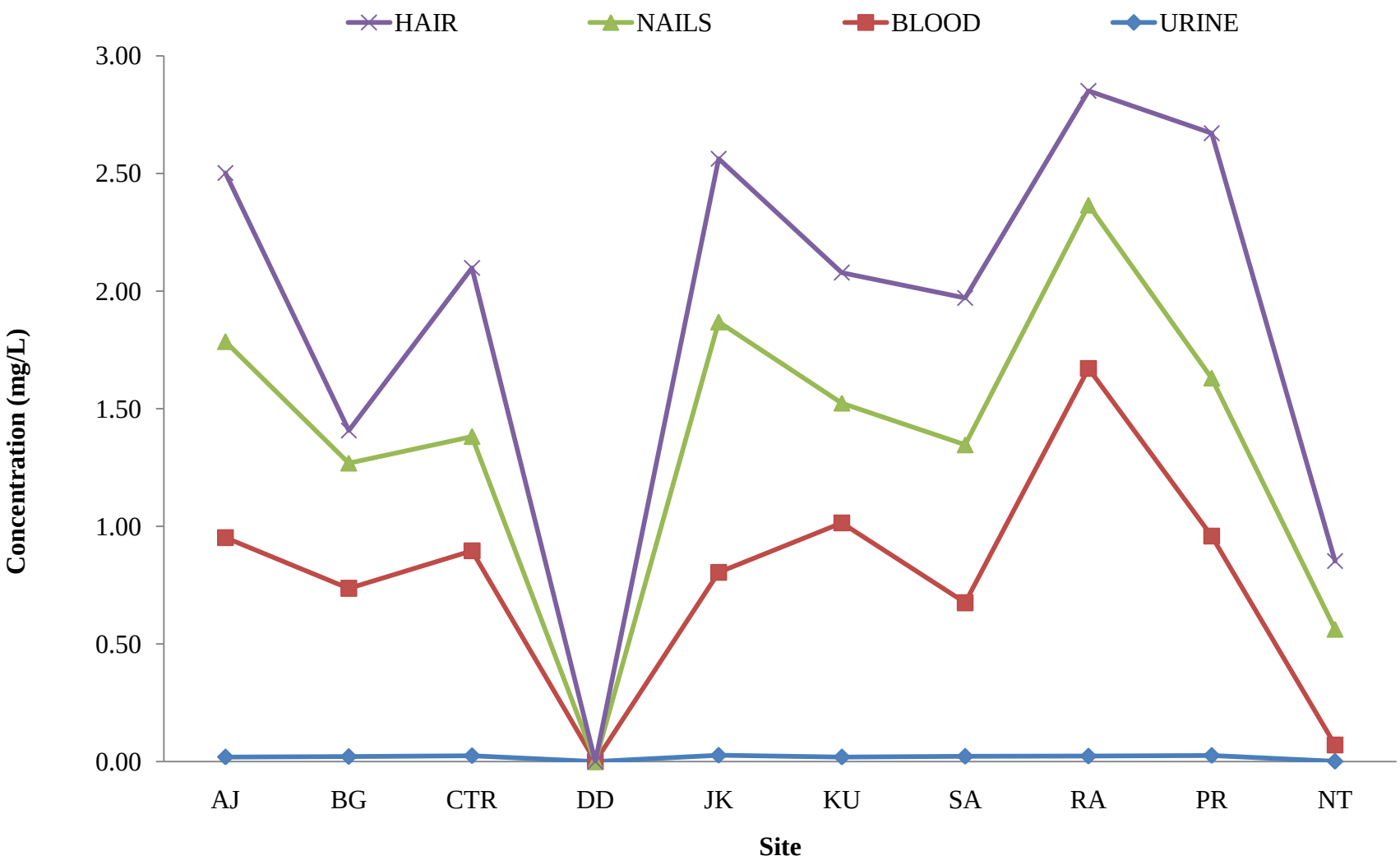


**Figure 4.58: Concentrations of cadmium in the tissues and urine of human residents' samples near the dumpsite during the wet season**

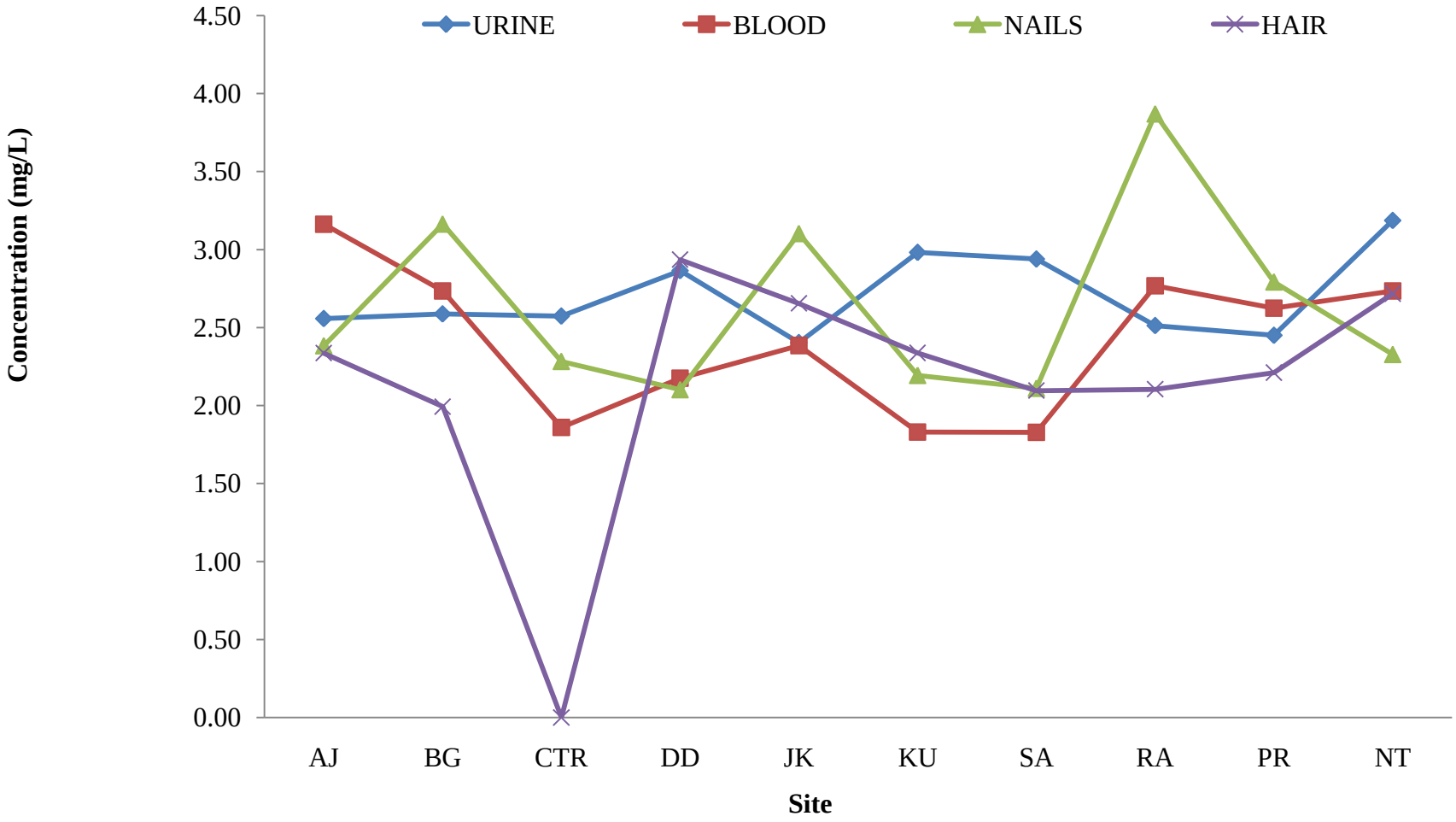


**Figure 4.59: Concentrations of mercury in the tissues and urine of human residents' samples near the dumpsites during the dry season**

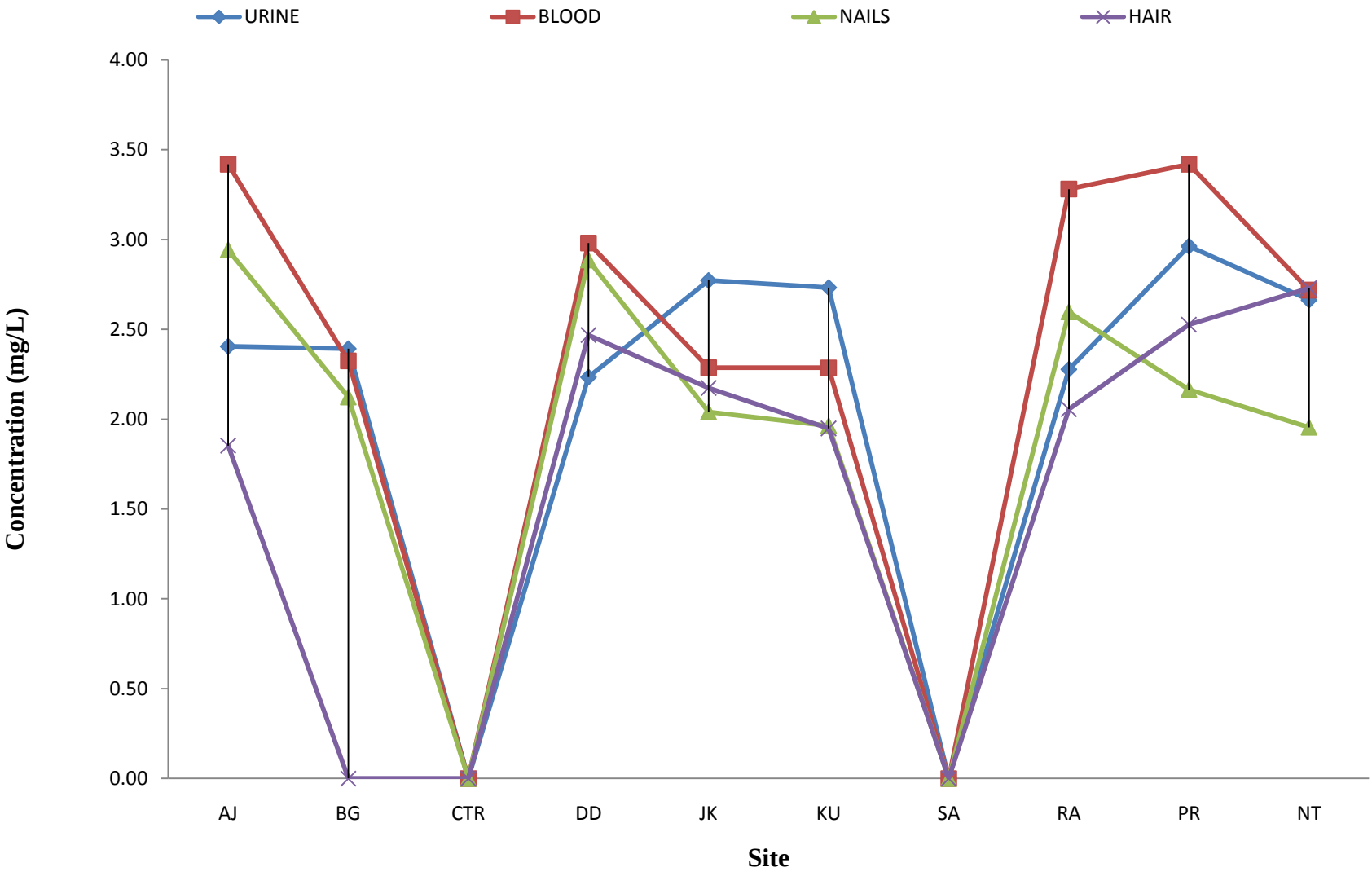


**Figure 4.60: Concentrations of mercury in the tissues and urine of human residents' samples near the dumpsite duringthe wet season**

4.11.1: Zn contents in the tissues of the residents

The concentration of Zn in the urine samples of the human residents across the sites and seasons (dry and wet) range from 0.414 (CTR) to 1.102 mg/L (RA) and 0.385(BG) to 0.807 mg/L (AJ), respectively, as presented in the Figures. Also, the concentrations range of Zn in the blood samples of the human residents at the viciny ofdumpsites range from 0.590 (RA) to 4.047 mg/L (RA) and 0.738 (RA) to 5.08 mg/L (DD) in both the dry and wet seasons across the sites as presented in Figures 4.51 to 4.52. Similarly, the concentration ranges of 0.521 (JK) to 8.568 mg/kg (DD) and 0.485 (JK) to 7.968 mg/kg (DD), respectively, were recorded for Zn in the nail samples of the residents across the sites as presented in the Figures. Also, the levels of Zn in the hair samples of the residents across the sites as presented in the Figures 4.51 and 4.52, respectively, range from 0.774 (CTR) to 14.667 mg/kg (NTC) and 0.719 (BG) to 13.641mg/kg (NTC) for the dry and wet seasons, respectively.

4.11.2 Pb contents in the tissues of the residents

Figures 4.53 and 4.54 show the levels of Pb in the samples of human residents at the vicinity of the dumpsites during both dry and wet seasons. The concentration ranges of Pb in the urine samples of the residents across the seasons were 0.060 (RA) to 0.158 mg/L (DD) and 0.066 (PR) to 0.183 mg/L (JK), respectively as presented in Figures 4.53 and 4.54, respectively. Also, the levels of Pb in the blood samples across the sites range from 0.011 (CTR) to 0.244 mg/L and 0.009 (CTR) to 0.198 mg/L as presented in the Figures. The concentration ranges of 0.090 (PR) to 0.900 mg/kg (DD) and 0.097 (NTC) to 0.192 mg/kg (NTC) were recorded for Pb in the nails samples of the dumpsite residents across the sites. Also, the levels of BDL (CTR) to 0.384 mg/L and BDL

(CTR) to 0.298 mg/L (NTC) were recorded in the hair samples of the dumpsites residents for the dry and wet seasons, respectively.

4.11.3 Cu contents in the tissues of the residents

As could be seen in Figures 4.55 to 4.56, the concentrations of Cu recorded in the urine samples of the dumpsite residents in both dry and wet seasons were 0.002 (AJ) to 0.056 mg/L (PR) and BDL (AJ,CTR, SH) to 0.113 mg/L (AJ), respectively. The levels recorded in the blood of the human residents at the vicinity of the dumpsites across the sites range from 0.02 (RA) to 0.096 mg/L (KU) and BDL (CTR, SA) to 0.171 mg/L (PR) for the dry and wet seasons, respectively. Also, the ranges of Cu recorded in the nails of the residents across the sites were: 0.014 to 0.091 mg/L (DD) and BDL (AJ, CTR, SH) to 0.491 mg/kg (KU), respectively as presented in the Figures 4.55 and 4.56, respectively.The levels of Cu in the hair samples of the residents across the sites in both the dry and wet seasons were 0.031 (AJ) to 0.32 mg/kg (PR) and BDL (CTR) to 0.171 mg/L (AJ), respectively.

4.11.4 Cd contents in the tissues of the residents

Figures 4.57 and 4.58, the concentrations of Cd in the urine samples of the human residents at the vicinity of the dumpsites in both the dry and wet seasons. The ranges of 0.667 (NTC) to 3.744 mg/kg (PR and BDL (DD) to 0.026 mg/L (PR) were recorded across the sites and seasons. The ranges of BDL (RA) to 1.144 mg/kg (KU) and BDL (DD) to 1.648 mg/L in the dry and wet seasons in the blood samples. Similarly, the concentration ranges of Cd in the nail samples of the human residents across the sites were BDL (RA) to 1.144mg/kg (KU) and BDL (SH, DD) to 1.064 mg/kg (JK), respectively, for the dry and wet seasons. Similarly, the ranges of Cd in the hair samples of the samples in both the dry and wet seasons were BDL (DD) to 1.041 mg/kg (PR) and 0.149 (CTR) to 1.119 mg/kg (NTC) as presented in Figures 4.57 to 4.58.

4.11.5 Hg contents in the tissues of the residents

Figures 4.59 and 4.60 show the concentrations of Hg in the analysed samples of urine, blood, nails and hair samples of the people at the vicinity of the dumpsites in both dry and wet seasons. The levels of Hg recorded in the urine samples of the residents range from 2.403 (JK) to 3.187 mg/L (NTC) and BDL (CTR, SH) to 2.96 mg/L (PR) for the dry and wet seasons, respectively. The ranges of 1.830 (KU) to 3.162 mg/L and BDL (CTR) to 3.46 mg/L for Hg were recorded in the blood samples of the residents in both dry and wet seasons, respectively. The concentration ranges of Hg in the nail samples of the residents as reflected in the Figures 4.59 to 4.60 were in the range of 2.11 (SA) to 3.87 mg/kg (RA) and BDL (CTR, SH) to 3.60 mg/kg (SA) for both the dry and wet seasons, respectively. The levels of Hg in the hair samples of the residents at the vicinity of the dumpsites in both the dry and wet seasons were BDL to 2.717 mg/kg (NTC) and BDL (CTR, SH, BG) to 2.729 mg/kg, respectively.

4.11.6 Correlation matrices of heavy metals in human residents' tissues and dust particulates across the sites and seasons

The correlation matrices of metals in Human Tissues and dust particulates are presented in Table 4.39. The correlation coefficients of 0.269, 0.023, 0.127, 1.00, 0.269, 0.023, 0.741, 0.674, 0.185, and 0.344 were recorded for the correlations of ZnUrineD vs ZnBloodD, ZnNailsD, ZnHairD, ZnUrineR, ZnNailsR, PbUrineD, PbBloodD, PbNailsD, and PbHairD, respectively, as presented in Table 4.39.

Similarly, the correlation coefficients of 0.621, 0.017, 0.422, 0.090, 0.172, 0.148, 0.108, 0.048, and 0.282 were recorded for the correlations of ZnUrineD vs PbUrineR, PbBloodR, PbUrineD, CuBloodD, CuNailsD, CuHairD, CuBloodR, CdUrineD, and CdBloodD, respectively, as presented in Table 4.39.

The correlation coefficients of 0.765, 0.019, 0.269, 1.00, 0.765, 0.029, 0.916, 0.374, 0.064, 0.483, 0.584, 0.094, 0.454, 0.549, and 0.147 were recrded for the correlations of ZnBloodD vs ZnNailsD, ZnHairD, ZnUrineR, ZnBloodR, ZnNailsR, PbBloodR, PbHairR, CuUrineD, CuBloodD, CuNailsD, CuHairD, CuUrineR, CdUrineD, CuBloodD, CuNailsD, CuHAirD, CuUrineR, CuUrineD and CdBloodD, respectively, as presented in Table 4.39.

Similarly, the correlations of ZnNailsD vs ZnHairD, ZnUrineR, ZnNailsR, PbUirne D, PbNailsD, PbHairD, PbBloodR, CuBloodD, CuNailsD, CuHairD, CuUrineR, CuNailsR, CdUrineR, CuNailsR, CdUrineD, and CdBloodD were 0.523, 0.023, 0.765, 0.252, 0.730, 0.183, 0.155, 0.396, 0.549, 0.244, 0.316, 0.196, 0.453, and 0.175, respectively, as presented in Table 4.39.

Other correlation coefficients recorded were 0.019, 0.523, 0.207, 0.127, 0.266, 0.217, 0.133, 0.318, 0.288, 0.689, 0.376, and 0.147 for ZnHairD vs ZnUrineR, ZnBloodR, ZnNailsR, PbUrineD, PbBloodD, PbHairD, PbUrineR, CuBloodD, CuHairD, CuBloodR, CuNailsR, CdUrineD and CdBloodD, respectively, as reflected in Table 4.39.

The correlation coefficients recorded for ZnUrineR vs ZnBloodR, ZnNailsR, PbUrineD, PbBloodD, PbNailsD, PbHairD, PbUrineR, PbBloodR, CuUrineD, CuBloodD, CuNailsD, CuHairD, CuBloodR, CdUrineD, and CdBloodD were 0.269, 0.023, 0.741, 0.674, 0.185, 0.344, 0.621, 0.017, 0.421, 0.017, 0.421, 0.090, 0.172, 0.149, 0.108, 0.483 and 0.283, respectively, as reflected in Table 4.39.

Similarly, as reflected in the Table, the correlation coefficients of 0.765, 0.426, 0.029, 0.916, 0.374, 0.064, 0.483, 0.584, 0.094, 0.454, 0.549 and 0.147, were recorded for ZnBloodR vs ZnNailsR, PbUrineD, PbBloodD, PbNailsD, PbBloodR, CuUrineD,

PbBloodR, CuUrineD, CuBloodD, CuNailsD, CuHairD, CuUrineR, CdUrineD and CdBloodD across the sites and seasons.

As reflected in the Table 4.39, the correlation coefficients of 0.282, 0.730, 0.00, 0.155, 0.396, 0.549, 0.244, 0.316, 0.196, 0.453, and 0.175 were recorded for ZnNailsR vs PbUrineD, PbNailsD, PbHairD, CuBloodD, CuNailsD, CuHairD, CuUrineR, CuNailsR, CdUrineD and CdBloodD, respectively.

The correlation coefficients of ZnHairR vs PbUrineD, PbBloodD, PbHairD, PbUrineR, CuUrineD, CuBloodD, CuNailsD, CuHairD, CuUrineR, CuBloodR, CuNailsR, CdUrineD, and CdB loodD recorded across the sites and seasons were 0.207, 0.127, 0.613, 0.217, 0.133, 0.318, 0.288, 0.689, 0.376, and 0.147, respectively.

The correlation coefficients of 0.726, 0.369, 0.091, 0.736, 0.358, 0.007, 0.297, 0.353, 0.493, 0.332, 0.046, 0.686 and 0.297 were recorded for PbUrineD vs PbBloodD, PbNailsD, PbHairD, PbUrineR, pbBloodR, CuUrineD, CuBloodD, CuNailsD, CuHairD, CuBloodR, CuHairR, CdUrineD, and CdBloodD, respectively, across the seasons as presented in Table 4.39.

The correlation coefficients recorded for PbBloodD vs PbNailsD, PbHairD, PbUrineR, PbBloodR, PbHairR, CuUrineD, CuBloodD, CuNailsD, CuHairD, CuBloodR, CuHairR, CdUrineD and CdBloodD were 0.004, 0.988, 0.789, 0.278, 0.013, 0.169, 0.358, 0.246, 0.151, 0.135, 0.521 and 0.446, respectively, as presented in Table 4.39.

Also, the correlation coefficients of 0.416, 0.479, 0.717, 0.533, 0.469 and 0.227 were recorded for PbBloodD vs PbNailsD, PbHairD, PbUrineR, PbBloodR, PbHairR,

CuUrineD, CuBloodD, CuNailsD, CuHairD, CuUrineR, CuBloodR, CuNailsR, CuHairR, CdUrineD and CdBloodD, respectively, as reflected in Table 4.39.

Also, the correlation coefficients of 0.00, 0.416, 0.479, 0.717, 0.533, 0.467 and 0.227 were recorded for PbNailsD vs PbHairD, PbBloodR, CuBloodD, CuNailsD, CuUrineD, and CdBloodD, respectively.

Similarly, the correlation coefficients of 0.756, 0.533, 0.209, 0.436, 0.095, 0.386, 0.650, 0.222, 0.185, 0.430, 0.325 and 0.501 were recorded for PbHairD vs PbUrineR, PbBloodR, PbHairR, CuBloodD, CuNailsD, CuHairD, CuUrineD, CuBloodR, CuNailsR, CuHairR, CuUrineD and CdBloodD, respectively, as presented in Table 4.39.

As presented in the Table, the correlation coefficients of ZnUrineD vs CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailR, HgHairR, ZnDustD, PbDustD, CuDustD, CdDustD, HgDustD, ZnDustR, PbDustR, CuDustR, CdDustR and HgDustR were 0.108, 0.445, 0.290, 0.543, 0.063, 0.278, 0.585, 0.464, 0.552, 0.598, 0.555, 0.510, 0.630, 0.536, 0.459, 0.056, 0.350, 0.387, 0.705, 0.445 and 0.289, respectively.

Also, as presented in the Table 4.39, the correlation coefficients o 0.211, 0.393, 0.450, 0.103, 0.541, 0.308, 0.464, 0.199, 0.143, 0.491, 0.338, 0.227, 0.441, 0.365, 0.203, 0.074, 0.118 and 0.080 were recorded for ZnBloodD, vs CdNailsD, CdHAirD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgUrineR, HgBloodR, HgNailsR, HgHairR, ZnDustD, PbDustD, ZnDustD, ZnDustR, CuDustR and HgDustR, respectively.

The correlation coefficients of ZnNailsD vs CdNailsD, CdHairD, CdNaisD, HgUrineD, HgBloodD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, PbDustD, CuDustD, CuDustR, and HgDustR were 0.120, 0.576, 0.239, 0.415, 0.213, 0.496, 0.186, 0.179, 0.266, 0.465, 0.005, 0.378, 0.141 and 0.283, respectively, as presented in Table 4.39.

Also, the correlation coefficients of 0.173, 0.654, 0.397, 0.278, 0.060, 0.362, 0.260, 0.079, 0.005, 0.426, 0.880, 0.558, 0.061, and 0.411 were recorded for ZnHairD vs CdNailsD, CdHairD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, ZnDustR, PbDustD, CuDustD, CuDustR, CdDustR, respectively, as presented in Table 4.39.

The correlation coefficients of 0.108, 0.445, 0.290, 0.542, 0.063, 0.278, 0.585, 0.464, 0.552, 0.599, 0.555, 0.511, 0.630, 0.536, 0.460, 0.056, 0.350, 0.387, 0.705, 0.445, and 0.289 were recorded for ZnHairD vs CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, CuDustD, CuDustR and CdDustR, respectively.

Similarly, the correlation coefficients of 0.271, 0.393, 0.450, 0.103, 0.541, 0.308, 0.464, 0.199, 0.143, 0.491, 0.338, 0.227, 0.441, 0.365, 0.203, 0.074, 0.118 and 0.079 were recorded for ZnBloodR vs CdNailsD, CdHairD, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HghairR, PbDustD, ZnDustR, CuDustR, and HgDustR as presented in Table 4.39.

Also, the correlation coefficients for ZnNailsR vs CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, ZnDustD, PbDustD, CDustD, ZnDustR, PbDustR,

CuDustR and HgDustR were 0.120, 0.576, 0.239, 0.415, 0.213, 0.496, 0.186, 0.179, 0.266, 0.465, 0.005, 0.378, 0.141 and 0.283, respectively, as presented in Table 4.39.

The correlation coefficients of 0.173, 0.654, 0.397, 0.278, 0.060, 0.362, 0.260, 0.079, 0.005, 0.426, 0.880, 0.588, 0.060, and 0.411 were recorded for the correlation of ZnHairR vs CdNailsD, CdHairD, HgUrineD, hgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, ZnDustD, PbDustD, CuDustD, CuDustR, CdDustR, HgDustR, respectively.

Also, the correlation coefficients of 0.457, 0.762, 0.349, 0.418, 0.357, 0.118, 0.770, 0.689, 0.653, 0.778, 0.664, 0.651, 0.689, 0.676, 0.366, 0.127, 0.336, 0.205, 0.275, 0.318 and 0.241 were recorded for PbUrineD vs CdnailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, PbDustD, PbDustR, CuDustR and CdDustR, respectively.

Similarly, the correlation coefficients of 0.617, 0.633, 0.198, 0.252, 0.044, 0.184, 0.567, 0.504, 0.476, 0.714, 0.633, 0.538, 0.506, 0.685, 0.420, 0.237, 0.470, 0.349, 0.326, 0.209 and 0.151, respectively, were recorded for PbBloodD vs CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, PbDustD, CdDustD, ZnDustR, PbDustR, CuDustR, CdDustR and HgDustR, respectively as presented in Table 4.39.

The correlation coefficients recorded for PbNailsD vs CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, PbDustD, CdDustD, ZnDustR, PbDustR, HgDustR were 0.147, 0.344, 0.546, 0.230, 0.631, 0.353, 0.413, 0.167, 0.164, 0.495, 0.258, 0.289, 0.498, 0.397, 0.166, 0.434, 0.228, 0.159, 0.097, 0.009, and 0.007, respectively as shown in Table.

In addition, the correlation coefficients of 0.144, 0.639, 0.107, 0.319, 0.268, 0.478, 0.807, 0.587, 0.657, 0.413, 0.783, 0.529, 0.709, 0.221, 0.478, 0.405, 0.206, 0.182, 0.224, 0.043, and 0.506, respectively were recorded for the correlations of PbHairD vs CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, ZnDustD, PbDustD, CuDustD, CdDustD, ZnDustR, PbDustR, CuDustR and CdDustR, respectively.

The correlation coefficients of 0.054, 0.169, 0.065, 0.395, 0.442, 0.011, 0.169, 0.419, 0.237, 0.429, 0.504, 0.084, 0.343, 0.535, 0.580, 0.614, 0.425 and 0.570 were recorded for PbUrineR vs PbBloodR, PbHairR, CuBloodD, CuHairD, CuBloodR, CuNailsR, CuHairR, CuUrineD, CdUrineD, CdBloodD, CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, HgUrineD, HgBloodD, HgNailsD, HgHairD and HgUrineR, respectively, as presented in Table 4.39.

Similarly, the correlation of Pb vs PbHairR, VCuBloodD, CuNailsD, CuHairD, CuUrineR, CuBloodR, CuNailsR, CuHairR, CdUrineD, CdBloodD, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD and HgUrineR revealed the correlation coefficients of 0.486, 0.010, 0430, 0.063, 0.166, 0.357, 0.248, 0.200, 0.200, 0.005, 0.267, 0.309, 0.279, 0.180, 0.682, 0.177, 0.017, 0.220, 0.215, 0.521 and 0.148, respectively, as reflected in Table 4.39.

Also, the correlation coefficients of 0.186, 0.170, 0.397, 0.372, 0.324, 0.153, 0.345, 0.371, 0.496, 0.251, 0.159, 0.403, 0.012, and 0.512 were recorded for CuUrineD vs CuBloodD, CuUrineR, cuBloodR, CdUrineD, CdBloodD, CdNailsD, CdUrineR,

CdBloodR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HghairD and HgUrineR, respectively, as presented in Table 4.39.

In addition, the correlation coefficients of 0.016, 0.201, 0.014, 0.145, 0.774, 0.704, 0.782, 0.453, 0.516, 0.029, 0.317, 0.512, 0.724, 0.392, 0.247, 0.407, and 0.702, respectively were recorded for the correlations of CuBloodD Vs CuNailsD, CuHairD, CuBloodR, CuHairD, CuUrineR, CuBlooR, CuNailsR, CuHairR, CuUrineD, CdBloodD, CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, CdUrineD, CdBloodD, CdNailsD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, hgUrineD, HgBloodD, HgNailsD, hgHairD and HgUrineD, respectively.

Similarly, the correlation coefficients of 0.350, 0.510, 0.093, 0.192, 0.095, 0.205, 0.387, 0.389, 0.715, 0.289, 0.214, 0.304, 0.175, 0.404 and 0.039 were recorded for CuNailsD vs CuHairD, CuUrineR, CuHairR, CdUrineD, CdBloodD, CdHairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, and HgUrineR, respectively, as presented in Table 4.39.

The correlation of CuUrineR vs CuBloodR, CdUrineD, CdUrineR, CdBloodR, CdNailsR, CdHairR and HgNailsD, across the sites had correlation coefficients of 0.097, 0.459, 0.697, 0.343, 0.215, 0.334, 0.452, 0.246, 0.031, 0.444, 0.598, 0.160, 0.346, and 0.311, respectively, as reflected in Table 4.39. Also, the correlation coefficients of 0.182, 0.053, 0.369, 0.298, 0.469, 0.270 and 0. 32 were recorded for the correlation of CuUrineR vs CuBloodR, CdUrineD, CdUrineR, CdBlooodR, CdNailsR, CdHairR and HgNailsD, respectively, as presented in the same Table 4.39.

The correlation coefficients of 0.016, 0.202, 0.479, 0.217, 0.269, 0.369, 0.177, 0.303, 0.320, 0.051, 0.357, 0.561, 0.685, 0.261, and 0.540, respectively, were recorded for the correlations of CuBloodR vs CuNailsR, CuHairR, CdUrineD, CdBloodD, CdnailsD, CdHairD, CdUrineR, CdBloodR,CdnailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD and HgUrineR, respectively, as reflected in Table 4.39.

The correlation coefficients of 0.349 and 0.198 were recorded for correlating CuNailsR Vs CuHairR and CuNailsR vs CdHairD, respectively across the sites as reflected in the Table 4.39. The correlation coefficients of 0.127, 0.353, 0.336, 0.092, 0.087, 0.006, 0.363, 0.309, 0.070, 0.490, 0.102, 0.135, and 0.240 were recorded for CuHairR vs CdUrineD, CdBloodD, HgNailsD, HgHairD and HgUrineR, respectively as reflected in the Table 4.39.

Also, the correlation coefficients of 0.493, 0.410, 0.404, 0.124, 0.206, 0.269, 0.145, 0.254, 0.370 and 0.251 were recorded for PbUrineR vs HgBloodR, HgNailsR, HgHairR, PbDustD, CuDustD, CdDustD, ZnDustR, CuDustR, CdDustR, respectively as shown in Table 4.39.

Similarly, the correlation coefficients of 0.041, 0.417, 0.174, 0.429, 0.346, 0.126, 0.205, and 0.425 were recorded for PbBloodR vs HgBloodR, HgHairR, ZnDustD, PbDustD, CdDustD, CuDustR, CdDustR and HgDustR, respectively as presented in Table 4.39. The correlation coefficients of 0.272, 0.865, 0.665, and 0.591, respectively were recorded for PbNailsR Vs HgHairR, CuDustD, CdDustR and HgDustR, respectivey as presented in the table

The correlation coefficients of 0.019, 0.148, 0.538, 0.148, 0.084, 0.217, 0.248 and 0.321, respectively were recorded for PbHairR vs HgBloodR, HgHairR, ZnDustD, PbDustD, CuDustD, ZnDustR, CdDustR and HgDustR, respectively as reflected in the Table 4.39.

Also, the correlation coefficients of 0.069, 0.128, 0.042, 0.045, 0.027, 0.173, and 0.441 were recorded for CuUrineD vs HgBloodR, HgNailsR, HgHairR, PbDustD, CdDustD, PbDustR and CuDustR, respectively.

As presented in the Table, the correlation coefficients of 0.539, 0.574, 0.429, 0.141, 0.256 and 0.079, respectively for CuBloodD Vs hgBloodR, HgNailsR, HgHairR, PbDustD, ZnDustR, PbDustR and HgDustR, respectively as presented in the Table.

The correlation coefficients of 0.356, 0.303, 0.337, 0.194, 0.548, 0.360, 0.219, 0.161, and 0.338 were recorded for CuNailsD vs HgBloodR, HgNailsR, HgHairR, ZnDustD, PbDustD, CdDustD, HgDustD, PbDustR and CdDustR, respectively as presented in the Table.

Also, the correlation coefficients of 0.542, 0.250, 0.338, 0.193, 0.292 and 0.048, respectively were recorded for CuHairD vs HgBloodR, HgNailsR, HgHairR, CuDustD, HgDustD and CuDustR, respectively. The correlation coefficients of 0.082, 0.377, 0.270 and 0.072 were recorded for CuUrineR vs PbDustD, CdDustD, HgDustD and CdDustR, respectively, as presented in Table 4.39.

Similarly, the correlation coefficients of 0.188, 0.275, 0.384, 0.283, 0.082, 0.446, 0.124 and 0.128 were recorded for CuBloodR vs HgBloodR, HgHairR, CuDustR, CdDustR, HgDustD, CuUrineR, CdDustR and HgDustR, respectively.

The correlation of CuNailsR vs HgHairR, CuDustD, CdDustR and HgDustR, respectively as presented in the Table, revealed correlation coefficients of 0.041, 0.662, 0.089, 0.398, 0.011, and 0.401, respectively.

Also, as presented in the Table, the correlation coefficients of 0.372, 0.201, 0.087 and 0.193 were recorded for CuHairR vs HgBloodR, HgHairR, PbDustD and HgDustD, respectively as presented in the Table 4.39.

The correlation coefficients of 0.674, 0.704, 0.734, 0.513, 0.295, 0.438, 0.464, 0.946, 0.717, 0.638, 0.692, 0.936, 0.661, 0.641, 0.678, 0.229, 0.122, 0.125, 0.000, 0.248, and 0.031, respectively were recorded for CdUrineD vs cdBloodD, CdNailsD, CdHairD, CdUrineR, CdBloodBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodR, HgNailsR, HgHairR, PbDustD, CuDustD and CdDustD, respectively, as presented in the Table 4.39.

Similarly, the correlation coefficients of 0.547, 0.285, 0.211, 0.257, 0.614, 0.407, 0.255, 0.442, 0.687, 0.372, 0.323, and 0.409, respectively were recorded for CdNailsD vs CdHairD, CdUrineR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR and HgHairR, respectively, as presented in Table 4.39.

Also the correlation coefficients of 0.012, 0.151, 0.757, 0.683, 0.504, 0.889, 0.655, 0.566, 0.516, 0.877, 0.200, 0.536, and 0.114, respectively were recorded across the sites for CdHairD vs CdUrineR, CdNailsR, HgUrineD, HgBloodD, HgNailsD, HgUrineR, HgBloodR, HgNailsR, HgHairR, ZnDustD, PbDustD, CuDustD and CdDustD, respectively, as presented in Table.

The correlation coefficients of 0.789, 0.779, 0.817, 0.437, 0.587, 0.240, 0.573, 0.583, 0.622, 0.205, 0.085, 0.600, and 0.360, respectively, were recorded for correlating

CdUrineR vs CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgnailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, ZnDustD, bDustD, CuDustD and CdDustD, respectively, as presented in Table 4.39.

Similarly, the correlation coefficients of 0.584, 0.616, 0.352, 0.510, 0.756, 0.237, 0.455, 0.585, 0.562, 0.229, 0.049, 0.716, and 0.650 were recorded across the sites for CdBloodR vs CdNailsR, CdHairR, HgUrineD, hgBloodD, hgNailsD, HgHairD, HgUrineR, hgBloodR, HgNailsR, hgHairR, ZnDustD, PbDustD, and CdDustD, respectively, as presented in Table 4.39.

Other correlation coefficients of 0.651, 0.324, 0.482, 0.450, 0.385, 0.398, 0.454, 0.302, 0.327, 0.143, 0.579 and 0.341 were recorded for CdNailsR vs cdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, ZnDustD and PbDustD, respectively.

Similarly, the correlation coefficients of 0.363, 0.338, 0.336, 0.200, 0.536, 0.474, 0.358, 0.219, 0.585 and 0.174, respectively for CdHairR vs HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, PbDustD and CdDustD, respectively. The correlation coefficients of 0.764, 0.667, 0.678, 0.905, 0.784, 0.803, 0.671, 0.251, 0.185 and 0.155, respectively were recorded for HgUrineD vs HgBloodD, HgNailsD, hgHairD, HgUrineD, HgUrineR, HgBloodR, HgNailsR, PbDustD, CuDustD and CdDustD, respectively as presented in Table.

The correlation coefficients of 847, 0.686, 0.818, 0.891, 0.636, 0.736, 0.427, 0.291 and 0.151 were recorded for HgBloodD vs HgNailsD, HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, PbDustD, CuDustD and CdDustD, respectively. The correlation

coefficients of 0.544, 0.786, 0.744, 0.661, 0.569, 0.482, 0.187, and 0.471, respectively were recorded across the sites for HgNailsD vs HgHairD, HgUrineR, HgBloodR, HgNailsR, HgHairR, PbDustD, CuDustD and CdDustD, respectively as presented in Table.

Also, the correlation coefficients of 0.656, 0.631, 0.555, 0.973, 0.572, 0.267 and 0.284 were recorded across the sites for HgHairD vs HgUrineR, HgBloodR, hgNailsR, hgHairR, PbDustD, CuDustD and CdDustD as presented in the Table. The correlation coefficients of 0.00, 0.248 and 0.031 were recorded for CdUrineD Vs PbDustR, CuDustR and HgDustR, respectively as reflected in Table.

In addition, the correlation coefficients of 0.217, 0.198 and 0.119 were recorded for CdBloodD Vs ZnDustr, PbDustR and CdDustR, respectively. Similarly as recorded across the sites, the correlation coefficients of 0.112, 0.05, 0.440, 0.207 and 0.353 were recorded for CdHairD vs ZnDustR, PbDustR, CuDustR, CdDustR and HgDustR, respectively.

The correlation coefficients of 0.064, 0.113 and 0.163 were recorded for CdUrineR vs HgDustD, ZnDustR and PbDustR, respectively as reflected in the Table. The correlation coefficients of 0.055, 0.066, 0.517 and 0.433 were recorded as presented in the Table for CdBloodR Vs hgDustD, ZnDustR, PbDustR and CdDustR, respectively.

Similarly, the correlation coefficients of 0.208, and 0.110 were recorded for correlating CdNails vs HgDustD and CdNailsR Vs HgDustR, respectively. The correlation coefficients of 0.060, 0.027, and 0.154 were recorded for CdHairR Vs HgDustD, ZnDustR and PbDustR. The correlation coefficients of 0.148, 0.186, 0.167, and 0.020 were recorded for HgUrineD vs ZnDustR, PbDustR, CuDustR, CdDustR and HgDustR, respectively across the sites and seasons as presented in Table 4.39.

Also, the correlation coefficients of 0.078, 0.210 and 0.220 were recorded for HgBloodD vs PbDustD, CuDustR and CdDustR, respectively. Similarly, the correlation coefficients of 0.764, 0.677, 0.678, 0.327, 0.077, 0.141, 0.037, 0.092 and 0.272, respectively were recorded for HgUrineR Vs HgBloodR, HgNailsR, HgHairR, PbDustD, CuDustD, CdDustD, ZnDustR PbDustR and CuDustR, respectively as presented in Table.

The correlation coefficients of 0.847, 0.686, 0.061, 0.588, 0.052, 0.178, 0.312, 0.324 and 0.234 were recorded across the sites for correlating hgBloodR vs HgNailsR, hgHairR, ZnDustD, PbDustD, CdDustD, ZnDustR, PbDustR and CdDustR, respectively. Also, the correlation coefficients of 0.544, 0.013, 0.495, 0.235, 0.564, 0.509 and 0.127, respectively across the sites for HgNailsD Vs HgHairR, ZnDuatD, PbDustD, CuDustD, CdDustD, HgDustD, ZnDustR, PbDustR, CuDustR, CdDustR and HgDustR, respectively.

The correlation coefficients of 0.071, 0.590, 0.356, 0.258, 0.205, 0.268, 0.329, 0.390 and 0.232, respectively recorded across the sites for HgHairR vs ZnDustD, PbDustD, CuDustD, CdDustD, HgDustD, ZnDustR, PbDustR, CuDustR, CdDustR and HgDustR, respectively. Also, the correlation coefficients of 0.457, 0.297, 0.124, 0.293, 0.133, 0.439, and 0.056 were recorded as presented in Table 4.39, for ZnDustD vs PbDustD, CuDustD, CdDustD, HgDustD, ZnDustR, PbDustR, CuDustR, CdDustR, and HgDustR, respectively, as reflected in Table 4.39.

Similarly, as presented in the Table, the correlation coefficients of 0.621, 0.338, 0.587 and 0.619 were recorded for PbDustD vs CdDustD, ZnDustR, PbDustR, CdDustR and HgDustR, respectively, as presented in the Table 4.39. Also, the correlation coefficients of 0.260, 0.542 and 0.821 were recorded for CdDustD vs CdDustD, PbDustR,

CuDustR, CdDustR, PbDustR, CuDustR, CdDustR and HgDustR, respectively. Also as presented in the Table, the correlation coefficients of 0.213 was recorded for HgDustD vs CdDustR across the sites and seasons.

The correlation coefficients of 0.260, 0.542 and 0.821 were recorded for ZnDustR vs PbDustR, CdDustR and HgDustR, respectively as presented in the same Table 4.39. Finally, the correlation coefficients of 0.604 and 0.424 were recorded for PbDustR vs CdDustR and CuDustR vs HgDustR, respectively across the sites and seasons as reflected in Table 4.39.

**Table 4.39a Correlation matrices of metals in human tissues and dust particulates at the vicinity of dumpsites across the sites**

| Sample | ZnUrineD | ZnBloodD | ZnNailsD | ZnHairD | ZnUrineR | ZnBloodR | ZnNailsR | ZnHairR | PbUrineD | PbBloodD | PbNailsD | PbHairD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ZnBloodD | 0.269 | 1 | | | | | | | | | | |
| ZnNailsD | 0.023 | 0.765** | 1 | | | | | | | | | |
| ZnHairD | 0.127 | 0.019 | 0.523* | 1 | | | | | | | | |
| ZnUrineRR | 1.000** | 0.269 | 0.023 | 0.128 | 1 | | | | | | | |
| ZnBloodRR | 0.269 | 1.000** | 0.765** | 0.019 | 0.269 | 1 | | | | | | |
| ZnNailsRR | 0.023 | 0.765** | 1.000** | 0.523* | 0.023 | 0.765** | 1 | | | | | |
| PbUrineD | 0.741** | 0.426* | 0.252 | 0.207 | 0.741** | 0.426* | 0.252 | 0.207 | 1 | | | |
| PbBloodD | 0.674** | 0.029 | -0.139 | 0.127 | 0.674** | 0.029 | -0.139 | 0.127 | 0.726** | 1 | | |
| PbNailsD | 0.185 | 0.916** | 0.730** | -0.114 | 0.185 | 0.916** | 0.730** | -0.114 | 0.369 | 0.004 | 1 | |
| PbHairD | 0.344 | -0.015 | 0.183 | 0.266 | 0.344 | -0.015 | 0.000 | 0.613 | 0.091 | 0.988 | 0.00 | 1 |
| PbUrineR | 0.621** | -0.249 | -0.341 | 0.217 | 0.621** | -0.249 | -0.341 | 0.217 | 0.736** | 0.789** | -0.324 | 0.533* |
| PbBloodR | 0.017 | 0.374 | 0.155 | -0.232 | 0.017 | 0.374 | 0.155 | -0.232 | 0.358 | 0.278 | 0.416 | 0.209 |
| PbHairR | -0.509* | -0.364 | -0.136 | -0.086 | -0.509* | -0.364 | -0.136 | -0.086 | -0.147 | 0.013 | -0.241 | 0.436* |
| CuUrineD | 0.422 | 0.064 | -0.232 | -0.012 | 0.421 | 0.064 | -0.232 | -0.012 | 0.007 | 0.169 | -0.104 | -0.348 |
| CuBloodD | 0.090 | 0.483* | 0.396 | 0.133 | 0.090 | 0.483* | 0.396 | 0.133 | 0.297 | 0.358 | 0.479* | 0.095 |
| CuNailsD | 0.172 | 0.584** | 0.549** | -0.129 | 0.172 | 0.584** | 0.549** | -0.129 | 0.353 | -0.145 | 0.717** | 0.386 |
| CuHairD | 0.148 | 0.094 | 0.244 | 0.318 | 0.149 | 0.094 | 0.244 | 0.318 | 0.493* | 0.246 | -0.013 | 0.650** |
| CuUrineR | -0.133 | 0.454* | 0.316 | -0.219 | -0.133 | 0.454* | 0.316 | -0.219 | -0.172 | -0.608** | 0.533* | -0.422 |
| CuBloodR | 0.108 | -0.021 | -0.024 | 0.288 | 0.108 | -0.021 | -0.024 | 0.288 | 0.332 | 0.151 | -0.114 | 0.222 |
| CuNailsR | -0.234 | -0.321 | 0.196 | 0.689** | -0.233 | -0.321 | 0.196 | 0.689** | -0.157 | -0.140 | -0.461* | 0.185 |
| CuHairR | -0.184 | -0.173 | -0.123 | -0.018 | -0.184 | -0.173 | -0.123 | -0.018 | 0.046 | 0.135 | -0.255 | 0.430* |
| CdUrineD | .0483* | 0.549** | 0.453* | 0.376 | 0.483* | 0.549** | 0.453* | 0.376 | 0.684** | 0.521* | 0.467* | 0.325 |
| CdBloodD | 0.282 | 0.147 | 0.175 | 0.147 | 0.283 | 0.147 | 0.175 | 0.147 | 0.297 | 0.446* | 0.227 | 0.501* |

**Table 4.39b Correlation matrices of metals in human tissues and dust particulates at the vicinity of dumpsites across the sites**

| Sample | ZnUrineD | ZnBloodD | ZnNailsD | ZnHairD | ZnUrineRR | ZnBloodRR | ZnNailsRR | ZnHairRR | PbUrineD | PbBloodD | PbNailsD | PbHairD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CdNailsD | 0.108 | 0.271 | 0.120 | 0.173 | 0.108 | 0.271 | 0.120 | 0.173 | 0.457* | 0.617** | 0.147 | 0.144 |
| CdHairD | 0.445* | 0.393 | 0.576** | 0.654** | 0.445* | 0.393 | 0.576** | 0.654** | 0.762** | 0.633** | 0.344 | 0.659** |
| CdUrineR | 0.290 | 0.450* | -0.020 | -0.558** | 0.290 | 0.450* | -0.020 | -0.558** | 0.349 | 0.198 | 0.546** | 0.107 |
| CdBloodR | 0.543** | 0.103 | -0.268 | -0.468* | 0.542** | 0.103 | -0.268 | -0.468* | 0.418 | 0.252 | 0.230 | 0.319 |
| CdNailsR | 0.063 | 0.541** | 0.239 | -0.405 | 0.063 | 0.541** | 0.239 | -0.405 | 0.357 | 0.044 | 0.631** | 0.268 |
| CdHairR | 0.278 | 0.308 | -0.069 | -0.430* | 0.278 | 0.308 | -0.069 | -0.430* | 0.118 | 0.184 | 0.353 | -0.038 |
| HgUrineD | 0.585** | 0.464* | 0.415 | 0.397 | 0.585** | 0.464* | 0.415 | 0.397 | 0.770** | 0.567** | 0.413 | 0.478* |
| HgBloodD | 0.464* | 0.199 | 0.213 | 0.278 | 0.464* | 0.199 | 0.213 | 0.278 | 0.689** | 0.504* | 0.167 | 0.807** |
| HgNailsD | 0.552** | 0.143 | -0.012 | 0.060 | 0.552** | 0.143 | -0.012 | 0.060 | 0.653** | 0.476* | 0.164 | 0.587** |
| HgHairD | 0.598** | 0.491* | 0.496* | 0.362 | 0.599** | 0.491* | 0.496* | 0.362 | 0.778** | 0.714** | 0.495* | 0.657** |
| HgUrineR | 0.555** | 0.338 | 0.186 | 0.260 | 0.555** | 0.338 | 0.186 | 0.260 | 0.664** | 0.633** | 0.258 | 0.413 |
| HgBloodR | 0.510* | 0.227 | 0.179 | 0.079 | 0.511* | 0.227 | 0.179 | 0.079 | 0.651** | 0.538** | 0.289 | 0.783** |
| HgNailsR | 0.630** | 0.441* | 0.266 | 0.005 | 0.630** | 0.441* | 0.266 | 0.005 | 0.689** | 0.506* | 0.498* | 0.529* |
| HgHairR | 0.536* | 0.365 | 0.465* | 0.426* | 0.536* | 0.365 | 0.465* | 0.426* | 0.676** | 0.685** | 0.397 | 0.709** |
| ZnDustD | -0.438* | -0.183 | -0.024 | -0.348 | -0.438* | -0.183 | -0.024 | -0.348 | -0.310 | -0.132 | 0.166 | 0.221 |
| PbDustD | 0.459* | 0.203 | 0.005 | -0.367 | 0.460* | 0.203 | 0.005 | -0.367 | 0.366 | 0.420 | 0.434* | 0.478* |
| CuDustD | 0.056 | -0.177 | 0.378 | 0.880** | 0.056 | -0.177 | 0.378 | 0.880** | 0.127 | -0.013 | -0.224 | 0.405 |
| CdDustD | 0.350 | -0.039 | -0.145 | -0.203 | 0.350 | -0.039 | -0.145 | -0.203 | 0.336 | 0.237 | 0.228 | 0.206 |
| HgDustD | -0.401 | -0.293 | -0.135 | -0.078 | -0.401 | -0.293 | -0.135 | -0.078 | -0.145 | -0.330 | -0.125 | -0.007 |
| ZnDustR | 0.387 | 0.074 | -0.057 | -0.197 | 0.387 | 0.074 | -0.057 | -0.197 | 0.205 | 0.470* | 0.159 | 0.182 |
| PbDustR | 0.705** | -0.055 | -0.128 | -0.078 | 0.705** | -0.055 | -0.128 | -0.078 | 0.275 | 0.349 | 0.097 | 0.224 |
| CuDustR | 0.445* | 0.118 | 0.141 | 0.558** | 0.445* | 0.118 | 0.141 | 0.558** | 0.318 | 0.326 | -0.188 | 0.043 |
| CdDustR | 0.289 | -0.270 | -0.073 | 0.061 | 0.289 | -0.270 | -0.073 | 0.060 | 0.241 | 0.209 | 0.009 | 0.506* |
| HgDustR | -0.304 | 0.080 | 0.283 | 0.411 | -0.304 | 0.079 | 0.283 | 0.411 | -0.096 | 0.151 | 0.007 | -0.174 |

**Table 4.39c Correlation matrices of metals in human tissues and dust particulates at the vicinity of dumpsites across the sites (continued)**

| Sample | PbUrineR | PbBloodR | PbNailsR | PbHairR | CuUrineD | CuBloodD | CuNailsD | CuHairD | CuUrineR | CuBloodR | CuNailsR | CuHairR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PbUrineR | 1 | | | | | | | | | | | |
| PbBloodR | 0.054 | 1 | | | | | | | | | | |
| PbHairR | -0.024 | 0.486* | 0.070 | 1 | | | | | | | | |
| CuUrineD | 0.169 | -0.155 | -0.042 | -0.579** | 1 | | | | | | | |
| CuBloodD | 0.065 | 0.010 | -0.081 | -0.206 | 0.186 | 1 | | | | | | |
| CuNailsD | -0.226 | 0.430* | -0.174 | 0.104 | -0.375 | 0.016 | 1 | | | | | |
| CuHairD | 0.395 | 0.063 | 0.203 | 0.316 | -0.389 | 0.201 | 0.350 | 1 | | | | |
| CuUrineR | -0.535* | 0.166 | -0.107 | -0.347 | 0.170 | -0.075 | 0.510* | -0.371 | 1 | | | |
| CuBloodR | 0.442* | 0.357 | 0.478* | 0.096 | 0.397 | 0.014 | -0.056 | 0.097 | 0.182 | 1 | | |
| CuNailsR | 0.011 | -0.144 | 0.716** | 0.386 | -0.368 | -0.339 | -0.120 | 0.459* | -0.377 | 0.016 | 1 | |
| CuHairR | 0.169 | 0.248 | -0.014 | 0.650** | -0.126 | 0.145 | 0.093 | 0.697** | -0.390 | 0.202 | 0.349 | 1 |
| CdUrineD | 0.419 | 0.200 | 0.223 | -0.302 | 0.372 | 0.774** | 0.192 | 0.343 | 0.053 | 0.479* | -0.227 | 0.127 |
| CdBloodD | 0.237 | 0.005 | -0.112 | 0.032 | 0.324 | 0.704** | 0.095 | 0.215 | -0.187 | 0.217 | -0.266 | 0.353 |
| CdNailsD | 0.429* | 0.267 | 0.131 | 0.039 | 0.153 | 0.782** | -0.251 | 0.334 | -0.392 | 0.269 | -0.119 | 0.336 |
| CdHairD | 0.504* | 0.309 | 0.554** | 0.054 | -0.083 | 0.453* | 0.205 | 0.452* | -0.288 | 0.369 | 0.198 | 0.092 |
| CdUrineR | 0.084 | 0.279 | -0.635** | -0.218 | 0.345 | 0.516* | 0.387 | -0.015 | 0.369 | 0.177 | -0.848** | 0.087 |
| CdBloodR | 0.343 | 0.180 | -0.542** | -0.191 | 0.371 | 0.029 | 0.389 | -0.031 | 0.298 | 0.303 | -0.679** | 0.006 |
| CdNailsR | -0.062 | 0.682** | -0.343 | 0.215 | -0.008 | 0.317 | 0.715** | 0.246 | 0.469* | 0.320 | -0.461* | 0.363 |
| CdHairR | -0.036 | 0.177 | -0.591** | -0.180 | 0.496* | 0.512* | 0.289 | 0.031 | 0.270 | 0.051 | -0.575** | 0.309 |
| HgUrineD | 0.535* | 0.017 | 0.168 | -0.352 | 0.251 | 0.724** | 0.214 | 0.444* | -0.064 | 0.357 | -0.213 | 0.070 |
| HgBloodD | 0.580** | 0.220 | 0.159 | 0.140 | 0.159 | 0.392 | 0.304 | 0.598** | -0.196 | 0.561** | -0.041 | 0.490* |
| HgNailsD | 0.614** | 0.215 | 0.016 | -0.100 | 0.403 | 0.247 | 0.175 | 0.160 | 0.032 | 0.685** | -0.400 | 0.102 |
| HgHairD | 0.425* | 0.521* | 0.248 | 0.086 | 0.012 | 0.407 | 0.404 | 0.346 | -0.192 | 0.261 | -0.015 | 0.135 |
| HgUrineR | 0.570** | 0.148 | 0.101 | -0.235 | 0.512* | 0.702** | 0.039 | 0.311 | -0.114 | 0.540** | -0.295 | 0.240 |

**Table 4.39d Correlation matrices of metals in human tissues and dust particulates at the vicinity of dumpsites across the sites (continued)**

| Sample | PbUrineR | PbBloodR | PbNailsR | PbHairR | CuUrineD | CuBloodD | CuNailsD | CuHairD | CuUrineR | CuBloodR | CuNailsR | CuHairR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HgBloodR | 0.493* | 0.041 | -0.178 | 0.019 | 0.069 | 0.539** | 0.356 | 0.542** | -0.239 | 0.188 | -0.257 | 0.372 |
| HgNailsR | 0.410 | -0.094 | -0.261 | -0.383 | 0.128 | 0.574** | 0.303 | 0.250 | -0.087 | -0.005 | -0.516* | -0.117 |
| HgHairR | 0.404 | 0.417 | 0.272 | 0.148 | 0.042 | 0.429* | 0.337 | 0.338 | -0.250 | 0.275 | 0.041 | 0.201 |
| ZnDustD | -0.365 | 0.174 | -0.357 | 0.538** | -0.509* | -0.022 | 0.194 | -0.277 | -0.013 | -0.332 | -0.215 | -0.046 |
| PbDustD | 0.124 | 0.429* | -0.513* | 0.148 | 0.045 | 0.141 | 0.548** | -0.021 | 0.082 | -0.047 | -.485* | 0.087 |
| CuDustD | 0.206 | -0.196 | 0.865** | 0.084 | -0.111 | -0.201 | -0.065 | 0.193 | -0.151 | 0.384 | .662** | -0.078 |
| CdDustD | 0.269 | 0.346 | -0.204 | -0.044 | 0.027 | -0.168 | 0.360 | -0.284 | 0.377 | 0.283 | -0.443* | -0.377 |
| HgDustD | -0.034 | -0.089 | -0.097 | 0.217 | -0.394 | -0.016 | 0.219 | 0.292 | 0.270 | 0.082 | 0.089 | 0.193 |
| ZnDustR | 0.145 | -0.267 | -0.451* | -0.224 | -0.109 | 0.256 | -0.106 | -0.090 | -0.488* | -0.676** | -0.324 | -0.277 |
| PbDustR | 0.254 | -0.277 | -0.343 | -0.429* | 0.173 | -0.130 | 0.161 | -0.222 | -0.039 | -0.310 | -0.319 | -0.469* |
| CuDustR | 0.370 | 0.126 | 0.667** | -0.195 | 0.441* | -0.175 | -0.277 | 0.048 | -0.221 | 0.446* | 0.398 | -0.023 |
| CdDustR | 0.251 | 0.205 | -0.008 | 0.248 | -0.243 | -0.368 | 0.388 | -0.045 | 0.072 | 0.124 | 0.011 | -0.161 |
| HgDustR | -0.123 | 0.425* | 0.591** | 0.321 | -0.132 | 0.079 | -0.293 | -0.178 | -0.198 | 0.128 | 0.401 | -0.038 |

**Table 4.39e Correlation matrices of metals in human tissues and dust particulates at the vicinity of dumpsites across the sites continued**

| Sample | CdUrineD | CdBloodD | CdNailsD | CdHairD | CdUrineR | CdBloodR | CdNailsR | CdHairR | HgUrineD | HgBloodD | HgNailsD | HgHairD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CdUrineD | 1 | | | | | | | | | | | |
| CdBloodD | 0.674** | 1 | | | | | | | | | | |
| CdNailsD | 0.704** | 0.449* | 1 | | | | | | | | | |
| CdHairD | 0.734** | 0.469* | 0.547** | 1 | | | | | | | | |
| CdUrineR | 0.513* | 0.535* | 0.285 | 0.012 | 1 | | | | | | | |
| CdBloodR | 0.295 | 0.409 | -0.118 | -0.019 | 0.789** | 1 | | | | | | |
| CdNailsR | 0.438* | 0.359 | 0.211 | 0.151 | 0.779** | 0.584** | 1 | | | | | |
| CdHairR | 0.464* | 0.612** | 0.257 | -0.101 | 0.817** | 0.616** | 0.651** | 1 | | | | |
| HgUrineD | 0.946** | 0.673** | 0.614** | 0.757** | 0.477* | 0.352 | 0.324 | 0.363 | 1 | | | |
| HgBloodD | 0.717** | 0.735** | 0.407 | 0.683** | 0.437* | 0.510* | 0.482* | 0.338 | 0.764** | 1 | | |
| HgNailsD | 0.638** | 0.615** | 0.255 | 0.504* | 0.587** | 0.756** | 0.450* | 0.336 | 0.677** | 0.847** | 1 | |
| HgHairD | 0.692** | 0.550** | 0.442* | 0.889** | 0.240 | 0.237 | 0.385 | 0.200 | 0.678** | 0.686** | 0.544** | 1 |
| HgUrineR | 0.936** | 0.788** | 0.687** | 0.655** | 0.573** | 0.455* | 0.398 | 0.536* | 0.905** | 0.818** | 0.786** | 0.656** |
| HgBloodR | 0.661** | 0.823** | 0.372 | 0.566** | 0.583** | 0.585** | 0.454* | 0.474* | 0.784** | 0.891** | 0.744** | 0.631** |
| HgNailsR | 0.641** | 0.628** | 0.323 | 0.516* | 0.622** | 0.562** | 0.302 | 0.358 | 0.803** | 0.636** | 0.661** | 0.555** |
| HgHairR | 0.678** | 0.680** | 0.409 | 0.877** | 0.205 | 0.229 | 0.327 | 0.219 | 0.671** | 0.736** | 0.569** | 0.973** |
| ZnDustD | -0.366 | 0.175 | -0.248 | -0.130 | 0.085 | 0.049 | 0.143 | -0.049 | -0.327 | -0.134 | -0.098 | -0.013 |
| PbDustD | 0.229 | 0.545** | -0.070 | 0.200 | 0.600** | 0.716** | 0.579** | 0.585** | 0.251 | 0.427* | 0.482* | 0.572** |
| CuDustD | 0.122 | 0.053 | -0.154 | 0.536* | -0.595** | -0.300 | -0.398 | -0.595** | 0.185 | 0.291 | 0.187 | 0.267 |
| CdDustD | 0.125 | 0.088 | -0.236 | 0.114 | 0.360 | 0.650** | 0.341 | 0.174 | 0.155 | 0.151 | 0.471* | 0.284 |

**Table 4.39f Correlation matrices of metals in human tissues and dust particulates across the sites continued**

| Sample | CdUrineD | CdBloodD | CdNailsD | CdHairD | CdUrineR | CdBloodR | CdNailsR | CdHairR | HgUrineD | HgBloodD | HgNailsD | HgHairD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HgDustD | -0.064 | -0.120 | -0.083 | -0.240 | 0.064 | 0.055 | 0.208 | 0.060 | -0.022 | -0.057 | -0.123 | -0.362 |
| ZnDustR | -0.035 | 0.217 | 0.104 | 0.112 | 0.113 | 0.066 | -0.274 | 0.027 | 0.148 | -0.054 | -0.041 | 0.213 |
| PbDustR | 0.000 | 0.198 | -0.382 | 0.057 | 0.163 | 0.517* | -0.168 | 0.154 | 0.186 | 0.078 | 0.271 | 0.251 |
| CuDustR | 0.248 | -0.094 | 0.166 | 0.440* | -0.373 | -0.193 | -0.283 | -0.276 | 0.167 | 0.210 | 0.202 | 0.369 |
| CdDustR | -0.084 | 0.119 | -0.439* | 0.207 | -0.018 | 0.433* | 0.110 | -0.072 | 0.020 | 0.220 | 0.334 | 0.343 |
| HgDustR | 0.031 | -0.166 | 0.360 | 0.353 | -0.500* | -0.693** | -0.213 | -0.399 | -0.159 | -0.241 | -0.332 | 0.253 |

| Sample | HgUrineR | HgBloodR | HgNailsR | HgHairR | ZnDustD | PbDustD | CuDustD | CdDustD | HgDustD | ZnDustR | PbDustR | CuDustR | CdDustR | HgDustR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HgUrineR | 1 | | | | | | | | | | | | | |
| HgBloodR | 0.764** | 1 | | | | | | | | | | | | |
| HgNailsR | 0.677** | 0.847** | 1 | | | | | | | | | | | |
| HgHairR | 0.678** | 0.686** | 0.544** | 1 | | | | | | | | | | |
| ZnDustD | -0.332 | 0.061 | 0.013 | 0.071 | 1 | | | | | | | | | |
| PbDustD | 0.327 | 0.588** | 0.495* | 0.590** | 0.457* | 1 | | | | | | | | |
| CuDustD | 0.077 | 0.052 | -0.053 | 0.356 | -0.110 | -0.258 | 1 | | | | | | | |
| CdDustD | 0.141 | 0.178 | 0.235 | 0.258 | 0.297 | 0.621** | 0.002 | 1 | | | | | | |
| HgDustD | -0.153 | -0.025 | -0.186 | -0.340 | 0.124 | -0.124 | -0.062 | 0.260 | 1 | | | | | |
| ZnDustR | 0.037 | 0.312 | 0.564** | 0.205 | 0.293 | 0.338 | -0.261 | -0.038 | -0.429* | 1 | | | | |
| PbDustR | 0.092 | 0.324 | 0.509* | 0.268 | 0.133 | 0.587** | 0.024 | 0.542** | -0.215 | 0.608** | 1 | | | |
| CuDustR | 0.272 | -0.107 | -0.110 | 0.329 | -0.653** | -0.254 | 0.495* | -0.204 | -0.615** | -0.183 | -0.051 | 1 | | |
| CdDustR | -0.037 | 0.234 | 0.127 | 0.390 | 0.439* | 0.619** | 0.340 | 0.821** | 0.213 | 0.031 | 0.604** | -0.136 | 1 | |
| HgDustR | -0.095 | -0.446* | -0.462* | 0.232 | 0.056 | -0.285 | 0.285 | -0.190 | -0.275 | -0.163 | -0.455* | 0.424* | -0.142 | 1 |

## 4.12 Performance of Bismuth Electrode in Electrochemical Analysis

### 4.12.1 Detection limit and SWV

The detection limits of the metal using bismuth working electrode were 0.181, 0.058, 0.082, 0.017 and 1.479 µM for Cd, Cu, Hg, Pb and Zn, respectively, as presented in Figure 4.61. The voltammograms of the standard solutions of lead in 100mM $NaNO_3$ solutions of the supporting electrolytes on the Bi working electrode was presented in Figure 4.62. The repeatability of the peaks were studied at various concentrations for all the heavy metals using standard solution of cadmium (30mM) as presented in Figure 4.60. The peak currents for 0.2, 0.6 and 0.8µM were 7.0, 9.0 and 10µA recorded at -0.25V as shown in the Figure.

### 4.12.2: Linearity of calibration curve

The calibration plots of the analysed metal ions (Pb, Cu, Cd, Hg, and Zn) were obtained by the square wave technique as presented in appendices LVIII the regression coefficients ($R^2$) revealed values of 0.96, 0.75, 0.92 and 0.80 for Cd, Cu, Pb and Hg, respectively. Studies were also conducted in the presence of 0.03M concentration of NaOH and the supporting electrolyte to confirm the presence of peak due to the hydrogen ion which was noted at -0.4V while bismuth reduction was recorded at -1.0 to -1.2V, respectively.

### 4.12.3: Percentage recovery

Table 4.26 shows the percentage recoveries of the metal ions using bismuth working electrode, Ag/AgCl reference electrode for SWV electrochemical technique.

**Table 4.40: The limit of detection of the analysed metal-ions by the ICP-OES technique**

| Metal | Detection limit (ppm) |
|---|---|
| Cu | 0.005±0.001 |
| Pb | 0.029±0.020 |
| Zn | 0.033±0.011 |
| Cd | 0.027±0.011 |
| Hg | 0.570±0.030 |

The percentage recoveries of Zn, Pb, Hg, Cu and Cd in the analysed water samples by the square wave stripping voltammetry using bismuth working electrode were 22.22, 66.67, 106.06, 98.73 and 95.00% , respectively.

**4.13: Comparative Studies of Heavy matals in Water By ICP-OES and SWV Techniques**

4.13.1: Concentration of metals in water by ICP-OES technique

The concentrations of heavy metal ions as recorded by the ICP-OES analytical method range from 0.036 (G) to 0.617 (O), 0.111 (H) to 1.156 (K), 0.001 (H) to 2.314 (O), 0.003 (G) to 0.048 (K), 0.109 (H) to 0.545 (N) for Cu, Pb, Zn, Cd and Hg, respectively, as presented in Figure 4.62. These concentrations were compared with those recorded by the square wave stripping (SWV) and were presented in Table 4.27.

Furthermore, the detection limits of Cu, Pb, Zn, Cd, and Hg of the ICP –OES used for the analysis were 0.005, 0.029, 0.033, 0.027 and 0.570 ppm, respectively as presented in Table 4.28.

4.13.2: Concentration of metals in water by SWV technique

Figure 4.65 shows that most of the soluble fractions of the water samples were lead, cadmium and copper at potentials -0.1, -0.35, 0.25V, respectively. Copper metal ion was predominantly found at I and G mine water samples with concentrations of 0.27 and 0.55 ppm, respectively, as presented in Table 4.42.

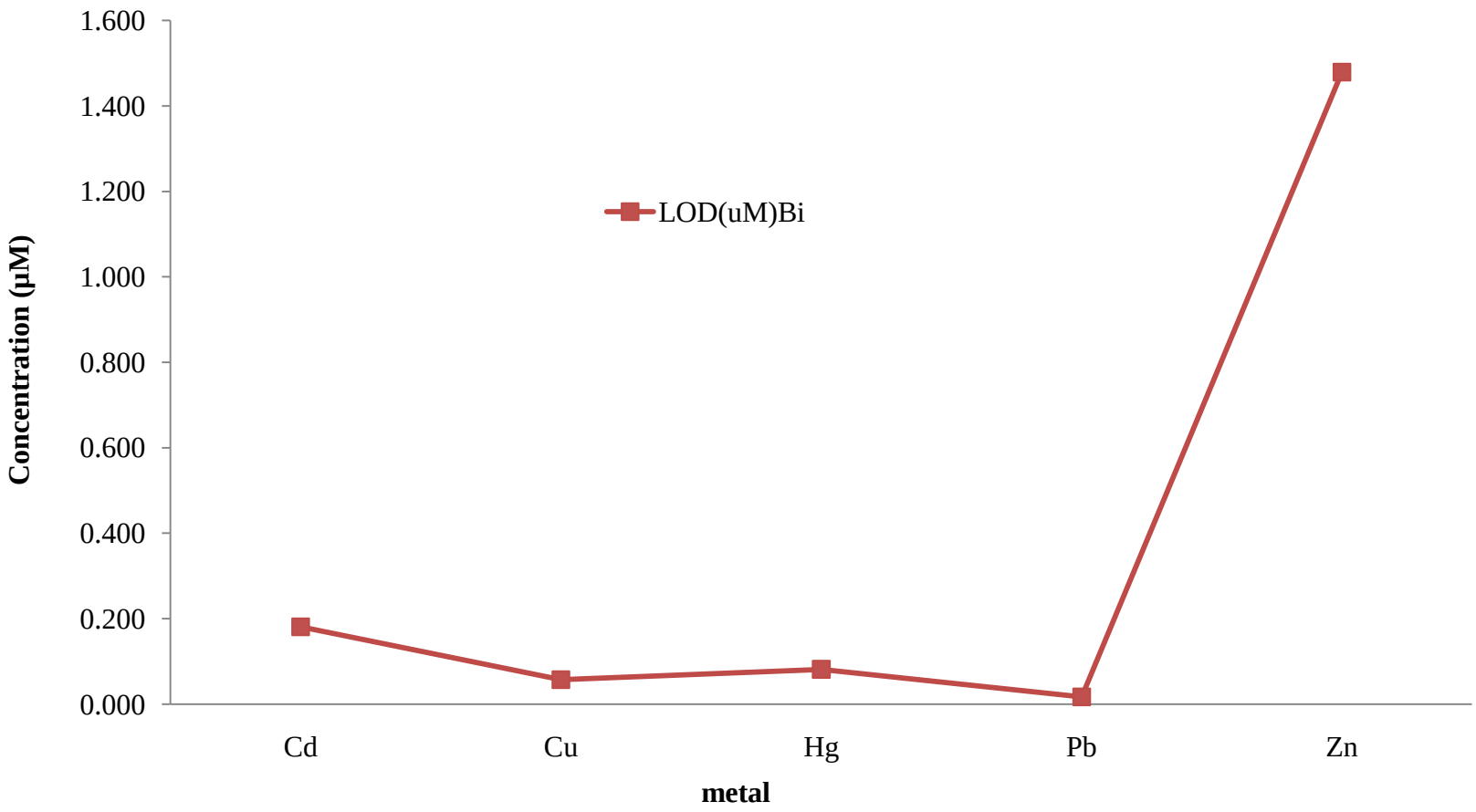


**Figure 4.61: Detection limits of the analysed metals for bismuth (Bi) working electrode**

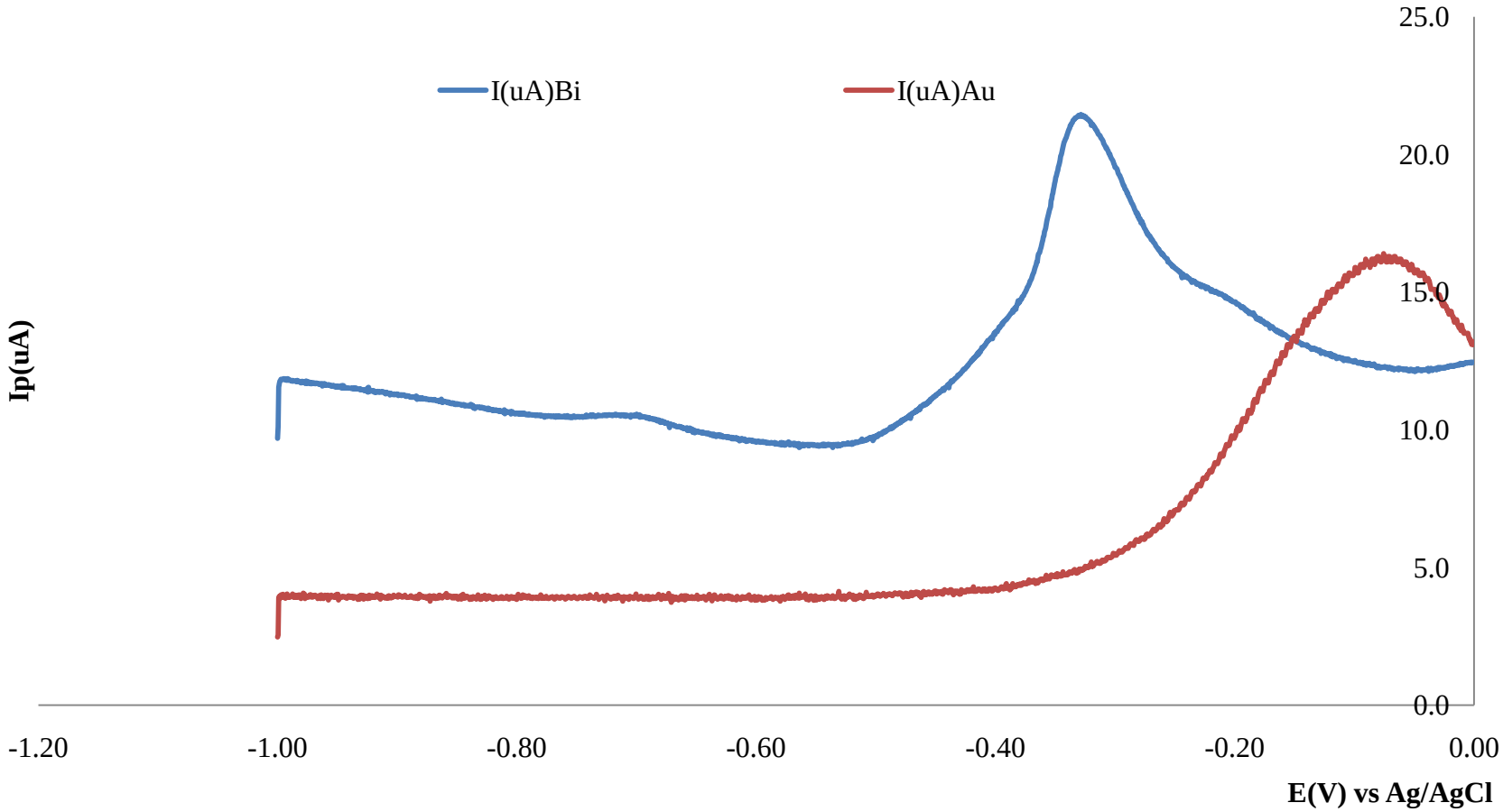


**Figure 4.62: comparative voltammograms of the standard solutions of lead in 100mM $NaNO_3$ solutions of the supporting electrolytes, the scan parameters wchere as follows; Estart = -1.0V, Efinal= +1.0V, pulse amplitude = 0.01V, SWV-frequency =80Hz, Estep = 0**

**Table 4.41: Percentage recoveries of metals using bismuth working electrode, Ag/AgCl reference and platinum counter electrode by SQWV technique**

| Metals (1µM) | spiked(µA) | unspiked(µA) | PRBLAG1.02 | spiked(µA) | Recovery |
|---|---|---|---|---|---|
| Zn | 0.02 ± 0.01 | 0.09 ± 0.01 | BDL | 0.02 ± 0.01 | 22.22 |
| Pb | 0.02 ± 0.02 | 0.03 ± 0.01 | BDL | 0.02 ± 0.01 | 66.67 |
| Hg | 9.80 ± 0.05 | 9.24 ± 0.06 | BDL | 9.80 ± 0.02 | 106.06 |
| Cu | 0.80 ± 0.02 | 0.79 ± 0.02 | 0.02± | 0.78 ± 0.04 | 98.73 |
| Cd | 0.19 ± 0.04 | 0.20 ± 0.02 | BDL | 0.19 ± 0.02 | 95.00 |

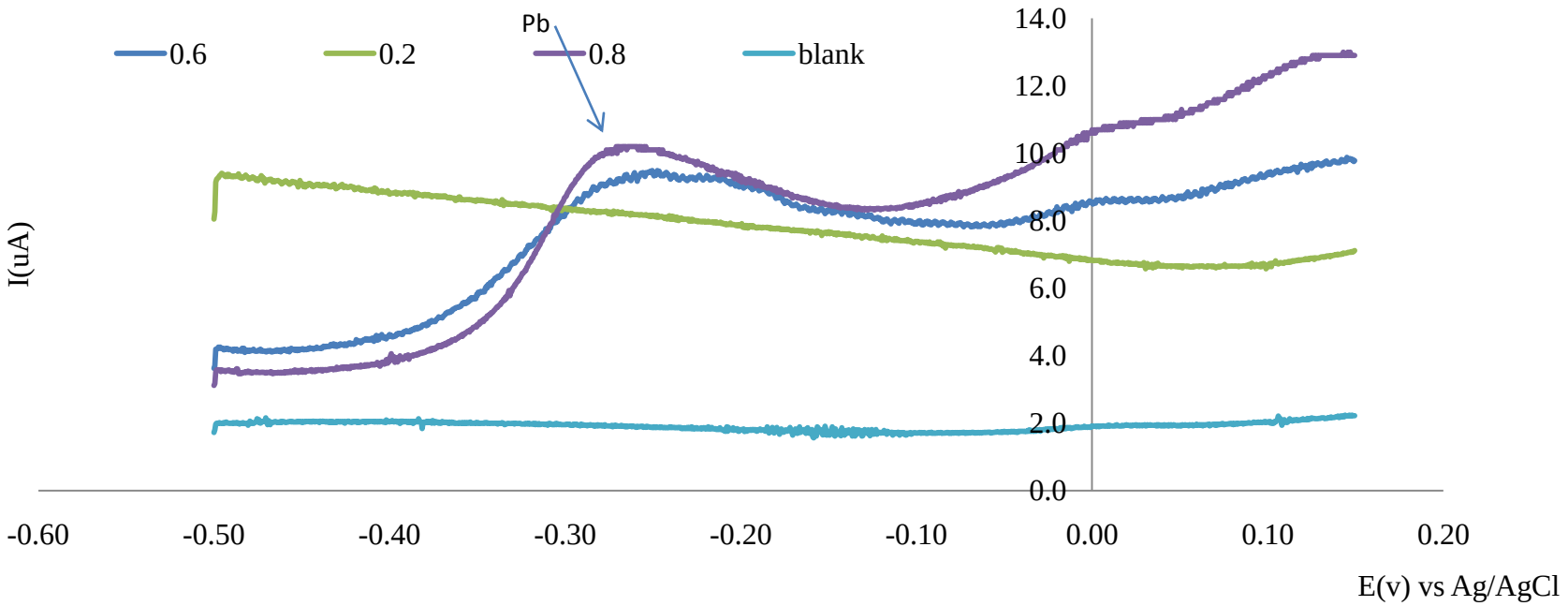


**Figure 4.63: The voltammogramm showing an increasing peak current with increase in the analyte concentration**

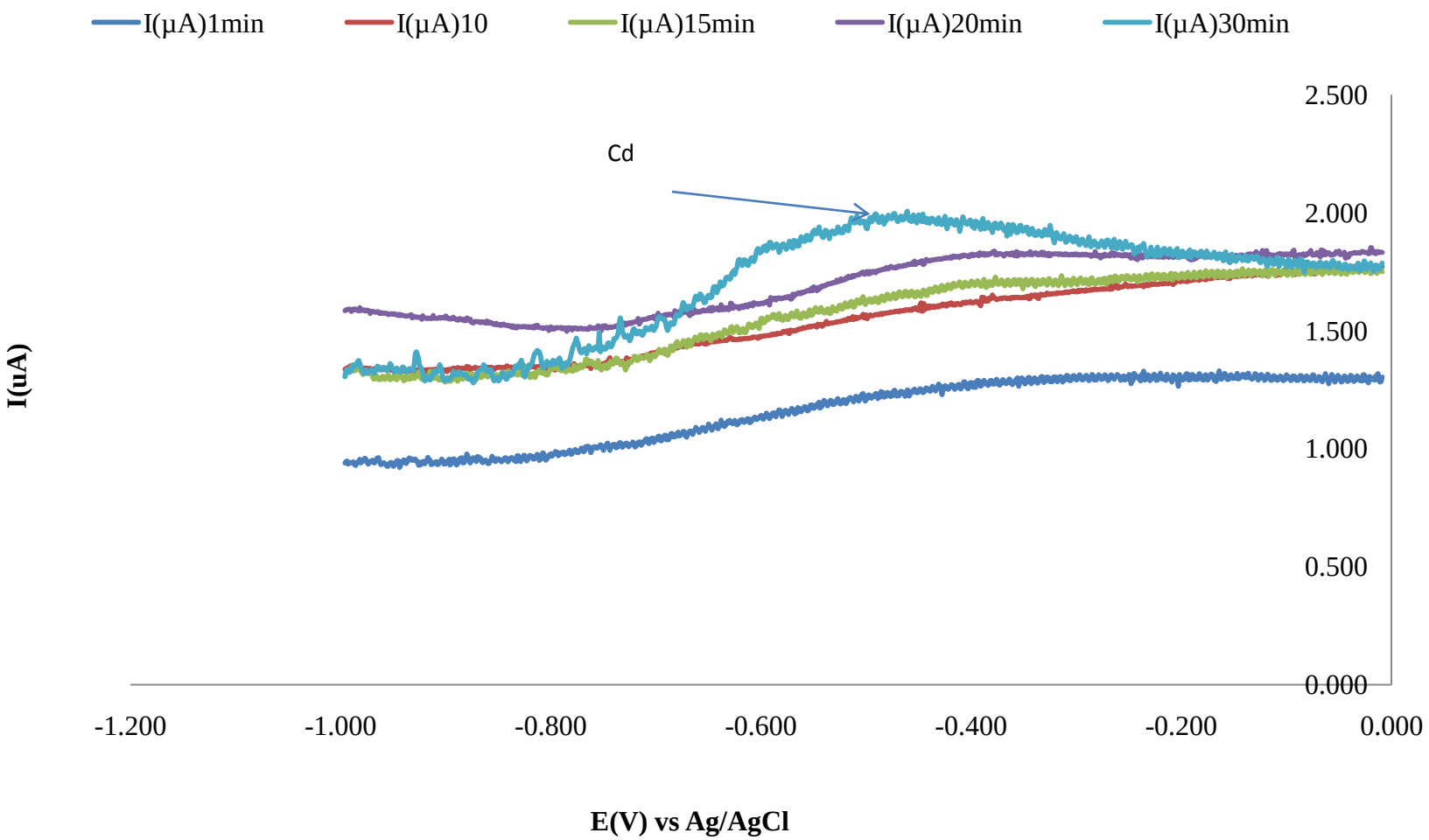


**Figure 4.64: Kinetic studies of cadmium concentrations at different deposition time (1, 10, 15, 20, and 30minutes respectively). Estart = -1.0V, Eend = 0, pulse amaplitude = 0.01V, SQRWV freq = 80V, Estep =0.01V and the current range is 10µA.**

**Table 4.42: Comparative studies of metal concentrations of the polluted water in ppm**

| Analytical method | samples | Cu | Pb | Zn | Cd | Hg |
|---|---|---|---|---|---|---|
| ICP-OES | F | 0.040 ± 0.002 | 0.131 ± 0.005 | 0.003 ± 0.012 | 0.005 ± 0.001 | 0.126 ± 0.017 |
| SWV | | BDL | 0.57±0.10 | BDL | 3.19±0.50 | BDL |
| ICP-OES | G | 0.036±0.037 | 0.204±0.029 | 0.003±0.018 | 0.003±0.008 | 0.135±0.295 |
| SWV | | 0.27±0.01 | 0.26±0.10 | BDL | BDL | BDL |
| ICP-OES | H | 0.042±0.001 | 0.111±0.027 | 0.001±0.009 | 0.005±0.012 | 0.109±0.017 |
| SWV | | BDL | BDL | BDL | BDL | BDL |
| ICP-OES | I | 0.041±0.004 | 0.202±0.024 | 0.004±0.012 | 0.005±0.008 | 0.115±0.016 |
| SWV | | 0.55±0.01 | 0.54±0.02 | BDL | BDL | BDL |
| ICP-OES | J | 0.053±0.044 | 0.346±0.017 | 0.211±0.022 | 0.011±0.003 | 0.428±0.221 |
| SWV | | 0.62±0.10 | BDL | BDL | BDL | BDL |
| ICP-OES | K | 0.351±0.007 | 1.156±0.043 | 2.163±0.014 | 0.048±0.011 | 0.758±0.037 |
| SWV | | BDL | BDL | BDL | BDL | BDL |
| ICP-OES | L | 0.038±0.009 | 0.118±0.018 | 0.005±0.019 | 0.006±0.009 | 0.191±0.017 |
| SWV | | BDL | BDL | BDL | BDL | BDL |
| ICP-OES | M | 0.325±0.007 | 1.007±0.016 | 2.102±0.018 | 0.042±0.008 | 0.517±0.406 |
| SWV | | BDL | BDL | BDL | BDL | BDL |
| ICP-OES | N | 0.056±0.001 | 0.471±0.059 | 0.162±0.06 | 0.016±0.016 | 0.545±0.016 |
| SWV | | BDL | 0.15±0.10 | BDL | BDL | BDL |
| ICP-OES | O | 0.617±0.006 | 0.965±0.048 | 2.314±0.016 | 0.043±0.013 | 0.45±0.014 |
| SWV | | BDL | BDL | BDL | BDL | BDL |
| Standard | S | 1.5 | 0.001 | 5 | 0.003 | 0.001 |

Key: F= TBUP1.02, G=INT1.03, H=TBUP.01, I = TBDNSTR.02, J = END1.01, K = UP1.02, L= INT1.01, M = PRBLAG1.02, N = END1.02, O = LAG3B.03, S = standard

**Table 4.43 Correlations of spectroscopic and electro-analytical methods in water samples**

| Metals | ICPCu | ICPPb | ICPZn | ICPCd | ICPHg | SWVCu | SWVPb | SWVZn | SWVCd | SWVHg |
|---|---|---|---|---|---|---|---|---|---|---|
| ICPCu | 1 | | | | | | | | | |
| ICPPb | 0.867** | 1 | | | | | | | | |
| ICPZn | 0.943** | 0.967** | 1 | | | | | | | |
| ICPCd | 0.903** | 0.991** | 0.985** | 1 | | | | | | |
| ICPHg | 0.600** | 0.872** | 0.740** | 0.837** | 1 | | | | | |
| SWVCu | -0.365 | -0.321 | -0.375 | -0.390 | -0.230 | 1 | | | | |
| SWVPb | -0.430 | -0.475* | -0.478* | -0.500* | -0.542* | 0.290 | 1 | | | |
| SWVZn | .a | .a | .a | .a | .a | .a | .a | | | |
| SWVCd | -0.207 | -0.288 | -0.234 | -0.252 | -0.319 | -0.204 | 0.639** | .a | 1 | |
| SWVHg | .a | .a | .a | .a | .a | .a | .a | .a | .a | .a |

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

a. Cannot be computed because at least one of the variables is constant.

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

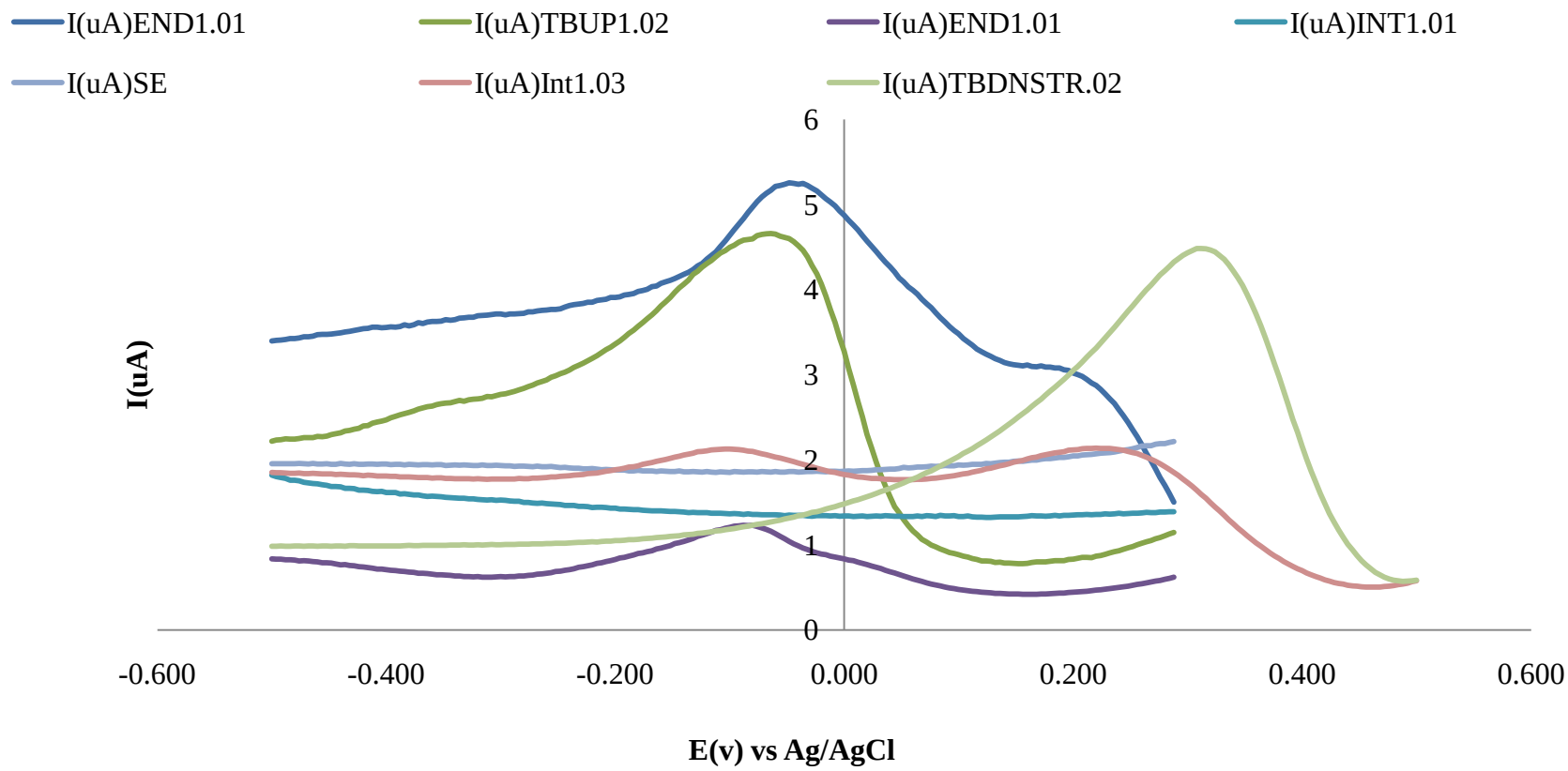


**Figure 4.65: The SWV voltamogramms of the water samples detected using bismuth working electrode, Ag/AgCl reference and platinum counter ; the scan parameters were $E_{start}$= -0.6v, $E_{final}$ = +0.6v, swv-frequency = 15hz**

4.13.3 Correlation matrices of metals in water by ICP-OES and SWV

The correlation analysis of metals by spectroscopic and (AAS) and Electro-analytical methods (SWV) are presented in Table 4.43. The correlation coefficients of 0.867, 0.943, 0.903 and 0.600 were recorded for ICPCu Vs ICPPb, ICPZn, ICPCd and ICPHg, respectively. The correlation coefficients for ICPZn Vs ICPHg, Vs ICPCd and ICPHg were 0.985, and 0.740, respectively, as presented in the Table. The correlation coefficient 0.837 was recorded for ICPCd Vs ICPHg. Similarly, the correlation coefficients of 0.290 and 0.639 were recorded for SWVCu Vs SWVPb and SWVPb Vs SWVCd, respectively, as presented in the Table.

## 4.14 Electrochemical Atomic Force, Tunneling, and Optical Microscopic Studies of the Bismuth Surface

4.14.1 Atomic force microscope (AFM) images

The surface area exhibited by the image was $101\mu m^{2,}$ surface area difference of 0.971% and root mean square (Rq) of 38.1nm as presented in Figures 4.64a and b, respectively.

4.14.2 Tunnelling electron microscope (TEM) images

Bismuth electrode untreated with the supporting electrolyte(0.1M $NaNO_3$) revealing clearly the interphase between the electrolytic material and the glass as shown in Figures 4.65a and b, respectively.

4.14.3 The optical microscope (OPM) images

Images of the electrode before (a) and after being treated (b, c) with the supporting electrolyte are presented in Figure 4.66

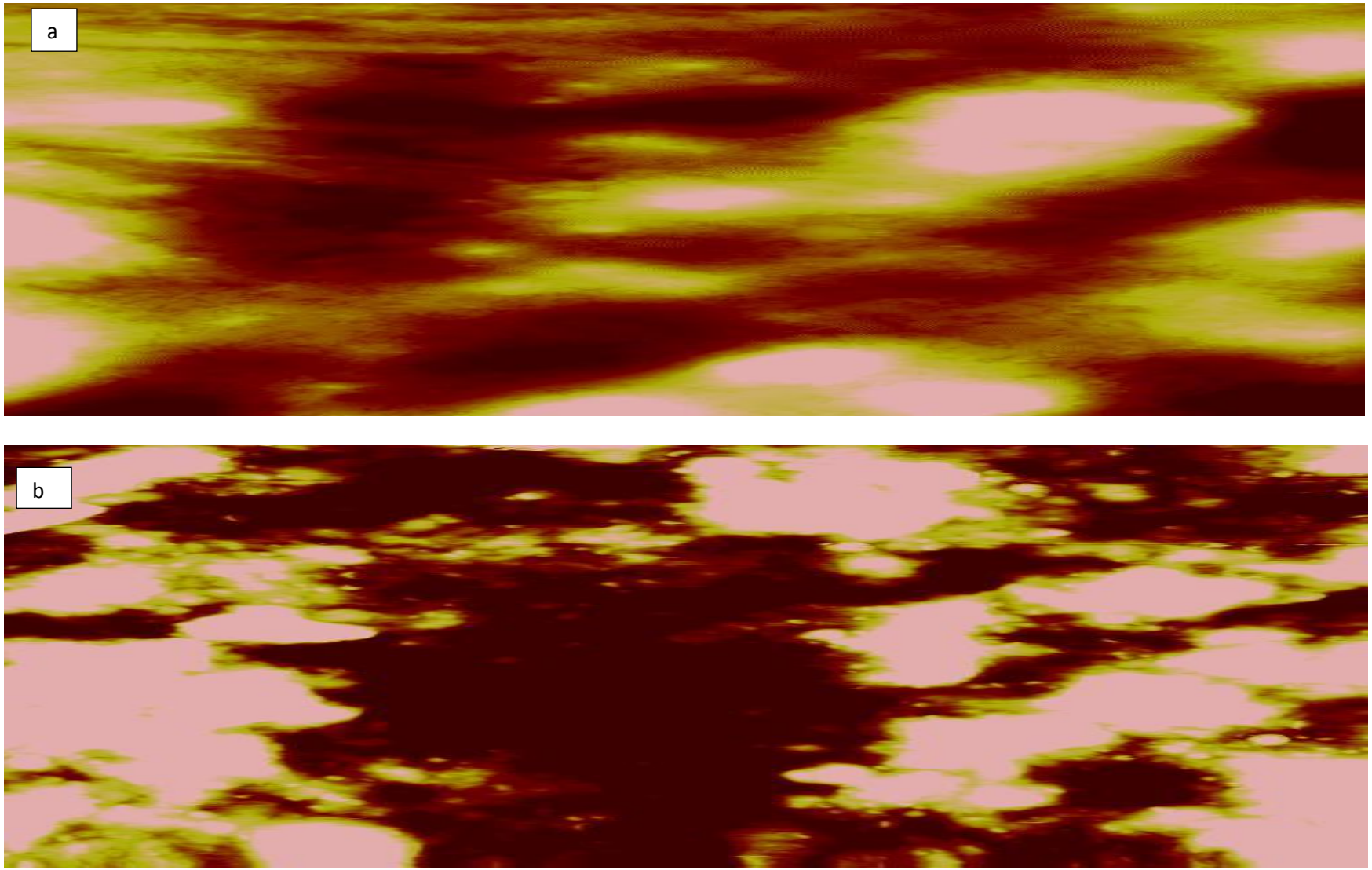


**Figure 4.66: The atomic force microscopic images of bismuth electrode surface before (a) and after (b) the electro-analysis**

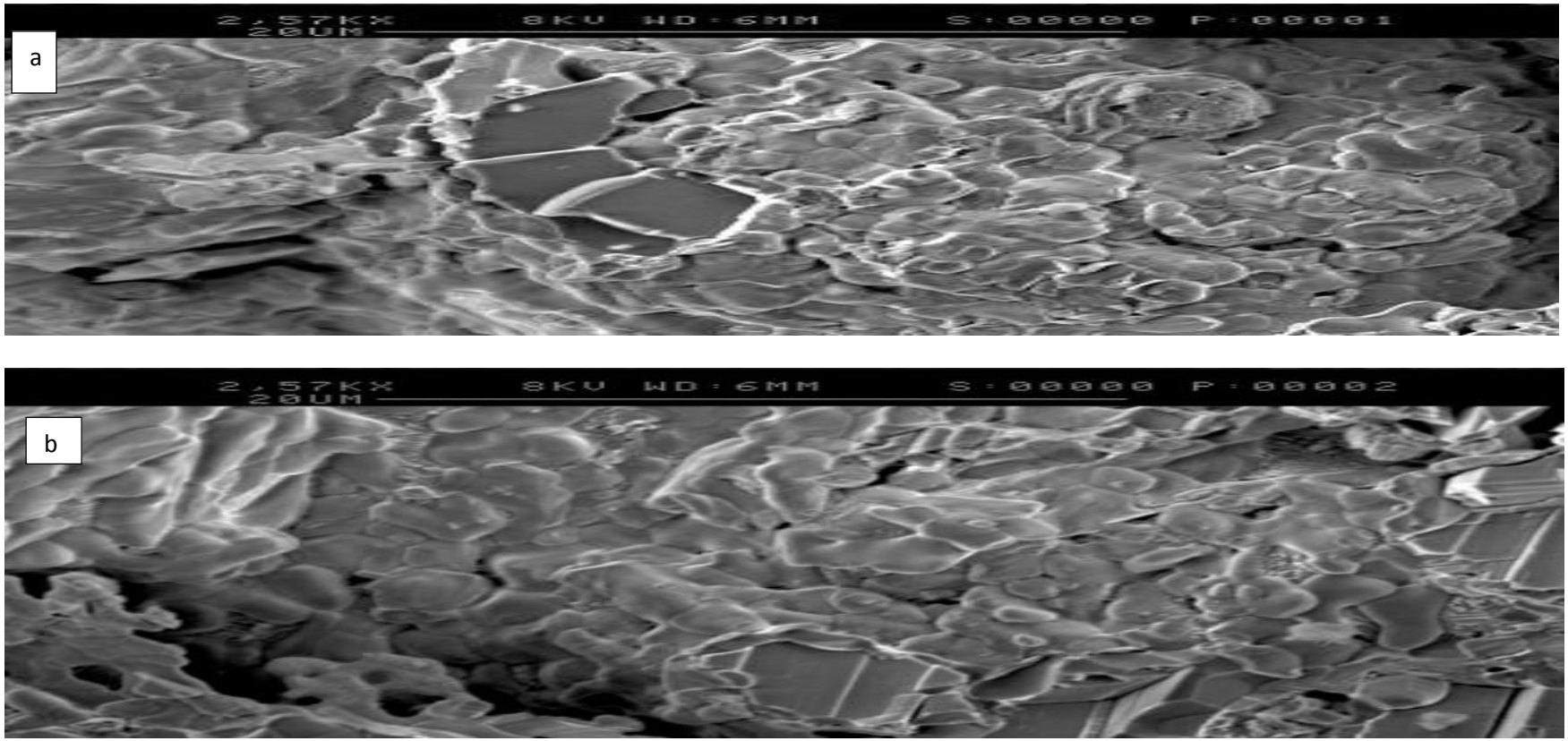


**Figure 4.67: The tunnelling electron microscope (TEM) image of the bismuth electrode surface before (a) and after the electro-analysis(b)**

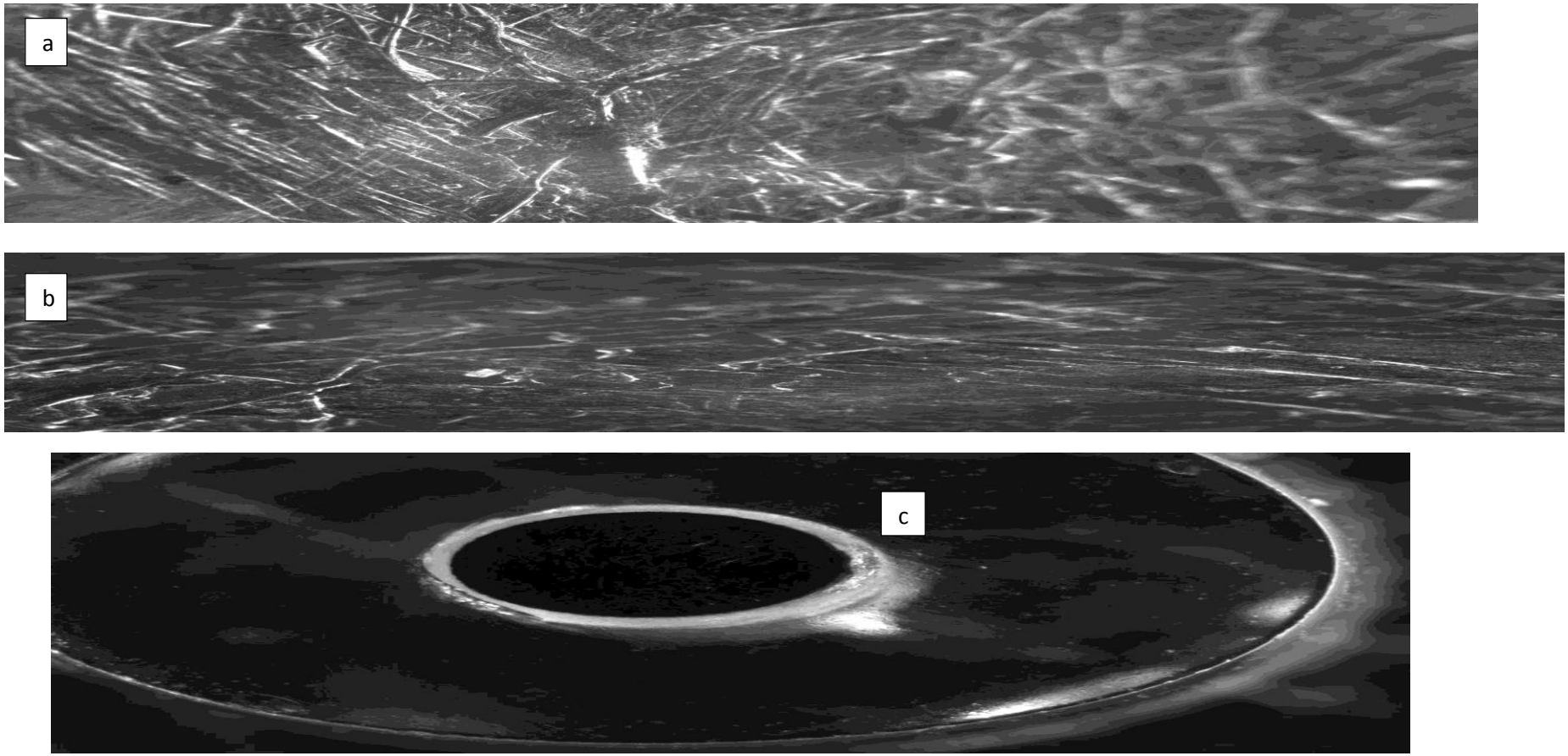


**Figure 4.68: Bismuth electrode surface before (a) and after the electro-analysis (b and c) as viewed under optical microscope**

# CHAPTER FIVE

## 5.0 DISCUSSION

### 5.1 Quality Assurance

The percentage recoveries results of the soil samples for the sequential extraction as compared to total metal contents were presented in Table 4.1. The highest percentage recovery was recorded for Zn metal ion (100.75 ± 2.30 %) while Pb had the least percentage recovery of 92.63 ± 0.02 %. The trend in percentage recovery of the metals in the soil sample was Zn > Cd > Cu > Hg > Pb. Similarly, the percentage recoveries of metals in the other samples investigated were presented in Table 4.2. In the case of well water, all the metals exhibited excellent recoveries in the following trend; Cu = Zn > Hg > Cd > Pb, Cu and Zn being the highest 100.05 ± 0.04 % while Pb had the least percentage recovery of 99.38 ± 0.27 %.

Furthermore, in the case of dumpsite leachates, the trend was Zn > Cd > Pb > Hg > Cu, and the highest and lowest recoveries of 99.98 ± 0.05 % and 99.35 ± 0.25 % were recorded for Zn and Hg, respectively. Also, the percentage recoveries of the metals recorded in the blood sample followed the trend Cu > Zn > Cd > Hg, thus, Cu and Hg showed the highest and lowest concentrations of 102.14 ± 0.10 and 92.79 ± 0.01%, respectively. Moreover, the trend of the percentage recoveries recorded in the urine and hair samples were; Zn > Cu > Pb > Hg > Cd and Cu > Zn > Pb > Hg > Cd, respectively, in which Cd exhibited the least percentage recovery while Zn had the highest as presented in Table 4.1. However, all the recorded percentage recoveries were within the acceptable ranges of > 90%. The ranges of the percentage recoveries as presented in Tables 4.1 and 4.2 were all within the acceptable range and the differences might be attributed to differences in leaching

time, reagents and total volume of extractions (Ciba *et al*., 1999). Similar ranges have already been reported in literature for sequential extraction (Albores *et al*., 2000)

## 5.2 Characterisation of Refuse Dumpsite

The results of the dumpsites characterisation revealed that polythene bags, wood, plastics and textile materials were the major dumpsites constituents across the sites. The emergence of plastics and polythene bags industries and the replacement of old household utencils by these modern facilities explain the high generation of such wastes in the environment and especially in Zaria city. The presence of this solid wastes, was also attributed to the socio-economic well-being of the populace in the metropolitan environment. Bones, waste leaves, rubber tubes, and charcoal were the most abundant solid wastes recorded in the study areas as presented in Table 4.3. The presence of these materials could alter the physico-chemical properties of refuse waste soils and heavy metal contents. The characterized solid wastes in this study were slightly different from those reported by Uba *et al*. (2008) and Ikem *et al*., (2002).

## 5.3 Gaseous Pollutants and other Field Data

The concentrations of CO recorded across the sites were generally higher during the dry season as presented in appendices III and IV. Also, the concentrations recorded for CO were below the U.S ambient air quality standard of 9.0ppm across the season with the exception of the samples from the RA – dumpsite during the dry and wet seasons respectively. The levels of CO recorded across the sites were significantly different at $p \leq 0.05$ without exception. The carbon dioxide recorded during the dry season was strongly positively correlated with flammable gas. FLD, $SO_2D$, $NH_3D$, partD and TempR as presented in Table 4.4. This indicates their common pollution source.

Also, the highest and lowest concentrations of $H_2S$ were recorded at the SA and CTR sites, respectively. The concentrations recorded were generally higher during the dry season, this was attributed to waste degradation within the solid waste due to rainwater percolation. The concentration ranges of these gases where higher than the standard limit of 0.03ppm $H_2S$, across the sites. High levels of these gases irritates the upper respiratory tracts, mucous membrane impairment and is responsible of headache, conductivities, red eyes, malodorous, etc. $H_2SR$, was positively correlated with other gases across the sites but was very weakly correlated with FLD.

Similarly, the concentrations of particulate dust recorded across the sites were generally high during the dry season without an exception. The highest and lowest concentrations were at the CTR and SH sites, respectively. This was attributed to the waste degradation and ageing. The concentrations of particulate recorded across the sites were significantly different across at $p \leq 0.05$. The flammable gas recorded was strongly correlated with $SO_2R$ as shown in Table 4.4. The highest and lowest concentrations of $SO_2$ were recorded at the CTR and SH – dumpsite, respectively. Generally, the concentrations of $SO_2$ recorded were above the USEPA toxic limit of 0.03ppm across the sites with the exception of samples from the control site (CTR). The $SO_2$ emissions largely depend on combustion process as reported by Watanabe *et al*., (2003) and bacterial process. The levels of $SO_2$ recorded were significantly different at $p \leq 0.05$ across the sites. The major health implications associated with $SO_2$ pollution is the increase in breathing rate and air starvation, suffocation and aggravation of asthma and bronchitis impairment and impairment in the pulmonary functions and irritation of throat and eyes (Dara, 2008). Also,

as presented in Table 4.4, $SO_2$ was significantly correlated with COD and $SO_2$R Vs $NH_3$R, respectively.

The highest concentrations of $NO_2$-N were recorded at JK and SA dumpsites during the dry season while the lowest concentration was recorded at the CTR as reflected in the appendix III. Also, the levels of $NO_2$ recorded across the sites were above the USEPA limit limit of 0.05ppm across the sites and seasons, respectively. Overall, the concentrations of $NO_2$ were higher in the wet season than in the dry season. This was attributed to enhanced waste degradation due to microbial actions. $NO_2$ emissions largely depend on combustion process as reported by Watanabe *et al*., (2003). The analysis of variance (ANOVA) showed that the concentrations of $NO_2$-N were not significantly different at $p \leq 0.05$ across the sites. This means other sources apart from the dumpsite might have contributed to the levels of $NO_2$-N recorded across the sites.

The highest concentration for $NH_3$ recorded at the PR dumpsite was attributed to the composition of the refuse waste. The lowest concentration of $NH_3$ was recorded at the CTR site as presented in the Table. The levels of $NH_3$ recorded across the sites were significantly different at $p \leq 0.05$ in both the dry and wet seasons, respectively. This indicates the common source of $NH_3$ across the sites. Ammonia sources in the atmosphere are animal wastes, ammonification of humus followed by emission from soils, loss of ammonia - based fertilizer from soils and industrial emissions (Okafor *et al*., 2009). High concentrations of ammonia in the air damage the respiratory tracts, eyes and it's corrosive to mucous membrane.

The lowest percentage of the relative humidity was recorded at the RA–dumpsite while the highest was noted at the CTR (control) site during the dry season. This clearly indicates that the relative humidity decreases with an increase in pollution as reflected in Figure 4.3. The highest percentage relative humidity was recorded at the SA–dumpsite while the lowest concentration was recorded at the CTR–dumpsite during the wet season as presented in Figure 4.4. The observed trend was attributed to an increase in the bacterial action during the wet season. On subjecting the results of the % relative humidity to statistical analyses, the concentrations were significantly different at $p \leq 0.05$ across the sites and seasons, indicating the common pollution source across the sites.

The temperature recorded across the sites and seasons revealed the highest temperature at the RA- dumpsite while the lowest temperature was recorded at the SA–dumpsite during the wet season as presented in appendix IV. This was attributed to intense bacterial action on the soil of the RA–dumpsite. The temperature of the refuse waste across the sites and seasons were strongly positively correlated with COD, FLD, $NO_2D$, $NH_3D$, HUMD, $NH_3R$ and PartR, respectively. This clearly indicates their common source of pollution.

The concentrations of the suspended particulates across the sites and seasons were significantly different at $p \leq 0.05$. Particulate dust was strongly positively correlated with $NO_2D$, HumD, COR and TempR, respectively, as reflected in Table 4.4. This clearly indicates their common pollution source across the sites.

## 5.4 Physicochemical Parameters of Dumpsite Soils

The soil composition was observed to vary from one season to another with the relative abundance of the particle size in the order; sand > silt > clay as presented in Table 4.5. This observation was in accord with those observations made by Rashad and Shalaby, (2007). However, the trend observed at the control site was different from that in the study area which shows that sand > clay > silt. The difference in the observed trend was attributed to activities taking place at the sites, as dumpsite soil are organically bound when compared to that in the control soil. The same observation was made by Awode *et al*., (2008); Oyedele *et al*. (2008) and Anake *et al*. (2009) in similar studies.

The high percentage of sand in the soil samples revealed that the refuse waste soils were of the texture class sandy loamy and this further suggested that the soils may have poor water and metal retention capacities, as the lower the clay contents the poorer the the retention capacity of the soils.

From the pH values recorded in both the dry and wet seasons, all the soils were alkaline in nature with the exception of control site which was basic in the wet season. The highest pH values were recorded at JK and DD dumpsites in the dry and wet seasons, respectively which was attributed to increased dumping activities and composition of the solid wastes as presented in Table 4.3. Studies have revealed that most metals in the pH range of 6.0 to 9.0 are always in the free form (Porteus, 1985), thus would be readily bioavailable to the environment. In addition, Sposito (1982) reported that Domino and Greenfield composted sites had pH values of 7.8 and 7.1, respectively, indicating that wastes contaminated soils have relatively higher pH values. High pH values might decrease the mobility of the metals in the soils as stated by Smith *et al.* (1996 ) and consequently contribute to lower transfer ratios of the metals in the refuse soils.

The higest level of the electrical conductivities was recorded at the RA dumpsite soils while the lowest was recorded at the CTR site as presented in Table 4.3 and was attributed to presence of metallic scraps releasing metals in either sulphate or chloride form into the soil. By comparison, Boulding (1994) classified electrical conductivities of soils (in µs/cm) as: non saline < 2000; moderately saline 2,000 to 8,000; very saline 8,000 to 16,000; extremely saline >16,000. The range of the electrical conductivities recorded indicate that the soil across the sites fall within the range of non saline to very saline as recorded in the RA soil across the sites. The highest level of the CEC were recorded at sites KU for the dry and wet seasons, respectively.

The highest concentrations of 11.60 (KU) and 14.14 Cmol/kg (DD) were recorded during the dry and wet seasons for the organic matter, respectively. Many studies conducted on physicochemical properties of waste soils on refuse dumpsites documented organic matter at different levels (Bamgbose *et al*., 2000; Elaigwu *et al*. 2007; Awode *et al*., 2008; Okunola *et al*., 2011; Gasu and Ntemuse, 2011). The ranges in this study were higher than those reported by Awode *et al*. (2008) who reported lower ranges of 0.10 to 2.20%. The levels of the CEC (Cmol/kg) were significantly lower than those of the dumpsites which were attributed to high organic matter contents at the dumpsites compared to control area which was in accord with the report of Brady and Weil (1999) that soils with high humus contents and pH have high CEC.

As presented in the Table 4.7, the highest concentration of $NO_2$-N was recorded at the DD–dumpsite while the lowest concentration of $NO_2$-N was recorded at the CTR site during the wet season. Similarly, during the dry season, the highest concentrations of $NO_2$-N were recorded at the SH and KU–dumpsites while the lowest concentration was recorded at the RA- dumpsite. The variations in the availability trends of $NO_2$-N across the seasons

were attributed to the bioavailability of the metals in the dumpsite soils. The highest level of $NO_2$-N was recorded during the wet season and was attributed to increasing bacterial action as presented in Tables 4.6 and 4.7, respectively. The levels of $NO_2$-N recorded across the sites and seasons were within the normal range obtainable in soils. The levels obtained in this study were also within the range of 0.10 ± 0.001 to 91.70 ± 0.06 reported by Uba *et al*. (2008) in similar studies.

Similarly, the lowest levels of $NO_3$-N were recorded at sites BG and CTR while the lowest concentration was recorded at the SH–dumpsite soil, respectively during the dry season as presented in Table 4.6. Conversely, the highest concentration of $NO_3$-N was recorded at the DD–dumpsite soil while the lowest concentration was noted at the CTR site respectively during the wet season as presented in Table 4.7. The variability in bioavailability trends $NO_3$-N in both the dry and wet seasons was attributed to intense bacterial actions during the wet season. The concentrations of $NO_3$-N recorded in this study were lower than the ranges recorded by Uba *et al.* (2008). On subjecting the results of $NO_3$-N to statistical analysis both across the sites and seasons, they were significantly different at $p \leq 0.05$. This clearly indicates their common source of pollution. The levels recorded in this study were within the range obtainable in a normal soil. The decomposition of plants containing wastes contributes significantly high levels of nitrogen in the dumpsite waste soils (Eddy *et al*., 2006).

Also, as presented in Tables 4.6 and 4.7, the levels of $SO_4^{2-}$-S across the sites, the highest concentration of $SO_4^{2—}$-S was recorded at the JK- dumpsite soil while the lowest concentration was recorded at the soil of the CTR site for dry and wet seasons, respectively. The concentrations were significantly different at $p \leq 0.05$, this also indicates the common

source of pollution. Similarly, the levels of $SO_4^{2-}$S reported in this study were lower than those recorded by Uba *et al*. (2008) in similar studies. Mineral sulphur is largely sulphate except under reducing conditions where sulphides and sulphites may be present (Williams and Steinberg, 1964). The total sulphur in soil varies widely from about 5 to 50,000 ppm.

The concentrations of $PO_4^{3-}$P recorded in the soil during the dry season was at the AJ–dumpsite while the lowest concentration was recorded at the CTR – site as presented in Table 4.6. Similarly, the highest concentration of $PO_4^{3-}$P was recorded at the AJ – dumpsite soil while the lowest concentration was recorded at the DD–dumpsite as reflected in the Table 4.7. The levels of $PO_4^{3-}$P were significantly different at $p \leq 0.05$ across the sites and seasons, indicating a common source of pollution. Also, the levels of $PO_4^{3-}$P recorded in this study were lower than the range reported by Uba *et al*. (2008), Okoronkwo *et al*., (2006), Eddy *et al*., (2006), respectively.

## 5.5 Total Metal Contents of Dumpsite Soils

As observed in Table 4.8, the highest concentration of Zn was recorded in the SA–dumpsite while the lowest concentration was noted at the CTR site during the dry season. Conversely, during the wet season, the highest concentration of Zn was recorded in the sample of the SH–dumpsite while the lowest concentration was observed at the CTR–site which was attributed to leaching activities, composition and bioavailability of the refuse waste soil. The concentrations of Zn were also significantly different at $p \leq 0.05$. Also as presented in Table 4.12, there were strong positive correlations of ZnD vs ZnR, PbR, CuR, CdDustD and ZnDustR, respectively. This indicates their common pollution source. The trend for the concentration of Zn across the sites during the dry season was SA > KU > NTC > RA > JK > SH > AJ > BG > PR > DD.The concentrations of Zn recorded in the AJ,

BG, JK, KU, SA, SH, RA and NTC–dumpsite soils were above the WHO (1997) tolerable limits of 300mg/kg during the dry season.

Similarly, As presented in Table 4.9, the highest concentration of Zn was recorded at the SA–dumpsite while the lowest concentration was recorded at the CTR site during the wet season, these concentrations were above the WHO (1997) tolerable limit in KU, SA and NTC–dumpsite soils, respectively; this was attributed to dumpsite compositions. The levels of Zn across the sites were also significantly different at $p \leq 0.05$. Also, as presented in Table 4.12, the concentrations of Zn across the seasons were strongly positively correlated and were attributed to their common source of pollution. Similarly, the levels of Zn recorded in soils were also correlated positively with Zn and Cd in the dust particulates. This also shows that Zn in the dust particulates emanated from the dumpsite soil. The levels of Zn reported in this work were below the levels of Zn reported by Uba *et al.* (2008).

The concentrations of Pb across the sites and seasons (dry and wet) are presented in tables 4.8 and 4.9, respectively. During the wet season, the highest concentration was recorded at the CTR- dumpsite soil while the lowest concentration was recorded at the AJ–dumpsite, respectively. The concentrations of Pb across the sites were significantly different across the sites at $p \leq 0.05$ in the wet season. Conversely, as presented in Table 4.8, the highest level of Pb was recorded at the RA – site while lowest concentration was recorded at the BG–dumpsite respectively during the dry season. This was attributed to dumpsite compositions, leachates migrations and the bioavailability of Pb in the soil. Generally, the concentrations of Pb recorded across the sites were below the WHO (1997) standard limit of 100mg/kg. The high concentration of Pb recorded at the control site during the wet season was attributed to leachates migration. On comparing the levels of Pb

in dumpsite soils across the seasons, the highest levels of Pb across the sites were recorded during the dry season, this was attributed to the dumpsite compositions. Also, the results were subjected to correlation analyses to establish the degree of interrelationship that exist among the metals and the results are presented in Table 4.12. From the Table, strongly positive correlations exist between PbD vs ZnD, CuD, ZnDustD, CuDustR and CdDustR, respectively. This clearly indicates their common pollution source. The concentrations of Pb reported in this study was above those reported by Uba *et al*., (2008), Okoronkwo *et al.*, (2006) but higher than the levels recorded by Ebong *et al.* (2007) and Odukoya *et al*. (2000), respectively. The availability trends observed for Pb in both the dry and wet seasons were RA > NTC > SA = DD > JK > AJ > CTR > PR > SH > KU > BG and CTR > KU > JK > PR > RA > DD > SH > SA > NTC > BG.

Also, the concentrations of Cu in dumpsite soils across the sites and seasons are presented in Tables 4.8 and 4.9, respectively. As reflected from Table 4.8, the highest concentration of Cu was recorded at the RA-dumpsite while the lowest concentration was recorded at the BG–dumpsite during the dry season. Conversely, the highest level of Cu was recorded at the JK while the lowest concentration was recorded at the SH–dumpsite, respectively. The difference observed across the seasons was attributed to the bioavailability of Cu in the dumpsite soil due to leachate migrations. Also, the concentrations of Cu recorded across the sites were above the WHO (1997) tolerable limit of 100mg/kg with the exception of RA–dumpsite soil during the dry season. This was attributed to the composition of the RA–dumpsite. The analysis of variance revealed significant difference in the concentrations of Cu across the sites and seasons at $p \leq 0.05$; this also indicates a common pollution source. The concentrations of Cu recorded in the

dumpsite soils were subjected to correlation analysis as reflected in Table 4.12. From the Table CuD was strongly positively correlated with HgDustD, PbDustD, CdDustR and CuR Vs ZnR, CdR vs ZnR, respectively, revealing their common pollution source. Also, The trend of Cu bioavailability during the dry and wet season were RA > NTC > DD > CTR > JK > PR > SH > SA > AJ > KU > BG and JK > NTC > SA > KU > PR > RA > AJ > DD > CTR > BG > SH, respectively.

Similarly, the levels of Cd recorded in the refuse waste soils across the sites and seasons are presented in Tables 4.8 and 4.9, respectively. As presented in the Table, the highest level of Cd was recorded at the AJ–dumpsite while the lowest concentration was recorded at the CTR-site during the wet season as presented in Table 4.9. Conversely, the highest concentration of Cu was recorded at the soil from the RA–dumpsite while the lowest concentration was recorded at the BG–dumpsite soil during the dry season. The difference in the availability trends of Cu across the seasons was attributed to bioavailability of Cu in the dumpsite soil. Generally, the concentrations of Cd recorded across the sites and seasons were below the limit of 3.0mg/kg for WHO (1997) as presented in the Tables. Generally, the concentrations of Cd recorded in this study were higher than the ranges reported by Yusuf *et al*. (2006), Ikem *et al*. (2002) and Ramos *et al*. (1994) were also lower than those reported by Uba *et al*. (2008) in waste soils. The observed trend of Cd across the sites and seasons (dry and wet) were: RA > SH > KU > PR > JK > DD > AJ > NTC > CTR > BG and AJ > SA > KU > RA > PR > NTC > JK > DD > BG > SH > CTR, respectively.

Similarly, the highest concentration of Hg was recorded in the AJ–dumpsite while the lowest levels of Hg were recorded at the BG–dumpsite soils during the dry season as

presented in Table 4.8. Conversely, the availability trend observed for Hg during the dry season was different, the highest concentration of Hg was recorded at the soil from the BG–dumpsite while the lowest concentration was recorded at the CTR–site during the wet season, this was attributed to the bioavailability of Hg in the dumpsite soils. The concentrations of Hg recorded in the soil of dumpsites across the sites were above the WHO limit across the sites and seasons. This indicates that the refuse waste soils were generally contaminated by Hg without an exception. The concentrations of Hg in soils were also significantly different at $p \leq 0.05$ across the sites.

Generally, the trends of the bioavailability of Hg in both the dry and wet seasons were AJ > SH . DD > NTC . SA > KU > PR > RA > CTR > JK > BG and BG > SH > PR > AJ > RA > SA > KU > NTC > DD > JK > CTR, respectively.

The concentrations of Hg were correlated across the sites and seasons as presented in Table 4.39 so as to establish the degree of relationship between Hg and other toxic metals. As shown from the Table, strongly positive correlation was recorded for CdR Vs HgR, which clearly indicates that both Cd and Hg have a common source of pollution.

## 5.6 Concentrations of Metals in Dumpsites Particulate Dust

The highest concentration of Zn in the dust particulates as presented in Table 4.10 during the dry season was recorded in the BG–dumpsite dust particulate while the lowest concentration was recorded at the JK–dumpsite. Conversely, the highest level of contamination was noted at the SA–dumpsite and the lowest concentration was recorded at the CTR–site during the wet season. These concentrations were also below the WHO (1997) tolerable limit of 300mg/kg for soils. On comparing the concentrations of Zn in the

dust particulates, the concentrations recorded during the dry season were higher than those recorded during the wet season; this was attributed to dumpsite compositions, bioavailability of metals in the soils and wind direction, this also leads to difference in the distribution trend of the metal in the particulate.

The trends recorded for the bioavailability of Zn in dust particulate in both the dry and wet seasons follow: BG > PR > SH > RA > DD > SA > KU > AJ > NTC > CTR > JK and SA > BG > DD > PR > JK > AJ > SH > KU > RA > NTC > CTR. The levels of Zn in dust particulates were correlated with those in the dumpsite soils across the sites and seasons. The results revealed strongly positive correlations between ZnD Vs ZnDustR, ZnDustR Vs PbR as presented in Table 4.39. They were also significantly different at $p \leq 0.05$.

The levels of Pb investigated in the in the dust particulates are also presented in Tables 4.10 and 4.11, for the dry and wet seasons, respectively. The highest concentration of Pb was recorded at the RA–dumpsite while the lowest concentration was recorded at the CTR site during the dry season. Also, during the wet season, the highest concentration of Pb was recorded at the SA–dumpsite while the lowest concentration was recorded at the CTR site as presented in the result section and Table 4.11. The concentrations for Pb recorded across the sites and seasons were above the WHO/USEPA toxic limit in dust, this shows that the residents might be subjected to lead poisoning, due to bioaccumulation. There were strongly positive correlation between PbDustD Vs CuD, PbDustR Vs CuD, PbDustD vs CdD, PbDustD Vs CdD and PbDustR Vs ZnR, respectively as presented in the Table 4.39. The levels of Pb across the sites and seasons were significantly different at $p < 0.05$. The trends of the availability of Pb across the sites were different across the seasons.

The trends observed for the dry and wet seasons were RA > PR > DD > AJ > SA > JK > KU > BG > SH >NTC > CTR and SA > RA > JK > PR > DD > AJ > NTC > KU > SH > BG > CTR, respectively.

The concentrations of Cd recorded in the dust particulates across the sites during the dry and wet seasons are presented in Tables 4.10 and 4.11, respectively. From the Tables, the highest concentrations of Cd was recorded in the samples of RA–dumpsite particulates and the lowest concentration was recorded at the CTR–site. On comparing the concentrations of Cd across the seasons, the highest concentrations across the seasons were recorded during the dry season as compared to those recorded during the wet season. This was attributed to dumpsite compositions, wind direction and bioavailability of Cd in the dust particulates. Also, the concentrations of Cd in the particulate dust were significantly different at $p \leq 0.05$.

Also, there were strong interrelationship between CdDustR vs ZnD, CdDustR vs PbD, CdDustD vs CdD, CdDustR vs CdD and CdR vs CdDustR, respectively as presented in Table 4.12. The levels of Cd recorded in the dust particulates across the sites and seasons were below the WHO (1997) toxic limit of 3.0mg/kg with the exception of concentrations recorded at the SH and RA–dumpsites. Also, the observed trend for the availability of Cd across the sites during the dry and wet seasons: RA > KU > DD > SA > JK > PR > BG > AJ > SH > NTC > CTR and RA > NTC > SA > AJ > KU > PR > SH > DD > BG > JK > CTR, respectively.

Similarly, the concentrations of Cu in the dust particulates are presented in Tables 4.10 and 4.11. The highest concentration of Cu was recorded at the NTC–dumpsite while

the lowest concentration was recorded at the KU–dumpsite during the dry season as presented in the Table 4.10. Also, during the wet season, the highest concentration of Cu was recorded in the particulate recorded from the JK–dumpsite while the lowest concentration was noted in the particulate dust of the CTR–site as presented in Table 4.11. Generally, the highest concentration of Cu across the season was attributed to the leachability of the soil, dumpsite composition and wind direction.

The concentrations of Cu in the dust particulate across the sites and seasons were significantly different at $p \leq 0.05$. This clearly indicates the common source of pollution of the metal across the sites. The degree of interrelationship of Cu in dust particulates across the sites were strongly positive for CuDustD Vs PbD and ZnR vs CuDustD, respectively as presented in Table 4.12. The trends observed for the availability of Cu in both the dry and wet seasons were: NTC > RA > BG > SH > JK > PR > DD > AJ > SA > CTR > KU and JK > NTC > RA > AJ > SA > DD > SH > PR > BG > KU > CTR, respectively.

The levels of Hg recorded across the sites and seasons are presented in Tables 4.10 and 4.1, respectively. The highest concentration of Hg was recorded during the dry season at the KU–dumpsite while the lowest concentration was recorded was recorded at the JK–dumpsite. Conversely, during the wet season, the highest concentration of Hg was recorded at particulate dust from the JK–dumpsite while the lowest concentration was recorded at the CTR–site. On comparing the concentrations of Hg in the particulate dust across the sites, the highest concentration of Hg was recorded during the dry season which was attributed to dumpsite composition. The concentrations of Hg across the sites were also significantly different across the sites and seasons at $p \leq 0.05$. There were strong positive correlations between HgDustD Vs PbD across the sites especially during the dry season as presented in

table 4.12. The concentration of Hg recorded across the sites and seasons were above the WHO (1997) tolerable limits of 0.13mg/kg for Hg in the particulate dust. The trends for the availability of Hg across the sites and seasons were different which was attributed to the bioavailability of Hg in the dumpsite soils. The observed trends during the dry and wet seasons were KU > CTR > AJ > RA > SH > NTC > BG > DD > PR > BG > SA and NTC > KU > SH > JK > PR > BG > DD > AJ > SA > RA > CTR, respectively.

## 5.7 Chemical fractionation of Metals in the Dumpsite Soils

Metal chemical speciation carried out by sequential extraction of the metals is essential in accessing the mobility and bioavailability of heavy metals in the waste soils. Figures 4.5 to 4.17 showed percentages of the bioavailable, residual and the non-residual fractions across the sites for Zn, Pb, Cu, Cd and Hg. The results obtained show that the amounts of heavy metals extracted from each fraction vary widely.

### 5.7.1 Chemical fractionation of Zn

Appendices V and VI revealed the concentrations of Zn by sequential extraction for wet and dry seasons, respectively. Among the non-residual fraction, the highest concentration of the total extractable fraction was found in the acid soluble fraction (fraction IV) with the exception of soil from the AJ–dumpsite during the wet season which concentrates more in the residual fraction. On comparing the concentrations of Zn in the residual and non-residual fractions across the sites, the non- residual fractions constitute the highest percentage of the total extractable fractions across the sites, this indicates that Zn would be released to the environment for contamination except the soil of the AJ-dumpsite. During the dry season, the highest percentage of Zn was also found in the non- residual fraction of the soil with exception of soil of the AJ–dumpsite.

Among the non-residual fractions, acid soluble fraction of Zn (fraction bound to carbonates) constitutes the highest percentage of the total extractable fraction of Zn as reflected in the Table; this was attributed to pH influence as the soils were alkaline in nature both across the sites and seasons. Overall, the percentages of the total extractable fractions of Zn across the seasons were predominantly found in the non-residual fractions of the soil. This clearly indicates that Zn in the analysed samples of soils would be readily bioavailable for environmental contaminations as reflected in appendices V and VI. Also, the total extractable fraction of Zn in the dumpsite soils across the sites and seasons were above the WHO (1997) tolerable limit of 300mg/kg both across the sites and seasons with the exception of samples from the SH and CTR dumpsites which were below the toxic limit as presented in the appendices. Among the residual fraction of the soil, AJ, BG, JK, SH, RA and PR had the highest amount of Zn in the reducible fractions which was partly attributed to high stability constants of zinc oxides in this study and was in accord with the report of several other workers who have also found zinc to be associated with reducible fractions (Kuo, *et al.,* 1983, Ramos *et al.,* 1994; Uba *et al.,* 2008)

### 5.7.2 Chemical fractionation of Pb in soils

The Appendices VII and VIII revealed the extractable fractions of Pb in refuse waste soils across the sites and seasons. Among the extractable fractions of Pb, the highest concentrations of Pb were recorded in the reducible fractions during the dry season. On comparing the levels of Pb recorded in the residual and the non–residual fraction, the later constitutes greater percentage of the total extractable fraction and this indicates that Pb at this site would be readily bioavailable for environmental pollution in dry season. Also, the levels of Pb recorded among the fractions and total extractable fractions were below the

USEPA toxic limit of 100mg/kg in this season. Similarly, as presented in appendix VII, the highest percentage of the bioavailable fraction was found in the soil of the CTR–site during the dry season indicating that this site has an environmental implication.

As shown in appendix VIII, the total exractable fraction of Pb among the fractions and across the sites were all below the USEPA toxic limit of 100mg/kg. Among the fractions, the highest percentage of the total extractable fraction was found in the residual fractions across the sites with the exception of JK, KU, SA, SH and NTC soils where Pb was predominantly found in the non-residual phases. The residual fractions represent metals largely embedded in the crystal lattices of the soil fraction and thus, not readiliy bioavailable for contamination in the environment except under very harsh conditions. Among the non-residual fraction, the acid soluble fraction (carbonates fraction) is influenced by pH. Appreciable amounts of Pb were found in the reducible and oxidisable fractions across the sites during the dry season. This finding is in agreement with what was reported by Kabata - Pendias and Pendias (1992) for the affinity of Pb to organic matter and that of Ramos *et al*., (1994) who found that Pb was associated with the reducible fraction.

The findings in this study are also similar to the findings of Ahumada *et al*. (1999), Karczewska *et al*. (1996), Chlopecka *et al*. (1993) and Sposito *et al*. (1982). In general, the oxide fractions scavenge Pb in natural and polluted soils (Xian, 1989; Kuo, *et al*., 1983) indicating the tendency of Pb to be released into the environment. On comparing the results of residual and non-residual fractions, the higher percentage of Pb across the sites were found in the non-residual fractions of the dumpsite soils, which clearly, indicates the potential bioavailability of the metal. Generally, the highest percentage of the bioavailable fraction of Pb was recorded at the BG-dumpsite.

### 5.7.3 Chemical fractionation of copper in soils

Appendices, IX and X revealed the concentrations of Cu in the extractable fractions as determined by sequential extractions for dry and wet seasons, respectively. The highest concentrations of copper was recorded during the dry season in the residual fraction, followed by acid soluble, this fraction involves a fraction which is bound to carbonate. In addition, appreciable fractions of Cu were also found in the reducible fraction, except soil samples of the JK and KU–dumpsites. Overall, the concentrations of the total extractable fractions of Cu were below the detection limits. The reducible fractions are excellent scavengers of trace metals and sorption by these oxides tend to control Cu, Mn and Zn solubility in soils (Pickering, 1986). Similarly, the total extractable fractions of Cu recorded across the sites were all below 100mg/kg USEPA toxic limit in the polluted sites. On comparing the concentrations of Cu in the residual and non-residual fractions, the higher percentage of the non-residual fraction was generally found in the dumpsite soils of BG, DD, JK, KU, SA, SH, RA and NTC, respectively, during the dry seasons. The bioavailability of Cu across the sites were generally very low, this clearly shows that the metal would be released into the environment only under very harsh conditions.

The levels of Cu for wet season in the refuse waste are presented in appendix X. The highest concentration of Cu among the fractions were determined in the residual fraction across the sites with the exception of BG–dumpsite soil which was predominantly found in the oxidisable phase which is fraction bound to carbonates. Metal in the residual fraction indicates that its largely embedded in the crystal lattice of the soil fraction and should not be available for environmental pollution except under harsh conditions. The total extractable fractions of copper as presented in the Table were all below the USEPA

toxic limit of 100mg/kg in soil. The levels of Cu recorded in the exchangeable and water soluble fractions were below the detection limit across the sites.

However, the highest percentages of the non-residual fractions are recorded at the AJ, BG, KU, SA, SH, RA, PR and NTC–dumpsite soils, respectively. The high amounts of Cu associated with the non-residual phases shows that they may be easily transferred into the food chain through uptake by plants growing in the soils. These characteristics plus hazards of Cu to human health, suggest that frequent examination of the levels of Cu in soils may determine potential health hazards to residents living near the polluted site. Since Cu is a cumulative poison, its main ways of entering into the food chain is through the refuse waste. Conversely, The highest percentage of Cu was recorded during the wet season in the residual fractions at the CTR, DD, and JK–dumpsites, respectively. This clearly shows that the metal would not be readily released into the environment for contamination except under very harsh conditions. In addition, high concentrations of copper were recorded in the oxidisable phase across the sites, this is the fraction which was bound to organic matter and living organisms (due to bioaccumulation) may be remobilized into the environment. The low bioavailabity of Cu recorded at the CTR, JK, SA, RA, PR, SH and AJ was attributed to high stability constant of Cu in soil. However, high bioavailability of Cu recorded at the NTC and BG–dumpsites indicate that Cu would be more bioavailable in these sites.

### 5.7.4 Chemical fractionation of cadmium in soils

Appendices XI and XII show the concentrations of Cd in the extractable fractions of the dumpsite soils across the sites and seasons, respectively. Among the six geochemical

fractions, the highest concentrations of Cd were recorded in the residual fractions of DD and JK, respectively, which shows that they would be released into the environment under very harsh conditions. Also, the percentages of the non- residual fractions of Cd were significantly high across the sites with the exception of soil of the JK, DD and CTR sites, respectively. This indicates that the Cd studied would be readily bioavailable to the environment for contamination in all but JK, DD and CTR sites respectively. Thus, Cd may be easily transferred into the food chain through the uptake by plants growing in the soils, or through inhalation of the particulate dust etc. These characteristics plus health hazards of Cd to human health, suggest that frequent examination of the levels of this element in soil samples may determine potential health hazards to residents living near the dumpsites.

The high percentage of the specifically adsorbed Cd in soils agrees with the findings of Harrison (1981), and Baron *et al*., (1990). Since Cd is a cumulative poison to mammals, its main ways of getting into the food chain is through dust, refuse waste disposal, etc. Comparing the levels of Cd for the extractable fraction in both the dry and wet seasons, significant amount of the total extractable fractions were predominantly found in the non-residual fractions, this clearly shows that in both seasons, Cd would be readily bioavailable to environment for contamination. Also, among the six geochemical fractions, the highest concentration of Cd was recorded in the acid soluble fraction, which is part of the bioavailable fraction. Overall, the total extractable fractions of Cd across the sites and seasons were above the USEPA limit of 3.0mg/kg for Cd in soils with few exceptions.

The presence of the appreciable percentages of cadmium in the mobile phase suggests that Cd in these soils was potentially highly bioavailable for plant uptake (Xian,

1989, Uba *et al*., 2008). The results obtained in this study was in agreement with the observations of Harrison (1981), Miller and Mcfee (1983), Kuo (1983).

### 5.7.5 Chemical fractionation of mercury in soils

The sequential extractions of Hg in refuse waste soil are presented in appendices XIII and XIV, for dry and wet seasons, respectively. During the dry season, as presented in appendix XIII, appreciable concentrations of Hg were recorded in all the six geochemical fractions, however, among the fractions, the highest concentration of Hg was recorded in the exchangeable fraction (Fraction II). In fraction II, Hg is held together by electrostatic adsorption and that it is specifically adsorbed. Generally, high amount of Hg recorded were associated with the first five fraction which constituted the non-residual fraction. The presence of appreciable amounts of Hg in the non-residual fractions of the refuse wastes indicate its potential bioavailability to environment for contamination as presented in the appendix XIII. Genrally,the concentrations of Hg recorded in the refuse waste soils were above the USEPA toxic limit of 0.13mg/kg for soils.

Comparing the results obtained across the seasons, the concentrations of Hg recorded during the dry season across the sites were higher than those recorded during the wet season, this was attributed to dumpsite composition and bioavailability of the metal in the refuse waste soil as presented in Table XIII. Similarly, the percentage of Hg in the bioavailable fraction during the dry season across the sites were higher than those recorded during the wet season, these were attributed to leachability of Hg in this season. Generally, the percentages of the residual fractions across the sites and seasons were low, this indicates that Hg is loosely bound in the crystal lattice of the soils and can be easily washed

away by rainfall to the immediate environment. This pollutes the surface, underground and plants which subsequently, affects the residents through food chain transfer.

Overall, the percentage of the bioavailable fraction of mercury across the sites was > 24.07% in the wet season. The potential mobility and bioavailability of the metal followed the pattern BG > JK > SA > AJ > CTR > DD > PR > KU > RA > NTC > SH and the availability pattern among the fractions was that oxidisable > exchangeable > water soluble > acid soluble > reducible > residual, the non-residual fraction had the highest percentage of the total extractable fraction of the metal ion. Among the non-residual fractions, the bioavailable fraction constitute more than 43 % with the exception of SH dumpsite indicating its potential bioavailability to the environment.

The non-residual fraction was the most abundant pool for all the metals studied. The potential mobility and bioavailability of Hg during the dry season followed the trend BG > SA > RA > KU > JK > DD > PR > CTR > NTC > SH > AJ. The highest bioavailable fraction was obtained at site BG and the least was noted at site AJ. The availability of the metal among the fractions followed the pattern; oxidisable > acid soluble > water soluble > exchangeable > reducible > residual. More than 49 % of the metal was bioavailable to the environment with the exception of site AJ which had the least fraction of the extractable fraction in the mobile phase. The t-test for comparing the mean concentrations at $P \leq 0.05$ showed that there was no significant difference among the fractions across the sites.

## 5.8 Water Quality

### 5.8.1 Physico-chemical parameters of leachates

The physico-chemical parameters of leachates investigated showed varying concentrations across the sites are presented in Table 4.13.

The pH recorded in the leachate samples across the sites indicates that the water was weakly acidic to alkaline across the sites, this was attributed to the composition of the dumpsite. The pH of the leachates recorded in this study is within the range of 7.0–9.2 across the sites with the exception of leachate samples from the RA–dumpsite which was below the above range. The pH of leachates can be upset by adding acid or alkaline from waste materials. Similar studies by Aiyesanmi and Imoisi, (2011) and Marien *et al*. (2008) revealed slightly lower values of 6.76 to 7.49 and 6.78 to 6.93, respectively. Moreover, slightly higher values of 7.74 to 7.91 and 8.17 were reported by Haun–Jung *et al*. (2005). Lower to higher values of 5.10 to 8.60 for pH were also reported by Al–Yaqout and Hamodoa (2003). pH enhances Solubility of metal in leachates, thus elevating their concentrations and possibly their toxicity.

Alkalinity in solid wastes help to resist changes in pH caused by the presence of acidic materials in domestic wastes. The concentration range of alkalinity reported in this study across the sites and seasons were above the range of 200 to 600mg $CaCO_3$/L reported by WHO (1997) with few exception. The concentration ranges in this study were below the range of 13.14 ± 4.17 to 23.34 ± 5.90 mg/L reported by Aiyesanmi and Imoisi, (2011).

The concentrations of $NO_3$-N and $NO_2$-N reported in this study across the sites were below the FEPA (1991) and WHO (1997) limits of 50 and 30 mg/L, respectively. In addition, the measured values of $NO_2$-N and $NO_3$-N were also lower than 9.5 to 20.9 mg/L reported by Haun – Jung *et al*., (2005) with the exception of BG, SA and RA dumpsites leachates in which concentrations above the tolerable limits were recorded. However, the levels of $NO_2$-N, $NO_3$-N reported in this study were above the range of 0.41 to 0.81 mg/L

and 0.09 mg/L reported by Aiyesanmi and Imoisi (2011). Incresing the amount of leachates in a small volume of water over may lead to toxicity of such water.

The levels of ammonium nitrogen ($NH_4$-N) recorded across the sites for leachate samples were highest at the PR–samples while the lowest concentration was recrded at the KU and NTC–dumpsites respectively. The levels of $NH_4$-N recorded in the RA, PR, BG, and SH–dumpsites were above the WHO toxic limit of 0.50mg/L, this was attributed to reduction of $NO_3$-N by bacterial actions in the leachate samples were lower than the range of 0.56 to 1.64 mg/L reported by Aiyesanmi and Imoisi (2011) 0.5mg/L recommended by WHO (1997) in the rest of the dumpsites.

The turbidity levels of the refuse wastes across the sites were within the range of 5–25 NTU. The turbidity levels recorded at the RA, NTC and BG leachate samples were very high indicating their high levels of pollution. The concentrations in this work were within the range reported by Aluko *et al*., (2003). Increasing, the amount of leachates in a small volume of water over long period of time may lead to toxicity of such water.

The levels of chlorides ($Cl^-$) recorded for leachates across the sites were above the WHO (1997) tolerable limit of 5–15 mg/L for $Cl^-$ in waste water except at sites AJ and BG – Dumpsites where lower concentrations were recorded as presented in table 4.13. Excess chloride in leachates is an index of pollution and is considered as tracer for groundwater contamination. The chloride levels as presented in the results section, were below the range reported by Aiyesanmi and Imoisi (2011) but higher than the range of 4.00 to 15.10 mg/L reported by Chu (1994) for landfill leachates. The higher Cl level in some dumpsites leachates reflects significant input of domestic wastes to the dumpsites.

The concentration range of $SO_4^{2-}$-S recorded in the leachate samples across the sites were below the WHO tolerable limit of 200–600mg/L for waste water except leachates of the JK- dumpsite which was above the tolerable limit as presented in Table 4.13. Concentrations of $SO_4^{2-}$-S recorded in this study was attributed to domestic waste. In addition concentrations recorded were also below the FEPA (1991) limits of 500 mg/L in the SA, JK and CTR sites.

As presented in Table 4.13, the colour intensity of leachate samples across the sites was above the stsndard limit of 0.01 for waste water. The highest and lowest colour levels were recorded at the AJ and CTR sites, this was also attributed to bacterial actions. The colour of the leachates recorded across the sites exceeded the WHO (1997) tolerable limits of 15CTU with the exception of CTR and BG - dumpsite. The high colour intensity may be attributed to leachate composition and dissolved substances. Similarly the values recorded in this study were higher than the limit of 15.0 CTU sets by the NSDWQ (2007) across the sites.

Also, the electrical conductivities (EC) of leachates recorded in this study were higher than the 1.20 to 14.00µs/cm recommended in waste water. The higher values of EC recorded in this study was attributed to the high levels of exchangeable bases in the leachates. This emerged due to composition of the dumpsite. The high electrical conductivity (EC) values of the leachates recorded across the sites might be attributed to high dissolved salts. The values of the electrical conductivities reported in this study were below those reported by Aiyesanmi and Imoisi (2011) and Haun - Jung *et al*. (2005).

The temperature range for leachates as presented in Table 4.13 were all within the APHA (2005) acceptable range of 5 – $50^0$C for waste water. The temperature range of the leachates measured across the sites fall within the FEPA (1991) limit of < $40^0$C for waste water. The high levels of temperature recorded in the leachates might be attributed to absorbed heat from the sun and possibly heat of dissolution of some waste materials in the study areas. However, the concentrations recorded in this study were lower than the range of 26.03 to 26.60$^0$C reported by Aiyesanmi and Imoisi (2011).

The high concentrations of the total solids (TS) recorded in the leachates samples in this study were attributed to the leachability of the solid wastes due to rainfall. The levels recorded in this study were above the WHO tolerable limit of 500mg/L for waste waters. The concentration of the total dissolved solids was reasonably high at RA dumpsite leachates and lowest at the control site which was attributed to the leaching of the various pollutants by the rainwater to the immediate environment especially the open wells of the residents. Varying concentrations of the physico–chemical parameters of leachates depends primarily upon the wastes composition and water contents in the solid wastes as reported by Mor *et al*. (2006) and Aiyesanmi and Imoisi (2011), respectively.

The correlation analyses of physicochemical parameters of leachates and water samples are presented in Table 4.15. From the Table, strongly positive correlations were recorded for ECL vs TSL, SSL, DSL, ALKL, $NO_2$NL, $NO_3$NL, $NH_3$NL, TurbidL, ECW, TSW, SSW, DSW, and alkw, respectively. This clearly indicates the common pollution source of these physicochemical parameters.

Also, strongly positive correlation was recorded across the sites for correlating TSL vs SSL, DSL, ALKL, $NO_2$NL, $NO_3$NL, $SO_4$SL, ClL, $NH_4$NL, $SO_4$SL, ColourL and TurbidL, respectively. This clearly indicates their common source of pollution.

Similarly, as presented in the Table, strongly positive correlation was recorded for TSL vs ECW, TSW, SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_4$NW, ColourW and TurbidW, this revealed their common pollution source and was attributed to bioavailability of the refuse waste soils.

The total suspended solid (SSL) across the sites were also positively correlated with DSL, ALKL, $NO_2$NL, $NO_3$NL, $SO_4^{2-}$-SL, ClL, $NH_3$NL, ColourL, TurbidL, ECW, TSW, SSW, ClW TurbidW and $NH_4$NW, respectively as presented in Table 4.15.

Similarly, strongly positive correlations were also identified for DSL vs ALKL, $NO_2$NL, $NO_3$NL, $SO_4$SL, $PO_4$PL, ClL, $NH_4$NL, ColourL and TurbidL, respectively as presentred in Table 4.15. This clearly indicates the common source of pollution across the sites.

Strongly positive correlations were recorded DSL vs ECW, TSW, SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_4$NW, ColourW and TurbidW, respectively. This was also attributed to the leachability of the solid waste by rainfall.

Also, as presented in Table 4.15, the alkalinity of leachates was compared with other physic-chemical parameters in soils, strongly positive correlations were recorded for ALKL vs $NO_2$NL, $NO_3$NL, ClL, NH4NL, ColourL, TurbidL, ECW, TSW, SSW, DSW, THW, $NO_2$NW, $NO_3$NW, ClW, $NH_4$NW, ColourW and TurbidW, respectively, indicating their common source of pollution, which is the refuse waste.

The degree of relationship between $NO_2$NL vs $NO_3$NL, $SO_4$SL, ClL, $NH_4$NL and TurbidL were investigated by correlation coefficients as presented in Table 4.15. The results revealed strong positive correlations among the parameters due to their common pollution source.

The correlation coefficients recorded for the $NO_3$NL vs $SO_4$SL, ClL, $NH_4$NL, TurbidL, ECW, TSW, SSW, DSW, THW, ALKW, $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, ColourW AND TurbidW, respectively as presented in Table 4.15. This clearly indicates that pollution of underground water was partly attributed to leachates percolation/seepage.

The levels of $NH_4$-N in leachates was also correlated with other physicochemical parameters in leachates and those in the underground water so as to establish the degee of interrelationship. There were strong correlations between $NH_4$-N vs TSW, $NO_2$NW, $NO_3$NW and $SO_4$SW were strongly positively correlated due to their common source of pollution. The source of pollution for underground water was partly attributed to leachates migration into the open wells.

The electrical conductivities of water (ECW) were strongly positively correlated with TSW, SSW, DSW, ALKW, $NO_2$NW, $NO_3$NW, ClW, ColourW and TurbidW, respectively. This was attributed common pollution source.

The TSS was also correlated with other parameters in the leachates and water, strongly positive correlations were recorded for TSS vs $NO_2$NW, $NO_3$NW, $SO_4$SW, $PO_4$PW, ClW, $NH_4$NW, ColourW and TurbidW, respectively, as presented in the result section.

The levels of nitrate nitrogen in water were also correlated with the rest of the physicochemical parameters in water and with other parameters in the leachates, the results revealed strongly positively correlations between $NO_2NW$ vs $NO_3NW$, $SO_4SW$, ClW, $NH_4NW$, $PO4^{3—}P$ and TurbidW, respectively. This clearly indicates their common pollution source of water and leachates.

5.8.2 Total heavy metal contents of dumpsite leachates

Hg, Zn, Pb, Cu and Cd were analysed in the leachate samples across the sites as presented in Figures 4.33 to 4.37. The concentrations range for Cadmium, (Cd) were higher than the toxic limits of 0.003 mg/L of the NSDWQ (2007). Higher values of 3.62 to 8.15 mg/L and 0.02 to 0.24 mg/L were reported by Ahlberg *et al*. (2006) and Aiyesanmi and Imoisi (2011) in Sweden and Benin city, respectively. However, lower values < 0.01 to < 0.15mg/L were reported in Taiwan (Haun–Jung, 2005). Cadmium is toxic when inhaled in small quantity particularly through dust generated through incineration of the dumpsites, it is carcinogenic in nature. However, the concentrations recorded for cadmium in this study were higher than the recommended limit (WHO, 1997) of 0.01 mg/L.

The concentrations range of Pb measured across the sites range from BDL (CTR) to 1.444 mg/L (BG) with highest concentration recorded at the BG and SH dumpsites while the least fraction was recrded at CTR. Also, it was noted that 90 % of the dumpsite leachates exceed the value of the WHO (1997) tolerable limits of 0.1mg/L. The most contaminated sites were at BG and SH – dumpsites, the concentrations reported in this study were higher than those reported by Aiyesanmi and Imoisi (2011) and Ahlberg *et al*. (2006) in Benin city and Sweden respectively. It was found that leaching significant amount of lead might caused cytogenetic alteration such as kidney and brain damage or

birth defects ingested through the food chain or drinking water (Ademoroti, 1996, Aiyesanmi and Imoisi (2011).

Zn concentrations across the sites range from 0.095 (PR) to 4.941 mg/L (AJ) with 50% of the analyzed samples across the sites revealed high concentrations exceeding <1.0 mg/L FEPA (1991). The highest concentration of Zn was recorded at the AJ-dumpsite while the least concentration was recorded at the PR site. The concentrations of Pb recorded in this study were higher than the range of 0.27 to 0.38 mg/L and 0.02 to 0.18 mg/L reported by Aiyesanmi and Imoisi (2011) and Huan-Jung *et al*., (2005). However, the values recorded in this study were below the concentration range of 5.07–19.09 mg/L reported by Ahlberg *et al*., (2006) in Sweden.

The dumpsite leachates were contaminated by Zn across the sites exceeding the WHO (1997) tolerable limit of 0.001mg/L. The control site however, had the least concentration below the detection limit (BDL). The highest concentration was recorded at JK–dumpsite. One–way ANOVA showed that the mean concentrations of all the analysed metals and those of the physico–chemical parameters were significantly different across the sites at $P \leq 0.05$.

5.8.3 Physicochemical parameters of well waters Near the dumpsites

The pH of the underground water in all the sites during the dry seasons were alkaline. Usually, the soil formation around savanna which Zaria belongs is of laterite which depicts possible alkalinity of the water. However, the acidity observed at CTR (in both the dry and wet seasons) and other sites (during the wet season) imply possible contamination through leaching and run-off from the dumpsites. The leaching potential of the soil might be due to their sandy-loamy nature. This observation was also made by Bolm *et al.* (1985) indicating that the leachability of the solid wastes to the immediate

environment was attributed contamination. The pH of the water across the sites and seasons varies and were significantly different at $P \leq 0.05$. The pH results showed that all the sites during wet season were below the tolerable limit of Nigeria Drinking Water Standard, APHA and WHO standards of 6.5 to 8.5, this means they were acidic, soft and corrosive (Yisa *et al.*, 2012).

The temperature recorded across the sites and seasons were above the ambient temperature prescribed by the National Drinking Water Quality Standard (NSDWQ, 2007).

The electrical conductivities (EC) of the well water during the dry and wet seasons are presented in Tables 4.14 and 4.16, respectively. The highest value of the EC during the dry season was recorded at the KU–dumpsite water while the lowest concentration was recorded at the AJ- dumpsite water a presented in Table 4.14. During the wet season, generally, the EC recorded were higher than those recorded during the dry season. This was also attributed to the leachates migration from the refuse waste to water. The highest value of the EC was recorded at the water samples of the SH–dumpsite while the lowest concentration of EC was recorded at the CTR–site, during the wet season. Also, the levels of EC recorded in both the dry seasons were above the FEPA/WHO standard limits of 1.2 to 14.0µs/cm across the sites with the exception of AJ–dumpsite as presented in Table 4.14.

Also, the levels of total solids (TS) recorded in the dumpsites across the sites during the dry season were above the toxic limit of 500 to 1500mg/L with the exceptions of samples at the RA, SA, PR and JK–dumpsites. The highest concentration of TS was recorded at the KU while the lowest concentration was recorded at the PR–water samples, during the dry season as presented in Table 4.14. Conversely, the highest level of TS was

recorded at the RA–water while the lowest concentration of the TS was recorded at the CTR site during the wet season as presented in Table 4.16. The variation in the presence of TS was attributed to leachates percolation/seepage into the underground water. Overall, across the seasons, the highest levels of TS was recorded during the wet season, this was attributed to leachates percolation/seepage to underground water.

Similarly, the levels of total hardness (TH) recorded in both the dry and wet seasons are presented in Tables 4.14 and 4.16, respectively. During the dry season, the TH levels across the sites were generally above the WHO (2006) tolerable limit of 500mg/L with the exception of CTR, KU, PR and SA, respectively as presented in Table 4.14. Conversely, during the wet season, the concentrations of TH across were above the tolerable limit of 100 to 500mg/L with the exception of the sample at the CTR–site which was below the tolerable limit a presented in Table 4.16. Also, the highest concentration of the TH was recorded from the well water at the vicinity of the AJ–dumpsite while the lowest concentration was recorded at the control site (CTR) as presented in the Table 4.16. This was attributed to seepage of leachates to the underground water during the wet season. The hardness in water is mainly due to slats and the most common are carbonates and sulphates of Ca and Mg which gets into the water due to indiscriminate disposal of municipal waste in the residential areas.

The levels of alkalinity in water across the sites and seasons are presented in the Tables 4.14 and 4.16. The levels of the alkalinity recorded during the dry season were below the WHO toxic limit of 100 to 500mg/L for water, this shows that the water across the sites in this season was not contaminated with respected to alkalinity level across the sites. Also, during the dry season, the highest alkalinity was recorded at the AJ–dumpsite

while the lowest alkalinity were recorded at the PR, JK, NTC, DD and CTR–waters respectively as presented in Table 4.14. Conversely, the levels of alkalinity recorded in well water during the wet season were higher than those recorded during the dry season. This was attributed to leachates percolation to the open wells. During the wet season, the highest levels of alkalinity was recorded at the water from the RA–dumpsite while the lowest concentration was recorded in the water at the vicinity of the KU-dumpsite. During the wet season, the alkalinity of the AJ, CTR, DD, JK and RA water were above the WHO tolerable limit of 100 to 500mg/L. High levels of alkalinity in water results in gastro-intestinal irritation in humans (WHO, 1997).

The levels of $NO_2$-N recorded during the dry season were above the WHO/FEPA (1997) toxic limit of 45mg/L across the sites as presented in table 4.14. Similarly, during the wet season, the levels of $NO_2$-N recorded across the sites were below the toxic limit of 45mg/L with the exception of water sample at the vicinity of BG–dumpsite as presented in Table 4.16. This was attributed to increase in bacterial actions, dumpsite compositions and leachates percolation to underground water.

Also, Tables 4.14 and 4.16, show the concentrations of $NO_3$-N of water in both the dry and wet seasons, respectively. On comparing the results of $NO_3$-N recorded in both the dry and wet season, the highest concentration was recorded during the wet season across sites; this was attributed to an increase in bacterial action during this season. Overall, the highest level of $NO_3$-N was recorded at the AJ and KU water samples during the dry season and these concentrations were above the WHO tolerable limit of 45mg/L. Similarly, during the wet season, the highest concentrations across the sites were recorded in the SH and RA

water samples, respectively. The availability trend of $NO_3$-N across the seasons were different, this was attributed to bacterial actions and dumpsite compositions.

The levels of $SO4^{2—}$-S recorded in water across the sites and season are presented in tables 4.14 and 4.16, respectively. During the dry season, the concentrations recorded for the $SO4^{2—}$-S across the sites and seasons were below the WHO toxic limit of 200 to 600mg/L with the exception of concentrations at the water samples of the SH and KU– dumpsites, respectively which were above the standard limit. Similarly, the levels of $SO4^{2—}$ S recorded during the wet season were below FEPA/WHO the toxic limit across the sites without an exception. Overall, the levels of $SO_4^{2—}$S recorded across the in both the dry and wet seasons shows that the high level of pollution due to $SO_4^{2—}$S an inorganic anion, was noted during the dry season, this was attributed to increase dumping activities and leachates percolation. High levels of $SO_4^{2—}$S in dumpsites was attributed to pollution due to domestic wastes.

Similarly, the levels of phosphate phosphorous $PO_4^{3—}$-P recorded in water samples in both the dry and wet seasons are also presented in Tables 4.14 and 4.16, respectively. The concentrations recorded were above the WHO/FEPA tolerable limit of 0.7mg/L across the sites and seasons without an exception. High levels of $PO_4^{3—}$-P was attributed to dumpsite compositions. During the dry season, the highest and lowest concentrations of $PO_4^{3—}$-P were recorded at the PR and CTR–sites, respectively. Similarly, during the wet season, the highest concentration of $PO_4^{3—}$-P was recorded at the AJ– dumpsite while the lowest concentration of was noted at the water samples from the SH and NTC–dumpsites respectively.

The levels of $NH_4$-N recorded in water samples across the sites during the wet season were presented in Table 4.16. The highest concentrations of $NH_4$-N during the wet season was recorded at the PR and SH water samples while the lowest concentrations were recorded at the JK and KU water samples, respectively as presented in the Table4.16. These concentrations were generally below the tolerable limit of 0.5mg/L for $NH_4$-N in water without an exception. Also, during the dry season, the levels of $NH_4$-N recorded across the sites were also below the WHO/FEPA tolerable limit of 0.5mg/L across the sites without an exception as presented in the Table 4.14. The highest and lowest concentrations during this season were recorded at the BG and SH water samples, respectively.

The colours of the water recorded at the vicinity of dumpsite in both the dry and wet seasons were all above the WHO/FEPA toxic limit of 0.01 to 0.02mg/L across the seasons as presented in the Table 4.14 and 4.16, respectively. This clearly indicates that the waters would be unpleasant for drinking.

The highest level of turbidity was recorded at the water samples from the AJ dumpsite while the lowest turbidity of the water across the sites during the dry season was recorded at the RA water sample as presented in Table 4.14. Similarly, the turbidity levels of water recorded during the wet season was highest at the RA and BG water samples. Generally, the turbidity recorded across the sites were all below the toxic limit of 5–25 NTU in both the dry and wet seasons, respectively with the exception of water sample at the AJ dumpsite during the dry season which was above the standard limit.

5.8.4: Total heavy metal contents of well waters for dry and wet seasons

The well waters at the vicinity of the dumpsites were analyzed for Hg, Zn, Cd, Cu and Pb, which are characterized as undesirable metals in drinking water. Zn concentrations in the well water samples were below the WHO (1997) limit of 3.0 mg/L across the sites and seasons without an exception. The concentrations reported in this study were lower than those reported by Glenn and Sia, (2008). Although Zn is not human carcinogenic, excessive intake of Zn in weter would lead to vomiting, dehydration, abdominal pain, lethargy and dizziness (ATSDR, 1994). Positive correlation was observed for Zn vs Cu, Zn vs Cd and Zn vs Hg across the sites ($r = 0.009$, 0.172 and 0.512 respectively) indicating the common source of pollution of this metal across the sites.

The concentrations range of copper was from BDL (CTR) - 2.59 mg/L (DD) with the highest concentration recorded at DD–dumpsites well water and the lowest concentration was recorded at CTR as presented in the results section. These concentrations were all below the WHO (2006) tolerable limit of 1.3 mg/L across the sites. The highest concentration of copper (2.9 mg/L) was recorded at the DD - dumpsite with concentration quite above the tolerable limit of 1.0 mg/L. The least contaminated site by this metal was CTR with the water samples having very low copper concentrations, this was not surprising as it was the control site where no dumping activity exists. Although low concentrations were recorded, there is a fear of bioaccumulation of the Cu if proper sanitary measures are not taken. The U.S. Environmental Protection Agency's Maximum Contaminant Level (MCL) of copper in drinking water is 1.3 mg/L. The MCL for copper is based on the expectation that a lifetime of consuming copper in water at this level is without adverse effect (gastrointestinal). The USEPA lists evidence that copper causes testicular cancer as

"most adequate" according to the latest research at Sanford-Burnham Medical Research Institute.

Lead is one of the poisonous trace elements found in the polluted natural water. The lead (Pb) concentrations in the the well water samples across the sites were above the WHO (1997) limit of 0.1 mg/L with few exceptions. The concentrations of Pb at the control site was within the WHO tolerable limit 0f 0.05 mg/L and above the National Standard of Drinking Water Quality (NSDWQ, 2007). This implies that the water is not suitable for drinking without treatment based on the high Pb concentration. Pb probably percolates into the water through the waste dumpsites through leachates percolation. High Pb concentration in human may lead to anaemia, kidney disease, cancer, affect mental development in infants and toxic to the central and peripheral nervous system (NIS, 2007). It was also reported that if significant quantity of Pb is consumed either through the food chain or drinking water, cytogenetic alteration such as kidney and brain damage or birth defects might occur (Ademoroti, 1996).

Cadmuim, another trace element of serious environmental concern was detected in all the water samples. The highest concentration of cadmium was recorded at KU-dumpsite and the least concentration was at the CTR well water. The concentrations of cadmium recorded across the sites have exceeded the WHO (1997) tolerable limit of 0.01 mg/L with the exception of CTR.

The concentrations of mercury recorded across the sites were above the tolerable limits of NSDWQ, (2007) and were positively correlated with zinc and copper ($r = 0.512$ and 0.159), respectively, this indicate the common source of contamination.

Overall, the concentrations of the essential elements Zn and Cu were below the WHO (2006) tolerable limits of 5 and 1.3 mg/L in the analysed water samples across the sites. However, the concentrations of Pb, Cd and Hg across the sites were above WHO tolerable limits of 0.001, 0.003 and 0.001 mg/L, respectively. Although the concentrations of Zn and Cu were below the tolerable limit, continuous release of leachates and consequent transportation via run off to groundwater could constitute threats to life. This showed that the hand-dug wells close to dumpsites in Zaria Metropolis are not safe for drinking, not just due to the unhygienic environment where it's sourced but also because heavy metals such as Pb, Hg and Cd contents were above the maximum tolerable limits across the sites. Other sources may be from the particulate matter emanating from the dumpsites which could easily get into the water due to poor coverage of the wells. However, positive correlations were recorded between Pb in water and Pb in leachates, Cd in water and Cd in leachates where r – values of 0.007 and 0.041were recorded.

### 5.8.5 Quality indices of well waters near the dumpsites

The water quality index (WQI) of the water samples showed that the analysed water samples for both dry and wet seasons were heavily contaminated and water quality indices were > 300 as presented in the results section (Tables 4.14 and 4.15) and were unfit for drinking unless subjected to further treatment such as boiling or addition of chemicals. However, the water samples in the wet season were contaminated the more as compared to those in the dry season. The high values of WQI recorded across the seasons might be attributed to leachates percolation to underground water.

## 5.9 Chemical Fractionation of Metals in Leachates and Well Waters

### 5.9.1 Chemical Fractionation of metals in dumpsite leachates

The total extractable fraction of Pb, Cd, Cu, Hg and Zn were investigated in the dumpsite leachate samples as presented in appendices XV to XIX. The results obtained for the extractable fraction of Zn in leachates across the sites as presented in appendix XV, were generally below the toxic limit of 5.0mg/L for WHO (1999) and USEPA (2000) standard limits. This suggest that the analysed leachates samples were not contaminated by Zn.

The total extractable fraction of Pb in this study was found to be higher than 0.05 to 0.12 mg/L reported by Manpanda *et al*. (2007) in Zimbabwe and lower than 0.35 to 0.97 mg/L reported by Ahlberg *et al*. (2006) in Sweden, respectively. Cytogenetic alterations such as kidney and brain damages or birth defects are some of the toxicological effects of lead if ingested through the food chain or drinking water (Ademoroti, 1996; Aiyesanmi and Imoisi (2011).

The concentrations of the bioavailable fractions of cadmium in the dumpsite - leachate in this study were below the ranges of 0.02 ± 0.01 to 0.24 ± 0.31 mg/L and 3.62 ± 0.01 to 8.15 mg/L reported by Aiyesanmi and Imoisi (2011) in Benin city and Ahlberg *et al*., (2006) in Sweden respectively. Analysis of variance (ANOVA) showed a significant difference (at $P < 0.05$) both among the fractions and across the sites. Inaddition, there was a positive correlation between the lead and Zinc (Pb-Zn) suggesting a common source of pollution.

The extractable fractions of copper in the analysed samples across the sites were presented in appendix XVIII. The trend was SA > NTC > AJ > KU > DD > CTR > JK > BG > RA > SH > PR. Generally, there was positive correlation in the concentrations OF Cu among the fractions and across the sites with few exceptions. Analysis of variance ($P < 0.05$) revealed a significant difference among the mean concentrations of the fractions across the sites. The levels of copper recorded in leachate in this study were lower than > 1.5mg/L reported by Ikem *et al*. (2002) in Lagos for his total elemental analysis. The distribution pattern among the fractions was Cu: Total > particulate > mobile > dissolved.

Appendix XIX showed the concentrations of mercury in the fractionated leachate samples. The bioavailability trend across the sites was PR > SH > SA > DD > RA > JK > AJ > BG > N TC > KU > CTR. It was observed that the levels obtained were well above the WHO (2006) limits both across the sites and among the fractions. The distribution trend among the fraction was: Particulate > Mobile > Total > dissolved. Similarly, one way ANOVA showed a significant difference among the fractions at $P < 0.05$.

Mercury in the dumpsite - leachates were positively correlated with the lead, however, negative correlation of the metal ion was recorded with copper, cadmium and zinc, revealing an inverse relationship. The high concentrations recorded at the sites may not be unconnected with dumpsites constituents where cadmium containing waste formed part of the constituents and the total fraction was significantly not different at $P < 0.05$. When this metal gets into the groundwater serious health problems such as chromosomal segregation, chromosomal disruption and inhibition of cell division may occur (Dara 2008).

Comparing the results obtained for zinc with the standard limits (USEPA, 2000; WHO, 2006), sites KU, SA, SH and PR were contaminated (concentration > 5mg/L). Thus, the concentration of zinc in the analysed leachate samples was readily bio-available to the environment contaminating especially, the underground water due to leachates percolation. Zinc pollution is known to induce vomiting, dehydration, abdominal pain, dizziness and lack of muscular co–ordination (WHO, 1999). Overall, the mobile fractions had the highest concentrations of the total extractable Zinc across the sites. The concentrations recorded were higher than the values of 0.37 to 0.65 mg/L reported by Aiyesanmi and Imoisi ( 2011) in Benin city for the total elemental analysis of leachates. The difference might be attributed to the different composition of the analysed dumpsites.

The concentrations of lead recorded across the sites in the leachates suggests that there was a common source of pollution by the metal ions as significant difference among the fractions was observed at $P < 0.05$. When the concentrations (total extractable) across the sites were compared with those of the international standard (USEPA, 2000 and WHO, 1999) they all exceeded the extractable fractions were higher than the range of 0.05 to 0.12 mg/L reported by Manpanda *et al*. (2007) in Zimbabwe and lower than 0.35 to 0.97 mg/L reported by Ahlberg *et al.* (2006) in Sweden, respectively. It was also noted that if significant quantity of lead was leached into the groundwater, cytogenetic alteration such as kidney and brain damage or birth defects results especially when ingested through the food chain or drinking water (Ademoroti *et al*., 1996; Aiyesanmi and Imoisi ( 2011).

The extractable fractions of cadmium were compared with the WHO (2006) standard limits of 0.003 and 0.001 mg/L (WHO, 2006; USEPA, 2003), respectively. Overall, the results showed higher values with few exceptions, the recorded concentrations

in this study were below the ranges of 0.02 to 0.24 mg/L and 3. 62 to 8.15 mg/L reported by Aiyesanmi and Imoisi (2011) and Ahlberg *et al*. (2006). Analysis of variance (ANOVA) showed a significant difference at $p < 0.05$ among the fractions and across the sites. In addition, there was a positive correlation between lead and Zinc (Pb - Zn) across the sites suggesting a common source of pollution.

The levels of copper recorded in this study were lower than >1.5 mg/L reported by Ikem *et al*. (2002) in Lagos. The distribution pattern among the fractions was Cu: Total > particulate > mobile > dissolved. Copper in the blood exist in two forms: bound to ceruplasmin (85 to 95%) and and the rest 'freely' loosely bound to albumin. The free copper is toxic as it generates reactive oxygen species such as superoxide, hydrogen peroxide and the hydroxyl radical, these damages proteins and DNA (Brew, 2010).

### 5.9.2 Chemical Fractionation of metals in well waters

The summary of the concentrations of the fractionated zinc, Pb, Cu, Cd and Hg in the well water samples across the sites and seasons are presented in Figures 4.41 to 4.50. The extractable fractions for zinc across the sites followed the pattern: Mobile > Dissolved > Particulate > Total, the range of the bioavailable fraction which is the sum of the dissolved and mobile fractions during the wet season were significant as presented in appendix XXI. Analysis of variance showed a significant difference among all the extractable fractions ($P < 0.05$). This observation suggests that the distribution of zinc depends partly on sources of contamination which is the dumpsite leachates. When the result was compared with the WHO (2006) standard limit (5 mg/L), all the concentrations recorded among the fractions were below the toxic limit but there is fear of bioaccumulation with the time. The potential

bioavailability of the metal across the sites followed the trend: AJ > DD > KU > SH > JK > PR > SA > BG > CTR > RA > NTC.

The bioavailable fraction of zinc, which is the most abundant pools of the metal with few exceptions, the percentage of the bioavailable fraction during the wet season range was significant. The potential mobility and bioavailability of the metal across the sites followed the trend BG > CTR > DD > JK > SA > NTC > RA > KU > SH > AJ > PR. Also, among the extractable fraction the distribution pattern is Dissolved > Total > Mobile > Particulate . The analysis of variance showed that the concentrations of all the extractable fractions of Zn were significantly different ($P < 0.05$) both across the sites and among the fractions. The values reported in this study were higher than 0.005 ± 0.03 mg/L reported by Abdulrafiu *et al.* (2011).

Furthermore, the levels of copper found in this study were below the WHO (2006) and USEPA (2003) limits of 1.5 and 1.3 mg/L respectively. The range of the bioavailable fractions across the sites shows that Cu were highly bioavailable at the DD, JK and the RA water samples. The distribution pattern of Cu was DD > JK > RA > AJ > PR > KU > NTC > BG > SA > SH > CTR. However the trend observed among the fractions was Total > Particulate > Dissolved > Mobile. The least concentrations were recorded at the control site.

Copper was also mostly associated with the last three fractions in the PR and NTC well water which was attributed to the formation constant of the organic copper complexes (Stumm and Morgan, 1981). Leachates from the dumpsites remain the major source of this metal based on its composition. There was strong correlation between copper and zinc ($r = 0.984$), copper and lead ($r = 0.850$) suggesting that they have a common pollution sources (dumpsites, Leachates and air). Furthermore, the values recorded in this study were higher

than the concentrations of 0.05 ± 0.03 and 0.12 ± 0.02mg/L reported in similar studies in the Ifo and Isolo from Ogun and Lagos, respectively.

The high concentration of cadmium was also noted at the control site. Compared to the standard WHO (2006) limit of 0.001 mg/L, the concentrations of cadmium in this study were above the toxic limit across the sites. Furthermore, availability pattern among the fraction is : Dissolved > Mobile > Total > Particulate. The primary targets for the toxicity of mercury and mercury compounds are nervous systems, the kidneys and the cardiovascular system. It is generally accepted that developing organ systems (such as the fetal nervous system) are the most sensitive to toxic effects of mercury. Other systems that may be affected include the respiratory, gastro intestinal, hematologic, immune and reproductive systems (UNEP, 2008).

The concentrations of cadmium, lead and mercury in the analysed water samples have exceeded the WHO (2006) tolerable limits, more than 50 % of the extractable fractions were in the bioavailable phase resulting in bioaccumulation in the tissues and organs of the inhabitants that usually use the water for drinking. In addition to other domestic use. Most of studied wells were open or poorly covered, this has made it easier for the heavy metals in the particulates to get into the water contaminating it. Other metals investigated in this study were within the WHO tolerable limits.

The bioavailable fractions across the sites and among the fractions were the most abundant pools for all the metals. More than 60 % of the total extractable fractions were not in the bioavailble fractions in most of the sites. The concentrations of the cadmium, lead and mercury were above the WHO (2006) tolerable limits in both the wet and dry seasons. However, higher concentrations of the entire metals were recorded during the wet season,

this was attributed to leaching of the contaminants to open wells contaminating the underground water.

Overall, the trend of the metals availability in both the dry and wet seasons were similar: Hg > Cd > Pb > Zn > Cu. The analysis of variance showed a significant difference among the fractions and across the sites ($P < 0.05$). Pollution of the well water samples in the vicinity of the dumpsites leading to serious health problems to consumers.

## 5.10 Heavy Metals in Chicken samples

### 5.10.1 Concentrations of heavy metals in chicken samples

Among the chicken samples, leg, head, intestine and feather were found to accumulate the highest amount of Zn, Pb and Cu, Cd, Hg, respectively, indicating the importance of these samples as bio-indicators to the study as presented in Tables 4.21 to 4.28, respectively.

The concentrations of zinc recorded in gizzard of the chicken samples across the sites and seasons were all below the Codex and WHO (1998) standards across the seasons. They were also below the concentrations of 85.934 mg/kg reprted by Salwa *et al*., (2012) but above the concentration of 1.9399 mg/kg reported by Nick *et al*. (2012) with few exceptions as presented in Figure 4.74.The order of average bioavailability of zinc in the contaminated chicken samples across the sites and organs followed the trend leg > skin > muscles > oesophagus > gizzard > intestine > feather > heart > head > kidney > liver > lung > brain > bones > wattle.

The mean concentrations of Zn in chicken samples for the dry and wet seasons were all below the permissible limits of 50 and 100 mg/kg for Codex and WHO (1998) as presented in Tables 4.19 and 4.20, respectively. However, the highest concentration of

zinc was recorded at site KU and the least concentration was recorded at the control site. The concentrations of zinc in the lungs of the analysed chicken samples were below the Codex permissible limit of 50 mg/kg, they were also below the concentration of 43.27 mg/kg reported by Salwa *et al*. (2012).

The highest concentration of zinc was thus, recorded at the RA samples across the seasons these concentrations were significantly different at $P \leq 0.05$ and were all below the Codex standard limit of 50 mg/kg and lower than both the Codex and WHO (1998) and lower than the concentrations recorded by Nick *et al*. (2012) as presented in Tables 4.19 and 4.20, respectively. These concentrations were lower than the concentration of 0.869 mg/kg reported by Salwa *et al.* (2012) in the local chicken feather samples.

The levels of lead recorded in the contaminated chicken organs were below the detection limit across the sites and seasons with the exception of samples at BG, KU and SH, in which concentrations above the FAO/WHO (0.01 mg/kg) were recorded ( BG, KU and SH).

Moreover, as presented in Table 4.21, the concentration ranges for lead across the sites in the heart of the analysed chicken samples were also above the FAO/WHO recommended limit of 0.01 mg/kg with few exceptions as presented in Table 4.22. The concentrations of lead recorded in the majority of the samples across the sites and seasons were above the value of 0.2151 mg/kg reported by Nick *et al*. (2012) with few exceptions. Similarly, as presented in Table 4.22, the concentration of lead in the samples of chicken legs were below the FAO/WHO standard limit of 0.01mg/kg with the exceptions of samples at sites AJ, KU, BG and SH respectively, in which concentrations above the tolerable limit were recorded.

The concentration of lead recorded in the liver samples across the seasons were all above the FAO/WHO (1996) limit of 0.2 mg/kg as presented in Tables 4.21 and 4.22, respectively. Similarly, the concentrations recorded were also higher than the concentrations of 0.304 mg/kg reported by Nick *et al.* (2012) in a similar study. These concentrations were above the FAO/WHO toxic limit of 0.01 mg/kg with the exception of samples at the AJ, KU, SH and RA dumpsites in which the concentrations recorded were all below the detection limit. Overall, the highest concentration of lead in this study was recrded in the brain samples.

The order of bioavailability of Pb across the sites and seasons followed the pattern: Brain > skin > muscles > intestine > oesophagus > heart > kidney > liver > feather > leg > wattles > lungs > bones > head. There was significant difference at $P < 0.05$ in lead concentration among the analyzed organ and tissue samples. The concentrations recorded for the metal ions across the sites were all above the WHO/FAO tolerable limit of 0.01 $mgkg^{-1}$ with few exceptions.

The high levels of lead in poultry products and meat might be attributed to contamination of feeds (solid wastes) and water sources (leachates) used to feed the chicken samples. The enhanced level of Pb in this study agrees with the findings of Uba *et al*., (2008) who reported high levels of Pb, Cd, Cu and Mn in the dumpsites waste soils which results in the enhanced absorption by the plants and consequently the animals which feed on them. This results to toxic reactions along the food chain (Duffus, 1980; Osuji, 1998).

The concentrations of lead in this study was in good agreement with the concentrations reported by Salwa *et al*. (2012), Uluozlu *et al*., (2009), Iwegbue *et al*.,

(2008), Akan *et al*. (2010). The levels of lead recorded were all below the values of 210mgkg$^{-1}$ recommended by the WHO (in organs such as muscle, liver, gizzard and lungs).

Lead is considered as one of the major environmental pollutants and it is also carcinogenic affecting the liver and thyroid functions (Eisler, 1988). In this study lead was found to concentrate more in brain of the analysed chicken samples.

The concentrations of cadmium in the oesophagus of the contaminated chicken samples across the sites and seasons were presented in Tables 4.23 and 4.24. The levels recorded were above the WHO (2011) permissible limit of 0.05 mg/kg in the meat samples and the highest concentrations across the sites and seasons were recorded at the JK–dumpsite chicken samples

These concentrations were all above the WHO (2011) permissible limit of 0.05 mg/kg with the exception of those at the control site. The concentrations recorded were lower than the concentration ranges of 0.129 to 0.403 mg/kg reported by Salwa *et al*. (2012) but higher than the concentration of 0.0236 mg/kg reported by Nick *et al*. (2012). Furthermore, the concentrations of cadmium recorded in bones of the contaminated chicken samples across the sites and seasons were below the permissible limit of WHO/FAO limit of 0.05 mg/kg. The analysis of variance showed a significant difference in the concentrations of this metal across the sites and seasons at $P \leq 0.05$.

Moreover, the concentration ranges of cadmium in the kidney of the contaminated chicken samples across the sites and seasons were lower than the ranges reported by Salwa *et al*. (2012) and above the concentrations reported by Nick *et al*. (2012), respectivelly. The concentrations of cadmium in the intestine of the contaminated chicken samples for the wet and dry seasons across the sites were presented in Tables. The highest concentrations above the permissible limit of 0.05mg/kg (European union, 2002) were recorded at the SA, SH,

RA, NTC and AJ intestine samples in both the wet and dry seasons respectively. Thus, the consumers of these samples might suffer health problems related to cadmium exposure such as renal dysfunction, chest pain, foamy blood sputum, bones defect etc. On subjecting the results to statistical analysis, one way analysis of variance (ANOVA), there was a significant difference in the concentrations of this metal both across the sites and seasons at $P \leq 0.05$.

Futhermore, the concentrations of Cd in the head samples of the contaminated chicken samples across the sites and seasons were above the tolerable limit of the European Uinion (0.05 mg/kg) across the season which was attributed, partly, to the dumpsites composition. These concentrations across the sites and seasons were significantly different at $p \leq 0.05$ and were positively correlated, a clear indication of their common source of pollution.

The levels of cadmium recorded in gizzard of the contaminated chicken samples were above the tolerable concentrations of 0.05 mg/kg across the seasons. However, concentrations above the permissible limits were recorded at the JK, DD and KU only in the dry season. Generally, the concentrations recorded in the gizzard samples were lower than the concentration of 0.157 mg/kg recorded by Salwa *et al*. (2012) in their comparative studies. However, the concentration of cadmium in this work were higher than the concentration of 0.0236 mg/kg recorded by Nick *et al*. (2012). One way analysis of variance (ANOVA) showed a significant difference in the concentration of the metals both across the sites and seasons at $P \leq 0.05$.

Moreover, the concentrations of cadmium in the feather of the contaminated chicken samples showed that highest and lowest concentrations were recorded at the control (CTR) and Babban Gwani (BG) dumpsites samples respectively. However, the

levels recorded recorded at sites BG, JK, KU and SH were above the European union tolerable limit of 0.05 mg/kg across the seasons. Generally, the concentrations recorded in this study were lower than the value of 0.403 mg/kg reported by Salwa *et al*. (2012) in their comparative studies of chicken with Quail samples. The concentrations recorded in this study both across the sites and seasons were significantly different at $P \leq 0.05$.

The concentrations recorded in the wattle samples of the contaminated chicken samples across the sites and seasons were presented in Table 4.23. Cadmium was not detected in most of the samples, however, concentrations above the EU toxic limit were recorded at the contaminated wattle sites AJ, BG and KU in both the wet and dry seasons, respectively.

Similarly, Table 4.23 shows the concentrations of cadmium in the skin of the contaminated chicken samples, lowest concentration was recorded at the control site while the highest concentration was recorded at the RA samples. On comparing the results with the standard limit of the European union (EU), the concentrations of the heavy metal in the contaminated skin samples of AJ, BG, JK, SH, RA and NTC were above 0.05 mg/kg toxic limit while sites DD, KU, SA, SH and PR had higher concentrations of the metal in the dry season respectively. Generally, the concentrations recorded across the sites and seasons were significantly different (at $P \leq 0.05$). However, the concentrations of cadmium recorded in the contaminated chicken skin samples were lower than the concentration of 24mg/kg reported by Salwa *et al.* (2012) in their comparative studies.

Cadmium is highly toxic, it is carcinogenic and potentially mutagenic (Salwa *et al*., 2012) with severe sub-lethal and lethal effects at low environmental concentration (Eisler, 1985). In this study, high concentrations were noted in the internal tissues of the chicken samples such as oesophagus , bones and intestine.

The least concentration range for cadmium was recorded in the liver during the wet season (0.055 $mgkg^{-1}$) at site BG. The highest cadmium concentration recorded in this study was lower than 0.15 to 0.23 $mgkg^{-1}$and 1 $\mu gg^{-1}$ reported by Salwa *et al*., (2012 ) and World Health Organization (WHO), respectively.

Food is one of the environmental sources of cadmium (Baykov *et al*., 1996), the dumpsite residents have been rearing chicken for domestic and commercial applications. The concentrations of cadmium recorded in the heart samples of the contaminated chicken samples across the sites and seasons were presented in Table 4.23 and 4.24, respectively. The concentration ranges were above the EU permissible limit of 0.05 mg/kg across the seasons with few exceptions in some sites. Thus, the heart samples in these sites were heavily contaminated by cadmium. However, cadmium were not detected across the seasons at AJ, BG, CTR, KU, PR and SH dumpsites.

Figure 4.95 shows the concentrations of cadmium in the muscles of the contaminated chicken samples across the sites and seasons (wet and dry sesons). The lowest concentrations were noted at the control sites, no dumping activity took place in this site and is a new settlement as shown in Figure 3.12. Generally, the concentrations recorded across the sites and seasons were above the EU permissible limt of 0.05mg/kg with the exception of the control sites and SA sample during the wet season. Similarly, the concentrations of cadmium in the muscles of the contaminated hicken samples in this study were above the concentration of 0.0162 mg/kg reported by Nick *et al*. (2012) and below the concentrations of 32.0 and 0.15 mg/kg reported by Salwa *et al*. (2012) respectively in similar studies. Moreover, the concentrations recorded were significantly different across the sites and seasons at $P \leq 0.05$.

The concentration ranges of Cd recorded in the leg samples of the contaminated chicken samples in the wet and dry seasons were above the EU permissible limit across the sites and seasons with the exception of DD, SA and control (CTR) samples as presented in Table 4.23 and 4.24, respectively. There was significant difference in the concentration of this metal at $P \leq 0.05$.

The levels of cadmium in the liver of the contaminated chicken samples acrosss the sites and seasons were presented in Tables 4.23 and 4.24. The levels of cadmium in the liver samples of the contaminated chicken at sites BG, KU, SA and SH were above the EU-permissible limit of 0.05mg/kg and heavily contaminated by this metal. The most contaminated sample across the site and season was recorded at the SH-dumpsite. The results obtained in this study was lower than the value of 0.159 mg/kg reported by Salwa *et al*. (2012) and above the concentration of 0.0457 mg/kg reported by Nick *et al*. (2012). Similarly, the concentration range of Cd recorded in the brain samples across the sites and seasons were above the EU toxic limit of 0.05 mg/kg were recorded at sites JK, SA and PR, respectively. Overall, the most contaminated sample was noted at the PR dumpsite and was attributed to the dumpsite composition. The concentrations across the sites and seasons were not significantly different with the exception of those samples at the JK, SA and PR dumpsites.

However, the highest concentration of Cd averagely was found in the oesophagus of the RA – dumpsites (0.110 $mgkg^{-1}$) followed by muscles and then the lowest concentration was found at the control site (CTR). One-way ANOVA showed that cadmium concentrations were significantly different across the sites at $P < 0.05$ and it was positively correlated across the sites in the different tissues and organs. Overall, the order of availability of cadmium across the sites and seasons, averagely, followed the pattern; lungs

> muscles > gizzard > kidney > oesophagus > intestine > leg > skin > feather > head > liver > heart > wattles > bones > brains. Overall the order of bioavailability of copper in the different chicken tissues and organs were: Liver > gizzard > head > oesophagus > leg > muscle > kidney = lungs = bones = kidney = heart > feather = wattles = brain respectively.

The highest concentration of copper was found in the liver of the NTC dumpsite followed by gizzard, head, oesophagus, leg and muscle and the least concentration was recorded in the brain as presented in Tables 4.25 and 4.26, respectively. One-way ANOVA showed a significant difference in the copper concentrations recorded at $P < 0.05$. Furthermore, there was a positive correlation among the tissues and organs with the exception of brain – wattles, brain – gizzard and oesophagus – brain which were negatively correlated. Overall the concentrations of copper in some of the analysed tissues and organs were found to exceed the WHO tolerable limits in chicken muscles ($30mgkg^{-1}$).

The organs and sites exposed to copper toxicity were oesophagus, head, gizzard, liver and brain of the chicken samples in the NTC dumpsites across the seasons (both dry and wet). The levels of the metal in these organs were found to exceed the $30mgkg^{-1}$ WHO tolerable limit with the highest concentration of $431.15mgkg^{-1}$ recorded in the liver. In all cases, the least concentrations of copper were found in the tissues and organs of the control site. The analysed chicken samples were mostly contaminated by mercury followed by copper, cadmium, lead and then zinc, thetrend to the bioavailable fractions of the metal in the soil.

Overall, brain, muscles, intestine, oesophagus accumulate higher lead both across the sites and seasons. Lungs, muscles, gizzard, kidney, oesophagus etc accumulates higher cadmium while higher concentrations of Hg, Cu and Zn were found in liver, gizzard, head, oesophagus, leg, muscles, kidney, skin, intestine and feather, respectively. The chicken

samples fed with dumpsites wastes and leachates were found to be heavily contaminated by mercury and copper in the leg, feather, head, kidney, liver, gizzard, oesophagus and muscles.

The concentration of mercury recorded in the chicken organs and tissues acrosss the sites were all above the safe limit for human consumption as presented in Tables 4.27 and 4.28, respectively. In addition, copper concentrations were also above the safe limit in the oesophagus, head and gizzard of NTC dumpsites. Overall, the order of bioavailability of the analysed metals in the chicken samples across the sites and seasons was Hg > Cu > Cd > Pb > Zn. There was significant correlation in the concentrations of zinc among the different organs and tissues at $P < 0.05$. In addition, positive correlations were recorded for the concentrations of the metals among the different organs. The concentrations of the metals in the chicken samples were below the World Health Organization (WHO) tolerable limits.

In this study, there was contamination of chicken samples by mercury, copper and cadmium. It was also noted that the amount of metals in feather was proportional to those found in the internal organs and tissues. Lead was found to accumulate more in the brain, skin, muscles, intestine, and oesophagus across the sites and seasons.

It is interesting to note that the organs that were mostly contaminated by all the analysed metals were muscles, gizzard, and oesophagus while kidney was contaminated by cadmium and zinc the brain were also polluted by lead metal ions. The mercury affects mostly the leg, feather, head, kidney etc.

Feather in this study was found to act as a suitable bio- indicator for metal accumulation in the internal tissues analysed and this was found to be in conformity with the report of Salwa *et al.,* (2012). However, zinc and copper which are essential elements were mostly found to accumulate more in the leg, skin, liver, gizzard and oesophagus and

the bioaccumulation was more in the liver which vbm might be attributed to the roles it plays in the entire body system (IAEA, 1980).

5.10.2 Bioaccumulation factor of heavy metals in chicken

a. Bioaccumulation of Zn in chicken samples

Table 4.29 exhibits the bioaccumulation factors (BAFs) of Zn across the sites during the dry season. The highest BAFs of Zn for Oesophagus during the dry season (OED) was highest at the sample from the KU–dumpsite while the lowest BAFs was recorded at the sample from the NTC–dumpsite. Also, during the dry season, the highest level of contamination was recorded at the DD while the lowest BAF was recorded at the AJ, BG, CTR, KU, SH, RA and PR oesophagus and lung samples respectively, during the wet season. This signifies the bioaccumulation of Zn in both the oesophagus and lungs of the contaminated chicken samples via soil. High bioaccumulation factor in the Table indicates high level of contamination and vice-versa.

The BAFs of Zn recorded in bones of the contaminated chicken samples in both the dry and wet seasons are presented in Tables 4.29 and 4.30, respectively. The highest BAFs recorded for Zn in bones was recorded at the AJ, BG, CTR, DD, JK, SA, SH and PR, respectively, while the lowest BAFs were recorded at the RA – site during the wet season. This indicates that they are more contaminated than the rest of the samples which was attributed to leachability of the dumpsite soils.

The levels of the BAFs across the sites and seasons (dry and wet) as presented in Tables 4.29 and 4.30, respectively. The levels of BAFs for Zn recorded in kidneys of the contaminated chicken samples during the dry season was highest at DD sample while

lowest level of kidney contaminations were recorded at the AJ, BG, CTR, DD, SA, SH and PR, respectively. Also, on comparing the levels of BAFs of Zn in bones of the contaminate chickens in both the dry and wet season, the highest BAFs was recorded during the wet season at the bone sample of the DD–dumpsite. This was also attributed to leachability, composition and ageing of the dumpsite.

Similarly, the BAFs in the intestine of the contaminated chicken samples during the wet season (INTR) are presented in Table 4.29. The highest BAFs in this season was noted at the RA–sample of the intestine and the lowest was recorded at the CTR-site. Generally, based on the BAFs recorded in both the dry and wet season, the highest level of contamination was recorded in the intestine samples as presented in the Tables.

The BAFs of Zn in the heart of the contaminated chicken samples was highest in samples of the DD–dumpsite, this was attributed to bioavailability of the Zn in the dumpsite soil. Also, the lowest BAFs of Zn was recorded in the sample of the PR-Dumpsite. On comparing the levels of BAFs recorded during the dry and wet seasons, the highest levels of heart contamination with Zn was recorded during the wet season.

The BAFs of Zn recorded in contaminated gizzard across the sites and seasons are presented in Tables 4.29 and 4.30, respectively. The highest level of BAFs for Zn was found at the contaminated gizzard of the JK–dumpsite. On comparing the BAFs of Zn in the contaminated gizzard samples across the sites, the highest level of contamination was recorded during the wet season, this was attributed to the bioaccumulative effects.

Similarly, the BAFs for Zn in feather of the contaminated chicken samples across the sites and seasons are presented in Tables 429 and 4.30, respectively. During the wet

season, the highest level of feather contamination was recorded at the AJ–dumpsite while the lowest BAFs of Zn in feather was recorded at the sample of the CTR. The trends observed for bioaccumulation of Zn in feather across the seasons differ, for example, the highest level of contamination of feather for Zn was recorded at the sample from DD-dumpsite while the lowest was recorded at the CTR site during the dry season which was not the case during the wet season.

Also, as revealed from Tables 4.29 and 4.30, the highest BAFs of Zn was recorded in the wattle samples of AJ–dumpsite during the dry season. This trend was attributed to bioavailability of the Zn in the refuse waste soil. The BAFs recorded for Zn in the contaminated skin of chicken was highest at the JK and lowest at the CTR–skin samples during the wet season. Conversely, the highest level of Zn was recorded DD-sample of skin while the lowest BAFs for Zn was noted at the CTR–site during the dry season. The variations in the bioavailability trend of Zn in the skin samples across the seasons were attributed to physiological functions of Zn in chicken system.

Similarly, the BAFs of Zn recorded in the head of the contaminated chicken samples are presented in Tables 4.29 and 4.30, respectively. Generally, the high level of contamination based on BAFs was recorded during the wet season across the sites with the exception of samples of AJ and BG–dumpsites which accumulate more Zn during the dry season as presented in the Tables. Also, the bioaccumulations of Zn in Muscles of chickens was highest at muscle sample from the PR dumpsite and were lowest at the NTC and CTR sites, respectively during the wet season, this was attributed to bioaccumulative effects and bioavailability of Zn in soils.

The BAFs of Zn were also recorded in the legs of the contaminated samples of chicken across the sites and seasons, the results are presented in Tables 4.29 and 4.30, respectively. The highest BAFs of Zn in the contaminated chicken legs in both the dry and wet seasons are recorded at the AJ and SH–dumpsite. The lowest levels of BAFs were recorded at the SA and BG – samples for wet season. Also, during the dry season, the lowest level of Zn was recorded at the contaminated leg sample of the CTR, DD, JK, SA, RA, PR and NTC, respectively. Thus, the most contaminated sample of legs due to zinc pollution were recorded at the AJ and SH sites, respectively during the dry season. This was attributed to the physiological functions of Zn in chicken systems.

Similarly, as presented in Tables 4.29 and 4.30, the highest BAFs of Zn in the contaminated liver was recorded during the dry season at the sample of JK–dumpsite while the lowest BAFs was recorded at the liver of KU-dumpsite as presented in Table 4.30. Overall, the higher levels of BAFs for Zn in the contaminated liver samples was recorded during the dry season while the lower levels of were recorded during the wet season. This was attributed to physiological functions of liver in the chicken system and dumpsite composition.

Similarly, the BAFs of Zn recorded in the brain of the contaminated samples of chicken across the sites are presented in Tables 4.29 and 4,30, respectively. The highest level of BAFs were noted during the dry season as compared to those recorded during the wet season. The most contaminated samples of brain due to Zn pollution were recorded at the NTC and DD dumpsite during wet and dry seasons, respectively. The lowest level of BAFs of Zn in brain were recorded at the AJ, BG, CTR, JK and PR, respectively while the lowest level of contaminations were recorded at the AJ, BG, CTR, DD, JK, KU, SH, RA

and PR during the wet season as presented in Table 4.29. This trend was also attributed to physiological functions of Zn in chicken systems.

b. Bioaccumulation Factors of Pb

Tables 4.31 and 4.32 revealed the bioaccumulation factors (BAFs) of Pb for wet and dry seasons, respectively. The levels of BAFs of Pb in the oesophagus during the wet season as presented in Table 4.31 was highest at the AJ–dumpsite while the lowest BAFs for Pb in oesopagus were recorded at the CTR, SA, RA, and PR, respectively. This was attributed to dumpsite functions and physiological functions of Pb in the chicken system. On comparing the levels of Pb recorded in both the dry and wet season, the highest level of BAFs were recorded during the wet season. This was attributed to dumpsite composition, leachate compositions and physiological function of the chicken system.

The BAFs of Pb recorded across the sites in lungs and bones of the contaminated chicken samples during the wet season are presented in Table 4.31. The results revealed insignificant levels of BAFs across the sites and seasons. The clearly indicates that the sample of lungs of chicken samples were contaminated by Pb in both the dry and wet seasons, respectively which was attributed to physiological functions of Pb in the chicken system. Also, the BAFs for Pb recorded in the kidney of the KU samples was the most contaminated sample in both the dry and wet seasons, respectively. On comparing the results obtained in both the dry and wet seasons, the highest BAFs for Pb was recorded in BG sample while the lowest levels of contaminations were recorded at CTR, SA, RA and PR–samples, respectively.

Similarly, the BAFs of Pb recorded in the intestine across the sites and during the wet season as presented in Table 4.31 indicate that the highest level of contamination was recorded in the intestine sample of the AJ–dumpsite while the lowest was noted at the CTR, JK, SA, RA and PR–sites respectively. On comparing the levels of BAFs across the seasons, the samples of intestine were mostly contaminated during the wet season. This was attributed to bioaccumulation of Pb, dumpsite composition and bioavailability of Pb in the dumpsite soils, respectively.

The levels of BAFs of Pb recorded in the contaminated heart samples during the wet and dry seasons were insignificant, this clearly indicates that they were not contaminated by Pb across the seasons, this was attributed to physiological functions of Pb in the chicken systems. Similarly, the levels of BAFs recorded for Pb in the contaminated chicken during the wet season was highest at the sample of the AJ–dumpsite and were lowest at the CTR, DD, JK, SA and PR–dumpsites, respectively. On comparing the levels of Pb recorded across the seasons, the highest BAFs were generally recorded during the wet season as compared to those recorded during the dry season, this was attributed to bioaccumulation of lead in gizzard and its bioavailability in soil.

The bioaccumulation factors of Pb in feather of the contaminated chicken samples across the seasons are presented in Table s 4.31 and 4.32, respectively. The highest levels of BAFs for Pb during the wet season were recorded in feather samples from the AJ, CTR, SA, RA and PR–sites, respectively. Also, during the dry season, the levels of BAFs for Pb recorded in feather samples were generally lower than those recorded in wet season. Also, during the dry season, lower levels of contamination were generally recorded in the feather samples as compared to those recorded during the wet season. Overall, feather samples of

BG and KU were mostly contaminated by Pb while samples of CTR, RA and PR were less contaminated during the dry season as presented in the Table. This was attributed to bioavailability of Pb in the soil as well as dumpsites compositions.

The wattle samples of the contaminated chicken samples were also investigated for possible bioaccumulation of Pb across the sites and seasons as presented in Tables 4.31 and 4.32, respectively. As presented in the Table, the highest level of BAFs for Pb during the dry season was recorded at the wattle sample of the BG- dumpsite while the lowest level of contaminations were recorded at the samples of the AJ, CTR, DD, JK, SA, RA, PR and NTC–dumpsites, respectively. Conversely, during the wet season, the highest level of contamination was recorded at the BG - dumpsite and the lowest was recorded at the AJ, CTR, DD, JK, SA, RA, PR, and NTC, respectively as presented in Table 4.31. On comparing the results of BAFs for Pb in the contaminated wattle samples across the sites, the highest levels of contaminations were recorded during the wet season.

Also, the skins of the contaminated chicken samples were investigated for possible Pb bioaccumulation across the sites and seasons as presented in Table 4.31 and 4.32. From the results, the highest level of contamination in the skin samples during the wet season was recorded at the NTC–dumpsite while the lowest were recorded at the CTR, SH and RA –dumpsites, respectively during the wet season. Similarly, the levels of BAFs for Pb in the skin samples of the contaminated chicken samples during the dry season were highest at the sample from the PR–dumpsite while the lowest level of contamination were recorded at the sample of the SH, RA and CTR–sites, respectively as presented in Table 4.32. The trend recorded for the bioaccumulation of Pb in the skin samples across the sites and seasons were different, this was attributed to physiological functions of Pb in the chicken system.

Similarly, on comparing the BAFs of Pb in the contaminated head across the seasons, the highest level of contamination was recorded during the wet season across the sites and was attributed to bioaccmulative effects and dumpsite composition. Also, the highest level of contamination of the chicken head during the wet season was recorded at sample from the SH–dumpsite while the lowest level of contamination was recorded at the CTR, DD, RA, and PR, respectively, as presented in the Tables.

Also, the BAFs of Pb recorded in the muscles samples across the sites and seasons were generally high across the season. Generally, higher levels of BAFs for Pb were recorded during the wet season as compared to those recorded during the dry season, this was attributed to bioaccumulative effects. Also, during the dry season, the highest BAFs of Pb in the muscle samples were recorded at the sample of the BG–dumpsite while the lowest BAFs was recorded at the CTR, JK, KU, PR and NTC, respectively. Conversely, during the wet the most contaminated muscle sample due to Pb pollution was noted at the RA–dumpsite while the samples of the CTR, JK, KU and PR were less contaminated. The difference observed in the bioaccumulative effects of Pb across the seasons was attributed to the physiological functions of Pb in the chicken system.

Similarly, the samples of chicken legs were investigated for possible Pb poisoning across the sites and seasons as presented in Tables 4.31 and 4.32, respectively. During the wet season, the highest BAFs for Pb was recorded in the leg sample of the AJ–dumpsite while the lowest were recorded at the CTR, DD, JK, SA, RA, PR and NTC–dumpsites, respectively. Similarly, during the dry season, the highest level of Pb was recorded at the sample of the KU–dumpsite while the lowest was recorded at the sample of the CTR, DD, JK, SA, RA, PR and NTC, respectively. The trends of Pb bioaccumulation in legs of the

contaminated chickens were different across the seasons, this was attribute to the physiological functions of Pb in the chicken systems.

The possibility of liver poisoning was investigated across the sites and seasons and the results are presented in Tables 4.31 and 4.32, respectively. On comparing the bioaccumulation of Pb in liver of the chicken samples across the seasons, the higher level of liver contamination was recorded during the wet season as compared to those recorded across the sites during the dry seaon, this was attributed to bioaccumulation effects. The observed trend on the bioavailability of Pb across the sites were also different, for example, the highest level of liver poisoning was noted at the sample of BG–dumpsite during the BG–dumpsite while the lowest level of contamination was noted at the samples of the NTC, PR, RA, JK, SA, DD and CTR–sites, respectively.

The brain of the contaminated chicken samples were also investigated for possible Pb poisoning as presented in Tables 4.31 and 4.32, respectively. The most contaminated brain was recorded was recorded at the chicken samples of the BG–dumpsite while samples of the AJ, KU, SH and RA had the lowest contamination factors (BAFs) during the wet season. This was attributed to the bioavailability of Pb in soil, its leachability and dumpsite compositions, respectively.

c. Bioaccumulation factor of copper

The bioaccumulation factors of copper were also investigated in the contaminated chicken samples as presented in Tables 4.33 and 4.34. The BAFs levels

recorded in the oesophagus across the sites during the wet season was highest at the samples from the BG–dumpsites while the lowest level of BAFs was noted at the CTR and PR–site, respectively. During the dry season, the highest level of contamination was recorded at the sample from the BG–dumpsite while the lowest contamination was recorded at the CTR, RA and PR dumpsites. On comparing the bioaccumulation factors of copper in the contaminated oesophagus sample across the seasons, the highest level of contamination was recorded during the wet season. This was attributed to bioavailability of copper in the dumpsite soils and physiological functions of Cu in the chicken systems.

The BAFs for Cu recorded across the sites and seasons are also recorded for lungs of the contaminated chickens across the sites and seasons. The levels of contamination during the dry season was highest at the lung samples of sample from the BG–dumpsite and was lowest at the CTR and RA–sites, respectively. Conversely, the highest level of BAFs for Cu was recorded at the lung sample of the SH–dumpsite while the lowest levels of contaminations were recorded at the sample of KU and CTR, respectively. This was attributed to the physiological functions and biochemistry of the chicken systems. Generally, the highest level of contamination for Cu in the lungs across the seasons were recorded during the dry season, this was also attributed to dumpsite compositions.

Similarly, the BAFs for Cu were recorded in bones of the contaminated chicken samples across the sites and seasons as presented in Tables 4.33 and 4.34, respectively. As can be observed from the Tables, the highest level of contamination across the seasons was recorded during the dry season at the bone sample from the BG–dumpsite while the lowest level of contamination was recorded at the samples of the CTR, DD, JK,

KU and RA–dumpsite, respectively as presented in the Table 4.34. This was also attributed to dumpsite composition and bioavailability of Cu in soils.

Also, the bioavailability of Cu in kidneys of the contaminated chicken were investigated across the sites an seasons, the results were presented in Tables 4.33 and 4.34, respectively. The highest level of BAFs for Cu during the dry season was recorded at the sample of the BG–dumpsite while the lowest were BAFs were recorded at the samples of the CTR, DD, JK, KU and RA–samples respectively. Conversely, the bioaccumulation trend in the kidney of the samples during the wet season was different. The highest level of BAF was recorded at the kidney sample from the SH–dumpsite while the lowest were recorded at the CTR, DD and JK–dumpsites, respectively. The observed trends across the seasons were attributed to bioavailability of Cu in the dumpsite soils and dumpsite compositions.

The levels of BAFs for Cu in the intestine samples across the sites and seasons are also presented in Tables 4.33 and 4.34, respectively. Overall, the highest level of BAFs for Cu in both the dry and wet seasons across the sites was recorded at the sample of the NTC–dumpsite while the lowest levels of contaminations were recorded at the intestine samples of the CTR and RA, dumpsites, respectively. The trends observed for the bioaccumulation of Cu in the intestine of the chickens across the seasons were the same; this was also attributed to physiological functions of Cu in this organ.

Also, the levels of bioaccumulation/contaminations were recorded in the heart samples of the contaminated chicken samples across the sites and seasons, respectively as presented in Tables 4.33 and 4.34, respectively. On comparing the contamination levels

across the sites, the highest level of contamination in the heart samples was recorded during the dry season across the sites. The highest level of contamination was recorded at the sample from the NTC–dumpsite, this was also attributed to dumpsite compositions and its age.

Similarly, the level of bioaccumulation investigated in gizzard samples for Cu during the dry season across the sites as presented in Table 4.33. The most contaminated sample of gizzard during the dry season was recorded at the sample from the NTC and the lowest level of contamination was recorded at the RA and CTR–samples, respectively. Also, during the wet season, the trend observed was different from what was observed during the dry season in which the most contaminated sample of gizzard due to copper pollution was recorded at the sample of the SH–dumpsite while the less contaminated samples were recorded at the CTR and RA–dumpsites, respectively as presented in the Tables.

The BAFs of Cu investigated in the wattles across the sites and seasons are presented in Tables 4.33 and 4.34, respectively. On comparing the levels of contamination of wattles of the contaminated chicken samples across the sites and seasons, the samples were not contaminated by copper across the seasons with the exception of the wattle sample from the SH–dumpsite in both seasons.

Similarly, the BAFs of Cu were also recorded for the samples of skin across the sites and seasons. The highest level of contamination was recorded during the dry season. The most contaminated sample of skin was recorded at the sample from the BG–dumpsite during the dry season which was attributed to dumpsite composition.

The head of the contaminated chicken samples were also investigated for Cu poisoning across the sites and seasons. The head samples of chicken were not contaminated by copper across the sites with exception of samples at the DD, SA, SH and NTC, respectively as presented in Tables 4.33 and 4.34, respectively. Also, the BAFs of Cu recorded at the DD, SA, SH and NTC–dumpsites were attributed to dumpsite composition and bioavailability of Cu in soils.

The muscles of the contaminated samples of chicken across the sites and seasons were also investigated for copper pollution as presented in Tables 4.33 and 4.34, respectively. The highest level of contamination due to copper in muscle samples of chicken was recorded at the PR–dumpsite and the lowest level of contamination was recorded at the CTR–site. Also, during the wet season, the highest level of bioaccumulation in muscles was recorded at the soil from the PR–dumpsite while the lowest was recorded at the CTR and RA–dumpsites, respectively as presented in Table 4.34. The BAFs of Cu on the contaminated leg samples of Cu across the sites and seasons are presented in Tables 4.33 and 4.34. The highest level of contamination of leg samples across the seasons were recorded during the dry seasons in the sample of the NTC– dumpsite while the lowest level of copper poisoning of chicken legs were recorded at the leg samples of the RA and CTR–sites, respectively.

The levels of BAFs for copper were recorded in liver of chickens across the sites and seasons are presented in Tables 4.33 and 4.34, respectively. On comparing the results of liver pollution/bioaccumulation across the sites and seasons, the highest level of bioaccumulation of liver was recorded during season, this was attributed to the physiological function of copper in the liver of the chicken systems. During the dry season,

the highest level of Cu pollution across the sites was recorded at the NTC–dumpsite while the lowest level of contamination was recorded at the RA and PR–dumpsites, respectively as presented in Table 4.34. The brain samples of the contaminated chicken samples were also investigated for possible copper poisoning across the sites and seasons as presented in Tables 4.33 and 4.34. The results showed that the brain samples of copper across the sites and seasons were not contaminated by this was attributed to physiological functions of Cu in chicken system.

d. Bioaccumulation Factor of Cadmium

The bioaccumulation factors of cadmium were also recorded in the chicken samples of chicken across the sites and seasons in both the dry and wet seasons. The level of bioaccumulation factors of Cd were investigated in oesophagus samples of chicken across the sites, the highest level was recorded at the sample from the SH–dumpsite while the lowest BAFs was recorded at the sample of the CTR–site during the dry season. Similarly, the highest level of Cd was recorded at the samples from oesophagus of the BG–dumpsite while the lowest level of contamination was recorded for the sample of the CTR–site. The variation in trend variability was attributed to physiological functions of Cd in chicken systems. On comparing the bioaccumulation of the samples across the seasons, the higher level of bioaccumulation was recorded during the dry season, this was attributed to dumpsite compositions across the sites.

Similarly, the levels of Cd recorded in the lungs of the contaminated chicken samples during the dry season were highest during the dry season as compared to those recorded during the wet season. The highest level of contamination for lungs was recorded

at the BG – dumpsite while the lowest was recorded at the CTR–dumpsite during the dry season as presented in Table 4.36. However, the highest BAFs was recorded from sample of the SH –dumpsite while the lowest was recorded at the CTR–site during the wet season as presented in Table 4.35 and 4.36, respectively. The levels of bioaccumulation recorded for Cd in bones of the contaminated chicken samples across the sites as presented in Tables 4.35 and 4.36, respectively, indicates that the bones of the chicken samples were not contaminated by Cd across the sites and seasons except the samples of SA, RA and NTC, respectively.

The levels of bioaccumulation due to Cd poisoning of the kidneys across the sites and seasons as presented in Tables 4.35 and 4.36, respectively. Generally, the highest levels of contamination were recorded at the sample from BG–dumpsite while the lowest was recorded at the CTR–site, during the dry season as presented in Table 4.35. Similarly, during the wet season, the level of Cd was highest at the SH–dumpsite and was lowest at the PR–dumpsite, respectively. The trends observed across the seasons were different, this was attributed to physiological functions of Cd in kidney/chicken system.

Similarly, the levels BAFs for Cd recorded in the intestine of the contaminated samples of chickens are presented in Table 4.35 and 4.36, respectively. From the results, the highest level of contamination was recorded at the SH–dumpsite while the lowest level of BAFs was recorded intestine of chicken sample from the SH–dumpsite during the dry season. Conversly, during the wet season, the highest level of contamination was recorded at the BG–dumpsite while the lowest level of contamination was recorded at the CTR–site. The variation in bioavailability trends of the samples in both the dry and wet seasons were attributed to the physiological functions of Cd in the chicken systems.

Similarly, the heart of the contaminated chicken samples across the sites and seasons were investigated for possible Cd poisoning as presented in Tables 4.35 and 4.36, respectively. On comparing the levels of bioaccumulation across the seasons, the highest level of bioaccumulation for the heart samples were recorded during the dry season across the sites. This was attributed to dumpsite composition.

Also, the contamination level of gizzard due to Cd poisoning were investigated based on the BAFs as presented in Tables 4.35 a,d 4.36, respectively. During the dry season, the most polluted sample of gizzard due to Cd poisoning was recorded at the sample of the BG–dumpsite while the lowest level of contamination was recorded at the sample from the CTR–site during the dry season, as presented in Table 4.36. On comparing the results BAFs recorded during the dry season with those recorded during the wet season, the higher contaminations of gizzard samples across the sites were recorded during the dry season, this was attributed to dumpsite composition, bioavailability of Cd in dumpsite soils and leachates and the physiological functions of Cd in the chicken systems.

The levels of pollution recorded in feather of the contaminated chicken were investigated for possible Cd poisoning across the sites and seasons. The highest level of contamination in feather was recorded at feather of the BG–dumpsite while the lowest BAFs was recorded at the sample from the CTR-site during the dry season as presented in Table 4.36. Similarly, the levels recorded in feather of the contaminated chicken samples during the wet season was highest at the SH–dumpsite sample while the lowest BAFs for Cd was recorded at the CTR–site as presented in Table 4.35. The variations in the bioaccumulation trend were attributed to physiological functions of Cd in the chicken

systems. On comparing the levels of contamination of feather due to Cd poisoning, the highest level of contamination were recorded during the dry season across the sites.

Similarly, the levels of contamination of the wattle samples of the chicken across the sites and seasons as presented in Tables 4.35 and 4.36, indicates the investigated samples of wattles across the sites and seasons were uncontaminated across the sites and seasons with exception of samples at the AJ, BG and KU, respectively. This was attributed to physiological functions of Cd in chicken systems.

Similarly, the level of contamination of the skin due to Cd pollution/bioaccumulation was investigated across the sites and seasons, the results indicates the highest level of contamination of the skin sample of the BG –dumpsite and the lowest level of contamination was recorded at the sample from the CTR – site during the dry season as presented in the Table 4.35. During the wet season, the highest level of contamination was recorded at the skin sample of the SH –dumpsite and the lowest level of contamination was recorded from the sample of the SA–dumpsite. When the results of BAFs were compared across the seasons, the highest level of contamination was recorded during the dry season, this was attributed to bioavailability of Cd in soils, dumpsite compositions and physiological functions of Cd in the chicken samples.

The head of the contaminated chicken samples were also investigated for Cd bioaccumulation as presented in Tables 4.35 and 4.36, respectively. The results obtained across the sites revealed that the samples were not contaminated by Cd with the exception of samples at the DD, JK, SA, RA and NTC, respectively. This was attributed to physiological functions and bioavailabiliies of Cd in the dumpsite environment.

Also, the levels of contamination were investigated in the muscles of the contaminated chicken samples as presented in Tables 4.35 and 4.36, respectively. During the wet season, the highest level of contamination was recorded in the oesophagus of sample from the SH- dumpsite while the lowest level of contamination was recorded at the CTR– site, respectively. Conversely, the highest level of contamination was recorded at the sample from the BG–dumpsite while the lowest level of contamination was recorded at the CTR–site during the dry season as presented in the Tables.

Similarly, the legs of the contaminated chicken samples were investigated for possible Cd poisoning as presented in Tables 4.35 and 4.36, respectively. The highest level of contamination was recorded at the sample from BG–dumpsite while the lowest level of contamination was recorded at the sample of the CTR site during the dry season, this was attributed to bioavailability of Cd in the dumpsite soils. On comparing the levels of contamination chicken across the seasons, the highest level of contamination was recorded at the leg of samples during the dry season across the sites. This was attributed to physiological functions of Cd in the chicken systems.

Similarly, the levels BAFs for Cd in the contaminated samples of liver were investigated for possible Cd poisoning, the highest level of contamination was recorded at the sample from the BG-dumpsite while the lowest level of contamination was recorded at the CTR and RA–sites, respectively during the dry season. The levels of BAFs for Cd recorded in the contaminated liver samples across the sites and seasons were generally lower than those recorded during the dry season and the highest level of contamination was recorded at the sample of the SH-site while the lowest level of contamination was recorded at the RA and CTR–site, respectively. The bioaccumulation trends observed across the

seasons were different, this was attributed to physiological functions of Cd in the chicken systems and the bioavailability of Cd in the dumpsite soils, respectively.

The brain of chicken samples were also investigated for possible Cd poisoning across the sites and seasons, respectively as presented in Tables 4.35 and 4.36, respectively. The results obtained revealed significant amount of levels of BAFs at the JK, SA, PR and DD–dumpsites, across the sites. Overall, the higher level of brain contamination across the sites was recorded during the dry season while the lowest as presented in the Tables. The most contaminated sample of the chicken due to cadmium pollution was muscles and then liver across the seasons as presented in the Tables.

e. Mercury bioaccumulation in chicken samples

The bioaccumulation factors (BAFs) of Hg in the samples of the contaminated chicken across the sites are presented in Tables 4.37 and 4.38, respectively.

As presented in the Table during the wet season, the highest level BAFs was recorded in the RA–sample of the oesophagus across the sites while the lowest BAFs was recorded at the AJ–dumpsite. This was attributed to dumpsite compositions, leachability of Hg in the refuse waste. The highest level of pollution due to Hg poisoning was recorded during the dry season at the RA–dumpsite and the lowest level of contamination was recorded at the AJ–dumpsite, as presented in the Tables, this was attributed to dumpsite composition, bioavailability of Hg in the dumpsite soils and physiological functions.

Similarly, the levels of Hg recorded in the lungs of the contaminated chicken samples across the sites as presented in Tables 4.37 and 4.38, respectively. During the wet season, the highest level of BAFs for Hg was recorded at the contaminated lung samples of

the JK–dumpsite while the lowest levels were recorded at the samples of the CTR, SA, SH, RA and PR–dumpsites, respectively as presented in the Table. The variation recorded in the trends across the seasons was attributed to compositions of the dumpsite, bioavailability of Cd in soils and physiological functions.

The levels of bioaccumulative effect of Hg in chicken bones were also recorded across the sites and seasons as presented in Tables 4.37 and 4.38, respectively. The highest level of contamination was recorded during the dry season at the bone sample of the SA–dumpsite and the lowest level of contaminations were recorded in bone samples of the AJ, BG, DD, JK and KU–dumpsite, respectively. The variations in the bioavailability trend of Hg across the site were attributed to dumpsite composition, and bioavailability of Hg in the dumpsite soil.

Similarly, the levels of bioaccumulation of Hg was recorded in kidney of the contaminated chicken samples across the sites and seasons as presented in tables 4.37 and 4.38, respectively. The most contaminated kidney samples across the sites were recorded during the dry season. The highest levels of BAF for Hg in the kidney samples were recorded at the RA–dumpsite and the sample at the CTR–site had the lowest bioaccumulative factor as presented in the Tables. This was attributed to dumpsite composition and bioavailability of Hg in the dumpsite soils, respectively.

The levels of contaminations were also investigated in the intestine chicken samples across the sites and seasons for possible Hg poisoning. The results of BAFs indicate highest level of contamination of the sample of the RA–dumpsite while the intestine sample of the CTR–site was not contaminated by Hg during the wet season as presented in the Table

4.37. The BAFs of Hg in the intestine samples across the seasons, the sample of the RA–dumpsite was the most contaminated and the sample at CTR site was not contaminated by Hg across the sites and seasons, this was attributed to dumpsite composition and the bioavailability of Hg in the refuse wastes.

The levels of contamination due to Hg were also investigated in the heart of the chickens both across the sites and seasons as presented in Tables 4.37 and 4.38, respectively. Generally, the highest level of contamination was recorded during the dry season especially at the heart samples of the RA–dumpsite and the sample of the CTR site was not contaminated as presented in the Tables. This was attributed to physiological functions of Hg in the chicken systems. Also, the level of Hg poisoning was investigated in gizzard of contaminated sample chickens both across the sites and seasons as presented in Tables 4.37 and 4.38, respectively. Generally, the highest levels of Hg contamination in gizzard samples were recorded during the dry season at the sample from the KU–dumpsite while the lowest level of contamination was recorded at the sample of the CTR–site. This was also attributed to physiological functions of Hg in gizzard of the chickens.

The bioaccumulative factors (BAFs) were also investigated in feather samples of the contaminated chicken samples across the sites and seasons. The results indicate the higher levels of feather contaminations during the dry season as presented in Table 4.37, this was attributed to dumpsite composition. The highest level of contamination was recorded at feather sample of the JK–dumpsite while the lowest level was noted at the control site (CTR) across the seasons. Similarly, the levels of Hg contamination was investigated in wattles samples across the seasons for possible poisoning as presented in Tables 4.37 and 4.38, respectively. From the results, the samples were not contaminated by

Hg across the sites and seasons. This was attributed to physiological functions of Hg in the sample.

Also, the levels of Hg poisoning in the contaminated skin samples were investigated across the sites and seasons as presented in Tables 4.37 and 4.38, respectively. From the results, the highest level of contamination was recorded at the sample of BG–dumpsite during the wet season while the lowest was recorded at the CTR–site, respectively. Similarly, the highest level of contamination was recorded at the RA–sample while the lowest level of contamination was recorded at the control site during the dry season. The trend observed was attributed to bioaccumulation effects of Hg and dumpsite compositions.

Similarly, the BAFs were also investigated in the head samples of chicken across the sites and seasons as presented in the Tables. The samples were not contaminated across the sites and seasons. This was attributed to physiological functions of Hg in the chicken system.

Also, Hg poisoning of muscles samples across the sites and seasons were investigated for possible bioaccumulations as presented in tables 4.37 and 4.38, respectively. From the results, the highest level of contamination was recorded at the samples of the SA–dumpsite while the lowest was recorded at the CTR–site during the dry season. Similarly, in both the dry and wet seasons, the lowest level of contamination was recorded at the CTR site, which was the uncontaminated site. The BAFs of Hg in the liver revealed significant level of contaminations at the sample of the DD–dumpsite and the sample lowest in contamination during the dry season was the sample of the DD–dumpsite. On comparing the level of contamination of liver across the seasons, the higher level of

contamination was recorded during the dry season and this was attributed to dumpsite compositions.

Also, the legs of the contaminated chicken samples investigated for possible Hg poisoning revealed high level of contaminations during the dry season across the seasons. This was attributed to dumpsite composition, physiological functions of Hg in the chicken systems and its bioavailability in the soil. The most contaminated sample of leg during the dry season was the obtained at the DD-dumpsite, this was also attribute to the bioavailability of Hg in the dumpsites environment.

The level of contamination of Hg in the brain was investigated across the sites and seasons for possible Hg poisoning as presented in Tables 4.37 and 4.38, respectively. The results revealed that the brain samples were not contaminated by Hg across the sites and seasons without an exception. This was attributed to physiological functions of Hg in the chicken systems.

## 5.11 Heavy Metals in Human Residents Tissues Near the Dumpsites

### 5.11.1 Concentrations of Zn in human tissues

The concentrations of Zn in urine residents near the dumpsites across the sites and seasons are presented in appendices XXXI and XXXVI, respectively. From the results, the highest concentration of Zn was recorded in the resident of the SA–dumpsite while the lowest concentration was recorded at the BG–dumpsite during the wet season. On comparing the concentrations of Zn recorded in the urine samples across the sites, the highest concentration was recorded during the dry season, this was attributed dumpsite compositions, bioavailability of Zn in soils and the physiological functions of Zn in the

human tissues. The bioavailability trend of Zn in urine samples across seasons was as follows SA > JK > RA > AJ > NTC > DD > KU > PR > CTR > BG. On comparing the levels of Zn in the urine samples across the sites and seasons with the WHO (1997) tolerable limit, the levels were lower than the tolerable limit.

Also, as presented in Figure 4.51 and appendix XXXI, the highest level of Zn was recorded in blood samples of resident from the DD-dumpsite during the dry season and the lowest concentration was recorded from the resident of the RA–dumpsite. On comparing the levels of Zn recorded in both the dry and wet seasons, the highest concentration of Zn in blood was recorded during the wet season, this was attributed to the dumpsite compositions and the bioavailability of Zn in the resident environment. The bioavailability trend of Zn in blood was DD > JK > KU > CTR > NTC > SA > BG > PR > AJ > RA. Overall, the concentrations of Zn recorded in dumpsite residents were lower than the WHO (1997) tolerable limit of 5mg/L across the sites and seasons.

Similarly, the levels of Zn investigated in the nail samples of human residents across the sites revealed significant amount during the dry season as compared to those recorded during the wet season, this was attributed to dumpsite compositions, bioaccumulation effects and physiological functions of Zn in the human tissues. Also, during the dry season, the highest concentration of Zn in the nail sample was recorded at the DD–dumpsite while the lowest concentration was recorded at the JK–dumpsite which was attributed to dumpsite composition and bioaccumulative effects. Generally, the concentrations of Zn in blood, urine and nail samples, the high concentration of Zn was recorded at the nail samples across the sites with the exception of samples at the JK, KU, SA and CTR sites, respectively. Zinc in nails originate from a number of sources such as

air, water, and food that we consume (Strain *et al*., 1972; Mough *et al*., 1978; Casey and Hambidge, 1980).

The bioavailability trend of Zn in the nail samples was DD > NTC > BG > PR > KU > SA > CTR > AJ > RA > JK. Zinc is essential for maintaining normal growth, reproduction and lactation performance (Miller *et al*., 1979). It is also associated with associated with taste and smell acuity, wound and burn healing. It is essential in the integrity of the immune system as it plays a role in stabilization of cell membranes and microtubule polymerization (Hambridge *et al*., 1987). It is also involved in nucleic and protein metabolism and in the fundamental processes of cell differenciation and replication. It plays a role in the production, storage and release of several other hormones as well as in the effectiveness of receptor sites and end organs responsiveness (Hambidge *et al*., 1987).

Similarly, the concentrations of Zn in hair of the dumpsite residents investigated was highest at the resident of the NTC–dumpsite and lowest at the hair sample of the BG–dumpsite during the dry season. Overall, the levels of Zn recorded in hair were higher than those recorded at the nails, blood and urine samples, with exception of those recorded at the CTR, DD and BG –dumpsites respectively where the higher concentrations of Zn was recorded at the nails. The concentrations of Zn recorded in nails and hair in this study were generally above the concentrations of 0.695 ± 0.330 (hair) recorded by Ayodele *et al*. (2009).

Moreover, the concentrations recorded in this study was also lower than the range of 57.7µg/g recorded by Nnorom *et al*. (2005) and 173 to 189, 156.48 and 21.40 to 176.96ppm reported by Chojnecka *et al*. (2005, 2006) and Ulvi *et al*., 2002, respectively. Similarly, the

concentration of Zn recorded in hair and nails in this study were also lower than the concentrations of 174(hair), 129(hair), 108(nails), 205(nails), 151 to 168, 121 to 247, 140.6 and 110.29 to 286.59µg/g (nails) reported by Ryabukin (1978), Wilhelm *et al*. (1991), DeAntanio *et al*. 1982, Sandra *et al*. 2002, Sukumar and Submanian (2003) and Mehra *et al*. (2005). The trend observed for the bioavailability of Zn in the hair of the dumpsite resident was: NTC > KU > SA > RA > DD > JK > AJ > PR > CTR> BG. Also, strongly positive correlations were recorded between ZnUrineD Vs PbUrineD and PbBloodD, ZnUrineD vs PbUrineD, CunailsD, ZnBloodD vs ZnNailsD, CuNailsD, CuBloodD, CuBloodR, PbBloodR and CuBloodD, respectively as presented in Table 4.39, clearly indicate the common pollution sources of the samples. Overall, the highest concentration of Zn was recorded in dust samples as compared to those recorded in human fluids and tissue samples, respectively. The bioavailability of Zn in the human samples followed the trend: Nails > Hair > Blood > Urine.

The mean concentrations of zinc reported in hair, nails, blood and urine samples in this study revealed that the metal in the tissues may be playing some physiological roles which were consistent with the report of Vivoli *et al.* (1990). In addition to the dust particulates, other source of zinc was the underground water used by the residents which was already established in the result section in this work to have been polluted by the metal.

5.11.2 Concentrations of Pb in chicken organs

The levels of Pb in the resident of dumpsites across the sites and seasons are presented in appendices XXXII and XXXVII, respectively. The highest level of Pb was recorded in the urine samples during the dry season as compared to those recorded during the wet season. During the dry season, the highest level of Pb was recorded in the urine

sample of the resident of the JK-dumpsite while the lowest concentration across the site was recorded at the sample of the PR–dumpsite as presented in appendices XXXII. The bioavailability of Pb in urine samples of the dumpsite residents followed the trend: JK > AJ > KU > RA > SA > DD = BG > NTC > CTR > PR.

The levels of Pb recorded in the blood samples of the residents across the sites and seasons are presented in appendices XXXII and XXXIII, respectively, and Figures 4.53 and 4.54, respectively. From the results, the highest level of Pb was recorded at the resident sample of the SA - dumpsite while the lowest concentration was recorded at the control site (CTR). The concentrations of Pb recorded in the blood samples of residents across the sites were significantly different at $p \leq 0.05$. On comparing the levels of Pb recorded in both the dry and wet seasons, the highest level of Pb were recorded during the wet season across the sites, this was attributed to bioaccumulation effects. The bioavailability trend of Pb in the blood samples across the sites and seasons was SA > JK = KU > AJ > BG > PR > NTC > RA > DD > CTR.

Also the levels of Pb recorded in the nail samples of the dumpsite residents across the sites was and season are presented in appendices XXXII and XXVII and Figures 4.53 and 4.54, respectively. The highest concentrations of Pb are recorded in nail samples of the resident while the lowest concentration was recorded at the sample of the NTC resident across the seasons. Generally, the levels of Pb in the resident samples were higher during the dry season, this was attributed to the dumpsite compositions. The bioavailability trend of Pb in nail samples was DD > KU > SA > BG > RA > PR > JK > CTR > AJ > NTC. On comparing the levels of Pb in nail with those in urine and blood samples, the highest level of bioaccumulation across the seasons and sites were recorded in nail samples with the

exception of samples at the JK, AJ and NTC–dumpsites, respectively. The levels of Pb across the sites and seasons were significantly different across the seasons at $p \leq 0.05$. Similarly, the levels recorded in this study were lower than the range of 9.1 to 194.5µg/g reported by Nnorom *et al*., (2005) but higher than the concentration of 0.464 (nail) mg/g reported by Ayodele *et al*. (2009), 1.046 mg/kg reported by Boris *et al*. (1994), 0.5 to 25.00ppm and 0.5 to 35.0ppm reported by Fergusson *et al*. (1990), respectively. Also, the levels of Pb reported in this study were lower than the ranges of 10.40 to 67.00µg/g and 14.42 to 48.30µg/g reported by Sukumar and Subraannian, (2003), Fergusson, (1990), and Boris, (1994), respectively.

Similarly, the levels of Pb investigated in the residents' hair across the sites and seasons as presented in the appendices. The highest concentration of Pb in the hair samples were recorded in the samples of the AJ–dumpsite and the lowest was recorded at the CTR – site during the dry season. The trend of the bioavailability of Pb during the dry season both across the sites was AJ > BG > RA > NTC > SA > DD > PR > JK > KU > CTR. The levels of Pb recorded in the hair samples across the sites during the dry season were lower than the range of 9.1 to 194.5µg/g reported by Nnorom *et al*. (2005). The results in this study were also higher than the ranges of 0.97 to 44.9ppm, 10.40 to 67.005µg/g, 14.42 to 48.305µg/g and 6.55 to 16.20 µg/g reported by Fergusson *et al*. (1990), Suleiman *et al*. (2003), Boris *et al*. (1994). Also, the ranges of 7.6 to 107.1 to 8.64 to 129.42 mg/kg were reported by Fergusson *et al.* (1990) and Chojnecka *et al*. (2006), respectively.

On comparing the concentrations of Pb in hair with those in nails across the sites, a significant difference was indicated across the sites at $p \leq 0.05$. The concentrations recorded in the hair samples were also above those recorded in the nail samples with the

exception of those at the CTR, DD, JK and KU, respectively. This was attributed to dietary effects, since human hair and nails are recording filaments over long periods of time and hence furnish a print out of post nutritional event (Strain *et al*., 1972) as dietary levels of some of the essential micro-element s have been reported to correspond to hair concentrations of the elements as reported by Reinhold *et al*. (1966), Strain *et al*. (1966), Potter *et al*. (1974), Maugh (1978), Katz *et al*. (1979), Hopps, (1977), Casey and Hamodoa (1980). The cosmetologists diagnose hair and skin related problems using this system. Also, the degree of relationship of Pb was determined among the samples both across the sites and seasons and strongly positive correlation was found between PbUrineD vs CdNailsD, CdHairD, CdNailsR, HgUrineD, HBloodD, HgNailsD, HgHairD, HgUrineR, CuDustD, PbDustD, PbBloodD vs CdNailsD, CdHairD, HgUrineD and HgBloodD, respectively. This clearly, indicates the common source of pollution of these samples, which is majorly, the dumpsite environment. The trend in the concentrations of lead across the sites for the dry season was Hair > Nails > Urine > Blood.

### 5.11.3 Concentrations of Cu in chicken

The concentrations of copper in the urine samples of the dumpsite residents across the sites and seasons as presented in the appendices XXXIII and XXXVIII were highest during the dry season across the sites. During the dry season, the highest concentration of Cu in the urine samples was recorded at the sample of the JK–dumpsite while the lowest was recorded at the CTR–site. The concentrations of Cu in the urine samples were significantly different at $p \leq 0.05$ across the sites. Also, the bioavailability trend of Cu across the sites was: JK > PR > CTR > SA > RA > NTC > KU > DD > BG > AJ.

Similarly, the concentration of Cu in the blood samples of the human residents was highest at the human urine sample from the KU–dumpsite while the lowest was recorded at the PR–sample during the dry season as presented in appendix XXXIII. Conversely, the highest concentration of Cu was recorded at the PR–dumpsite while the lowest concentrations in the blood samples were recorded at the CTR–site during the wet season. On comparing the levels of Cu in the blood samples of human residents across the seasons and seasons, the concentrations were significantly different at $p \leq 0.05$. The bioavailability trend of Cu in blood were different in both the dry and seasons. During the wet season, the trend was: PR > RA > JK > NTC > KU > AJ > BG > DD > CTR = SA. Also, during the dry season, the trend was: PR > KU > DD > SA > BG > CTR > NTC > AJ > JK > RA.

Also the levels of Cu in the nail samples of the human residents were recorded across the sites and seasons as presented in appendices XXXIII and XXXIII and Figures 4.55 to 4.56, respectively. The results presented revealed the highest concentration of Cu in the nail samples of the DD–dumpsite during the dry season and the lowest concentration was recorded at the CTR–site. On comparing the concentrations of Cu in the nail samples with those in blood and urine samples, the highest level of bioaccumulation was recorded at the nail samples during the dry season. The bioavailability trends recorded in nail samples in both the dry wet seasons were : DD > AJ = RA > KU > SA > NTC > BG > PR > CTR > JK and SA > JK > KU > AJ > RA > PR = NTC > BG > DD > CTR. The variations in the bioavailability trends of Cu were attributed to the bioavailability of Cu in the dumpsite environment. The human nails are recording filaments that can reflect metabolic changes of many elements over long periods of time and hence furnish a printout of post nutritional event (Strain *et al*., 1972). The concentration of Cu in the nails of residents across the sites

and seasons, they were significantly different at $p \leq 0.05$ which indicates the common source of pollution.

Also, the levels of Cu in the hair samples were investigated in the hair samples of the residents across the sites and seasons as presented in Figures 4.55 and 4.56, respectively. On comparing the levels of Cu recorded in hair samples of the dumpsite resident across the seasons, the concentrations recorded in the hair samples during the dry season were higher as compared to those recorded during the wet season, this was attributed to bioaccumulation effects. The highest concentration was also recorded at the hair sample of the AJ–dumpsite during the dry season. Also, the levels of Cu in the hair samples were compared both across the sites and seasons, the y were significantly different at $p \leq 0.05$, this indicate their common source of pollution. The concentrations of Cu in the hair samples with those in nails, blood and urine, the highest concentration were recorded in the nail samples both across the sites and seasons with the exception of samples at the AJ, DD and KU–dumpsites, respectively.

The bioavailability trends of Cu were different in both the dry and wet seasons, respectively, this was attributed to physiological functions of Cu in the human tissues. The bioavailabilities during the dry and wet seasons are: AJ > NTC > BG >DD > CTR > KU > SA > RA > JK > PR and AJ > BG > JK > KU > SA > DD > RA = PR = NTC > CTR. From the levels of Cu recorded in the hair samples across the seasons, it is reasonable to believe that Cu in human tissues may be playing some physiological roles. It is also possible to suggest that Cu in the hair and nails originate from a number of sources such as the particulate dust, water and food we consume (Strain *et al*., 1972; Maugh *et al*., 1978; Casey and Hambidge, 1980). There were strongly positive correlations between CuHairD vs

CuNailsR, CuHairR, HgNailD; CuUrineR vs CdNailsR, CuBloodR Vs CuHairR, CuBloodR vs HgUrineD, CuNailR Vs CuDustD, HgDustR, respectively. This clearly indicates their common pollution source.

5.11.4: Concentrations of Cd in chicken

The concentrations of Cd in the urine samples of human residents as presented in appendices XXXIV and XXXV revealed the highest concentration of Cd at the sample of the KU–resident while the lowest was recorded at the sample of the RA–resident across the sites. On comparing the results of Cd in the urine samples of the across the seasons, higher levels of Cd were recorded across sites during the dry season. This was attributed to physiological functions of Cd in the human tissues and bioavailability of Cd in the dumpsite environment. Conversely, the highest level of Cd was recorded at the sample of the JK–dumpsite during the wet season and the lowest concentration was recorded at the sample of the DD–dumpsite. The levels of Cd were significantly different at $p \leq 0.05$ across the seasons, this clearly indicates their common pollution source. Also, the bioavailability trends of Cd in the dry and wet seasons were KU > NTC > DD > PR > JK > CTR > AJ > BG = SA > RA and JK > PR > CTR SA > BG > BG > AJ = KU > NTC > DD, respectively. The variation in the bioavailability of Cd in the urine samples was attributed to the physiological functions of Cd in the human tissues.

Similarly, the levels of Cd recorded in the blood samples of the human residents at the vicinity of dumpsite were significantly different both across the sites and seasons at $p \leq 0.05$. During the dry season, the highest level of Cd was recorded at samples of the PR–resident and the lowest was recorded at the sample of the resident of the RA–dumpsite. The bioavailability trends of Cd recorded in the blood samples of human residents in both the

dry and wet season were: PR > SA > AJ > BG = NTC > RA > DD > KU > CTR > JK and RA > KU > PR = AJ > CTR > JK > BG > SA > NTC > DD, respectively as presented in the Figures and appendices. Thus, the highest concentration in blood samples was recorded in the urine sample of the resident of the RA–dumpsite. The variation in the bioavailability trend of Cd in the urine samples across the seasons was attributed to physiological functions of Cd in human tissues and the bioavailability of Cd in the dumpsite environments.

Also, the levels of Cd investigated in the nail samples of human residents across the sites and seasons were significantly different at $p \leq 0.05$. The highest concentration of Cd was recorded at the sample of the KU–resident and the lowest was recorded at the sample of the resident of the RA–dumpsite during the dry season, this was attributed to dumpsite composition. The bioavailability trend of Cd in both the dry and wet seasons were KU > BG > PR > NTC = JK > AJ > CTR > SA > DD > RA and JK > AJ > RA > SA = PR > BG > KU > NTC > CTR > DD, respectively. Thus, the highest concentrations of Cd were recorded at the residents of the KU and PR–dumpsite in both the dry and wet seasons, respectively. The variation in the trends across the seasons was attributed to the bioavailability of Cd in the dumpsite environment.

Similarly, the levels of Cd in the hair samples of the human resident were significantly different at $p \leq 0.05$ across the seasons. The highest level of Cd was recorded during the dry season at the sample of the NTC-dumpsite and the lowest was recorded in the hair sample of the CTR - resident. The levels of Cd recorded in the hair samples during the dry season was higher than those recorded during the wet season, this was attributed to physiological functions of Cd in the human tissues and its bioavailability in the dumpsites

environment. The observed trends for the bioavailability of Cd in both the dry and wet seasons were: NTC > BG = DD > KU > JK > AJ > SA > RA > PR > CTR and PR > AJ = CTR > JK > SA > KU > RA > NTC > BG > DD, respectively.

The levels of Cd recorded in human hair and nails were below those recorded in the blood as presented in Figures 4.57 and 4.58, respectively. This is because the concentrations of Cd in the blood signify short term exposure while those in the nails and hair show long term exposure. In addition, blood contains components absorbed and temporarily in circulation before excretion and/or storage (EPA, 1980). The hair and nails in which minerals are stored can be used to effectively monitor the highest priority toxic metals (Barrett, 1985; Afridi *et al*., 2006 a, b; Kazi *et al*., 2008). Also Cd in hair and nails is the simple laboratory test which helps to monitor how well bodies are responding to our diets and environment (EPA, 1979).

There were strongly positive correlations between CdUrineD vs CdBloodD, CdnailsD, CdhairD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, CdUrineR, CdBloodR, CdNailsR, CdHairR, HgUrineD, HgBloodD, HgNailsD, HgHairD, HgUrineR, HgBloodR and HgHairR, CdBloodR Vs CdnailsR, HgUrineD, HgNailsD, PbDustD and CdDustD, respectively. This indicate their common pollution sources which is the dumpsite and its environment.

5.11.5: Concentrations of Hg in chicken

The concentration of Hg in human tissues are presented in Figures 4.49 and 4.60, respectively. The level of Hg in the urine sample of the resident during the dry season was highest at the sample of the SA–resident while the lowest concentration was recorded at the

PR–residents. On comparing the bioavailability trends of Hg across the seasons, the higher level of contamination was recorded during the dry season, which was attributed to dumpsite composition. The bioavailability trend of Hg in both the dry and wet seasons were NTC > KU > SA > KU > DD > BG > AJ > RA > PR > JK and PR > JK > KU > NTC > AJ > BG > SA > RA > DD > CTR, respectively.

The levels of Hg in urine samples were significantly different at $p \leq 0.05$ across the seasons. The correlation analyses of HgUrineD vs HgBloodD, HgNailsD, HgHairD, HgUrineD, HgUrineR, HgBloodR, HgNailsR and HgHairR, respectively, this clearly revealed common pollution source. Also, strongly, positive correlation was recorded between HgUrineR vs HgBloodR, HgHairR, PbDustD, this clearly indicates the common pollution source, which is the dumpsite environment. Hg poisoning was affirmed by elevated urine/blood contamination. Mercury inhalation results in pulmonary damage in addition to muscular effects. Mercury ions produce toxic effects by protein precipitation, enzyme inhibition and generalized corrosive action (Hirada., 1995).

The levels of Hg in the blood samples as presented in Figure 4.59 was highest at the residents of the AJ–dumpsite and lowest at the residents of the KU–dumpsite, respectively. On comparing the levels of Hg in blood across the seasons, the highest level was recorded during the dry season and was attributed to bioavailability of Cd in the dumpsite environment. The bioavailability trend of Hg recorded in both the dry and wet seasons were AJ > RA > NTC = BG > PR > JK > DD > CTR > KU > SA and SA > AJ > PR > RA > DD > NTC > JK > KU > JK > CTR. The variation in the bioavailability trend of Hg was attributed to dumpsite composition and Hg in the particulate dust. The levels of Hg recorded across the sites were significantly different at $p \leq 0.05$, indicating the common

pollution source of Hg. If elemental mercury is lipid soluble, a characteristic that facilitates its diffusion across the alveli into the circulation as well as distribution throughout the liphophilic compartments of the body, penetrates the blood brain barrier, it is ionized and becomes trapped in the compartment where it is available to exact its neurotoxicity (Takahata and Watanabe, 1970). Elemental mercury has longest retention in brain with the detectable levels present for years following exposure (Takahata and Watanabe, 1970; Rothstein *et al*., 1960; Matsuo, *et al*., 1989).

Also, the levels of Hg investigated in the nail samples of the residents across the seasons are presented in Figures 4.59 and 4.60, respectively. From the results, the highest level of Hg was recorded in nail samples of the RA–residents while the lowest concentration was recorded in the resident of the DD–dumpsite, respectively, during the dry season. The concentrations of Hg recorded in nail samples across the sites were significantly different at $p \leq 0.05$. The high concentration of Hg was generally, recorded during the dry season across the sites as presented in the Figures. The bioavailability trends of Hg in human nail samples in both the dry and wet seasons were RA > BG > JK > PR > AJ > NTC > CTR > KU > SA > DD and SA > AJ > DD > RA > PR > BG > JK > NTC > KU > CTR, respectively. The variation in the bioavailability trend was attributed to the forms of Hg in the dumpsite environment.

The concentration of Hg in hair samples of residents are presented in Figures 4.59 and 4.60, respectively. The highest concentration of Hg was recorded at the DD–dumpsite while the lowest concentration was noted during the dry season. Comparing the levels of Hg recorded in both the dry and wet seasons, the concentrations recorded during the dry season was higher than those in the wet season and was attributed to bioavailability of Hg

in the dumpsite environment. The concentrations were also significantly different at $p \leq 0.05$. The levels of Hg in nails were positively correlated with those in the blood which clearly indicates their common source of pollution. The bioavailability trend of Hg in both the dry and wet seasons in hair samples follow the trends of DD > NTC > JK > AJ > PR > RA > SA > BG > CTR and NTC > PR > DD > JK > RA > SA > KU > AJ > BG = CTR, respectively. Overall, there was strongly positive correlation between HgHairR vs HgUrineR, HgHairD vs HgUrineD and HgHairD vs HgnailsD across the sites, these indicate their common pollution source.

### 5.12.1 Performance of bismuth electrode for electrochemical analysis

The development of electro-analytical method for real-time determination of heavy metals contents in water and other environmental samples is imperative especially with the cost of analysis using atomic absorption spectroscopy. As shown in the result section, the SWV has lowest limit of detection compared to ICP-OES technique. Zn exhibited the highest, this was attributed to more negative reduction potential of zinc as predicted in the electrochemical series compared to the rest of the metal ions investigated. Comparative voltammograms of the standard solutions of lead in 100mM $NaNO_3$ solutions of the supporting electrolytes on the Bi working electrodes are presented in Figure 4.62. The repeatability of the peaks were studied at various concentrations for all the heavy metals using standard solution of cadmium (30mM) as presented in Figure 4.63.

Malakhova *et al.* (2007) made a comparison between microscopic and electrochemical data and suggested that different surface microstructure of the electrodes have a considerable effect on their electrochemical properties.

5.12.2 Linearity of calibration curve

SWV showed good linearity for Pb, Cu, Cd and Zn. However, good linearity was not obtained in the calibration plot of Hg as $Hg^{2+}$ oxidises Bi. The bismuth electrode adopted for the determination of Zn in this work was not satisfactory as reflected by the calibration plot. This was attributed to reduction of hydrogen on the surface of bismuth electrode. The SWV voltammograms of cadmium conducted at different deposition times revealed increased peak current with time this was found to be proportional to the deposition time.

## 5.13 Comaparative studies of Heavy Metals in Water by ICP-OES and SWV Techniques

The concentrations of heavy metals determined by both the spectroscopic and electrochemical methods are presented in Table 4.42. From the results, the levels of Cu detected by the spectroscopic method were higher than those reported by the electrochemical method (SWV) at the samples of the F, H, K, L, M, N, O, which means that the metals would not readily be released into the environment except under very harsh conditions. Conversely, the concentrations of Cu recorded at G, I, J samples were higher using electrochemical method as compared to spectroscopic method, this was attributed to the lability of the metal in these samples. Overall, the concentrations of Cu recorded in water samples were all below the WHO tolerable limit of 1.5ppm. This clearly indicates that the analysed samples were not polluted by copper. Also, the levels of copper detected across the sites were strongly positively correlated with Zn, Cd, Pb and Hg, as presented in Table 4.43, this indicate their common pollution source.

Similarly, the concentrations of Pb were determined by both the electrochemical and spectroscopic methods as presented in Tables 4.42. The results revealed significantly high concentration of Pb at the G, I and F – samples by the electrochemical method (SWV) indicating that the levels of Pb in these samples would be readily release into the environment for contamination. Conversely, the levels recorded in the J, K, L and O samples were by spectroscopic method, this also, clearly shows that they are not readily bioavailable for environmental contamination as they are present in the organic phase which is very harsh to release into the environment. The most bioavailable fraction of Pb was recorded at the F –sample, which is the most polluted/contaminated sample. The levels of Pb in the analysed water samples were above the WHO (1997) tolerable limit of 0.001 by spectroscopic method while the concentrations of Pb in the samples of F, G, I and N samples were above the tolerable limit using the electrochemical method, this clearly indicates that these samples were the most polluted samples in terms of Pb pollution. Also, strongly positive correlations were recorded between Pb vs Zn, Cd and Hg, respectively, which clearly indicates their common pollution source.

Also of significance, are the comparative analyses of water samples by both the spectroscopic and electrochemical methods (SWV). The concentrations recorded revealed higher concentrations by electrochemical method as compared to spectroscopic method. This was attributed to the form in which the metals exist, which is the bioavailable fraction. Overall, the concentrations of Zn recorded in the samples were below the toxic limit of 5ppm which indicates that the metal is not contaminated by Zn as presented in Table 4.43. The levels of Zn was strongly positively correlated with those of Cd and Hg, this also clearly indicates their common pollution source.

The levels of Cd recorded by both the SWV and spectroscopic are presented in Table 4.42. From the results, Cd was not detected in G, H, I, J, K, L, M, N, by the SWV technique which indicates that Cd in these samples would be released into the environment under very harsh condition. However, Cd was detected in the water sample of the F–site which was above the WHO (1997) toxic limit of 0.003ppm. Similarly, the concentrations of Cd in the samples were positively correlated with Hg and Zn. Also, the concentrations of Cd in water were also strongly positively correlated with Pb as presented in Table 4.43, which clearly indicates their common pollution source.

Also, the levels of Hg were investigated in the water samples using both the spectroscopic and electrochemical methods as presented as presented in the Table 4.42. The results revealed that mercury was detected by spectroscopic as compared to electrochemical method, this clearly indicates that Hg in these samples would be released into the environment under very harsh conditions. The correlation coefficients of Hg with other metals were negative, indicating an inverse relationship with the exception of Cd and Cu. The total concentrations of Pb, Hg, and Cd in the water samples were above the standard limits of 0.001, 0.001 and 0.003ppm, respectively for water samples. However, the Hg and Cd were not detected by SWV technique and hence would not be readily bioavailable under normal condition except at site F for Cd. Thus, the analysed samples of waters were contaminated by Pb without an exception hence becomes a serious threat to consumers.

## 5.14 Electrochemical Atomic Force, Tunnelling and Optical Microscopic Studies of the Bismuth Surface

As presented in the results section, electrode surface before and after the square wave experiment shown by the tunnelling electron microscope clearly indicate a

remarkable difference from the interphase between electrolytic material and the glass. During the electrochemical experiment, the concentration of any metal of interest can be investigated and its concentration determined using current-time relationship and Beer–Lambert's law. There was surface modifications after the treatment as observed in b and c images, this was attributed to adsorption of the metal ions onto the electrode surface during the experiment which could be determined quantitatively.

# CHAPTER SIX

## 6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

## 6.1 SUMMARY

The study attempts to assess the impact of dumpsites to their immediate environments in Zaria Metropolis. In the cause of the research a questionnaire was administered as a guide to get some specific information about the residents (such as residency period, presence of wells, smokers, non-smokers etc). Findings from the study indicated that the major constituents of the dumpsites were polythene bags, wood, plastics and textile materials and the composition of the refuse wastes vary from one season to another with the relative abundance of the particle size in the order sand > silt > clay, this shows that the refuse waste soils were sandy-loamy in nature and may have poor water and metal retention capacities. Also, the bioavailability studies were carried out on the refuse waste soils, leachates and well water samples to determine the metals that would be easily released into the environment. Overall, the trend of the bioavailability of the metals in dumpsite leachates was Zn > Cd > Pb > Hg > Cu. The levels of Zn, Cd, Cu and Hg in the dust particulates were positively correlated with those in the soil with few exceptions, indicating their common pollution sources. In addition, the transfer of toxic metal ions through the food chain was investigated using chickens as bio-indicators across the sites and seasons. It is interesting to note that the organs that were mostly contaminated by all the analysed metals in the chicken samples were muscles, gizzard, and oesophagus while kidney was mostly contaminated by cadmium and zinc, the brain samples of the chickens were also polluted by lead metal ions. The mercury affects mostly the leg, feather, head, kidney, etc. However, zinc and copper which are essential elements were mostly found to accumulate more in the leg, skin, liver, gizzard and oesophagus and the bioaccumulation

was more pronounced in the liver which was attributed to the roles it plays in the entire body system. Similarly, the urine, blood, nail and hair samples of human residents were investigated for possible metal poisoning, the concentrations of Cu and Zn in these samples were below the standard limits while those of Cd, Pb and Hg were generally above the standard limits across the sites. Excellent recoveries were obtained for Pb, Cd, Cu and Hg while, the % recovery was very poor for Zn which was attributed to its reduction potential. The non-toxic bismuth electrode was designed and tested which shows the detection limits of 0.005, 0.029, 0.033, 0.027 and 0.570µM for Cu, Pb, Zn, Cd and Hg, respectively.

## 6.2 CONCLUSION

Overall, the results of the analyses revealed that leachates, refuse waste soil, underground water, particulate dust and chicken samples were heavily polluted by Cd, Pb and Hg. Similarly, the samples of human residents' urine, blood, nails and hair samples were also contaminated by same toxic metals and this would pose serious health threat to the populace at the vicinity of these dumpsites resulting in metabolic disorder. Also, the pollution of the particulate dust, underground water and chicken samples at the vicinity of the dumpsite consequently affect the residents through the food chain transfer. The electro-analytical method could be used to determine the bioavailable fractions of these metals at cheaper rate especially when the sample size is large. Low concentrations were generally detected by the SWV as compared to ICP-OES technique indicating that an electro-analytical technique would be suitable for speciation studies of metals in the environmental samples. There is need to improve the detection limit of bismuth electrode to accommodate more metals with high degree of precision.

## 6.3 RECOMMENDATIONS

It is recommended that

i. The well water at the vicinity of the dumpsites should be treated thoroughly before use to minimize the adverse health effects such as kidney impairment, cancer, mental development in infants, toxicity to the central and peripheral nervous system associated with mercury, cadmium and lead bio-accumulations.

ii.The novel electrochemical method (especially the stripping method) should be adopted to save the cost of analysing large number of samples as the method was validated with good recoveries with the exception of Zinc, thus more work should be done to improve the performance of the electrode.

iii. Kaduna State Environmental Agency (KEPA) should ensure that the generation of hazardous waste is minimized and also provides adequate refuse waste disposal facilities.

iv.KEPA should also ensure environmentally sound management of wastes by preventing and punishing illegal traffic.

## REFERENCES


Abdulrafiu, O. M., Adeleke, A. K., Lateef, O.G. (2011). Quality assessment of groundwater in the vicinity of dumpsite in Ife and lagos, Southwestern Nigeria. *Advance Applied Science Research*, 2(1), 289–298

Ademoroti, C. M. A (1996). Environmental chemistry and toxicology. Foludex Press Limited Ibadan, *Nigeria.Advances in Soil Science* (B.A stewart ed), Springer–verlag, Pp. 4.

Afridi, H.I., Kazi, T.G., Jamali, M.K., Kazi, G.H., Arain, M.B., Jalbani, N., Memon, A.R. (2006a). Atomic absorption spectrometric determination of Zn and Cr levels in scalp human hair samples. Influence of ageing gender and diabetic condition. *Journal of Indian Chemical Society*, 83(10), 1062–1064

Afridi, H.I., Kazi, T.G., Jamali, M.K., Kazi, G.H., Shar, G.Q. (2006b). The status of trace and toxic elements in boil. Samples (Scapl hair) of skin–disease patients and normal subjects. *Turkish, L. Medical Science*, 36(4), 223–230

Agbenin, J. O. (1995). Laboratory manual for soil and plant analysis. Department of Soil Science , *Ahmadu Bello University, Zaria*. Pp.15-52

Ahlberg, G., Gustafssion, O. and Wedel, P. (2006). Leading of metals from sewage sludge during one year and their relationship to particle size. *Journal of Environmental Pollut*ion, 144 (2), 545–553.

Ahmadu Bello University (2013). At a glance. *Retrieved from www.abu.edu.ng* on the 8 April, 2014

Ahnstrom, Z.S., Parker, D.R. (1999). Development and asessesment of a sequential extraction procedure for the fractionation of soil cadmium. *Soil Science Society of America Journal*, 63, 1650

Ahumada, I.J., Mendoza, I.A. (1999). Sequential extraction of heavy metals in soils integrated with wastewater. *Commun. Soil and Plant Anal*yses, 30, 150 –1519

Aiyesanmi A. F, Imoisi, O.B. (2011). Understanding leaching behaviour of landfill leachates in Benin–city, Edo state, Nigeria through Dumpsites Monitoring. *Paris, Journal of Environment and Climate Change*, 1 (4)**,** 190–200.

Akan, J.C., Abdulrahman, F.I., Sodipo, O.A., Chiroma, Y.A. (2010). Distribution of heavy of metals in the liver, kidney and meat of beef, mutton, caprine and chicken from Kasuwan Shanu market in Maiduguri metropolis, Borno state, Nigeria. *Research Journal of Applied Sciences, Engineering and Technology*, 2(8), 743- 748.

Albores, A. F., Perez- Cid, B., Gomes, E. F., Lopez, E. F. (2000). Comparison between sequential extraction procedures and single extraction procedures and for metal partitioning in sewage sludge samples. *Analyst*, 125, 1353–1357

Allen, S.E. (1974). Chemical analysis of ecological materials. *Blackwell scientific publications, Oxford*, Pp 13–16

Alloway, B. J. and Davies, B. E. (1971). Heavy metals content of plants growing on soil contaminated by lead mining. *Journal of Agricultural Science Cambridge*, 76, 321 - 323.

Alloway, B.J. (1996). *Heavy metals in soils*. Halsted Press John wiley and Sons Inc. London, Pp. 240.

Alloway, B.J., Jackson, A.P., Morgan, H. (1990). The accumulation of cadmium by vegetables grown on soils contaminated from a variety of sources. *Science Total Environment*, 91, 223-236

Aluko, O.O., Sridhar, M.K.C., Oluwande, P.A. (2003). Characterisation of leachates from a municipal solid wastelandfill site in ibadan, Nigeria. *Nigerian Journal of Environmental Health Research*, 2(1), 32–37

Al–yaqout, A. F., Hamodoa, M. F. (2003). Evaluation of landfill leachate on acid climate–a Case Study, *Env. Int*. 29, 593–600.

Amadi, A.N. (2011). Assessing the effects of aladimma dumpsites on soil and groundwater using water quality index and factor analysis. *Australian Journal of Basic and Applied Science*, 5 (2)**,** 763 –770.

Amadi, A.N. Ameh, M.I. and Jisa, J. (2010). The impact of dumpsites on groundwater quality in Makurdi metropolis, Benue state. *Nature, Appied. Science J*ournal, 11 (2), 143–152.

American Water Works Association (AWWA) (2000*).* Standard Methods for the Examinations of waste water, Washington D.C: *American Public Health*: retrieved from http://www.awwa.org/about-us.aspx on June, 5, 2012

Amusan, A. A., Ige, D.V., and Olawale, R. (2005). Characteriscics of soils and crop uptake of metals in municipal waste dumpsites in Nigeria *Journal of Human Ecology*,17, 167-171.

Anake, W.U., Adie, G.U., Osibanjo, O. (2009). Heavy metal pollution at municipal solid waste dumpsites in Kano and Kaduna States, Nigeria. *Bulletin of Chemical Society, Ethiopia*, 23(1), 281–289

Anonymous (1999). *US law solid waste act 2, definition of solid waste for RCRA subtitle C. Hazardous waste* retrieved from http: //www.epa.gov./osw/hazard/dsw/, 1 January, 2013

Anonymous (2014). *What a waste: a global review of solid waste management*, retrieved from http/: //www.epa.gov./osw/hazard/dsw/, 1 April, 2013

APHA (2005). *Standard methods for the examination of water and waste water*. 20th ed. *APHA – AWWA – WPCF, Washington, D.C USA.*

Arakel, A.V. and Hongjum, T. (1992). Heavy metal geochemistry and deposition pattern in coastal sediments, soils and water of Kedron brook floodplain area, Brisbane, *Australia Journal of Environmental Geology and Water Science,* 20, 219 - 231

Asadi, H., Moussavi, A., Ghadiri, H., Rose, C.W. (2007b). *Flow driven soil erosion processes and the size selectivity of sediment.* Retrieved from www98.griffith.edu.au/dspace/bistream/handle/10072/42591/73978_1.pdf;jsessionid=00E49BCDF57205DE_F71418446AEa10B9?sequence = 1 on the 1st January, 2013

ATSDR (2001). Landfill gas primer: An overview for environmental health and human services, agency for toxic substances and disease registry. Division of health assessment and consultation.*www.atsdr.cdc.gov/HAC/landfill,html/toc.html accessed on the* 10th July, 2009

Awode, U. A., Uzairu, A., Balarabe, M. L., Harrison, G .F. S. and Okunola, O. J. (2008). Assessment of peppers and soils for some heavy metals from irrigated farmlands on the bank of river challawa, Northern Nigeria. *Pakistan Journal of Nutrition*, 7, 244–248

Awofolu, O.R. (2005). A survey of trace metals in vegetation, soil and lower animals along some selected major roads in metropolitan city of lagos. *Env. Monitoring and Assessment*, 105, 431-437

Awokunmi, E. E., Asaolu, S. S., Ipinmoroti; K.O (2010). Effect of leaching of heavy metal concentrations of Soils in some Dumpsites. *African Journal of Environmental Science and Technolology*, 4 (8), 495 – 499.

Awomeso, J. A., Taiwo, A. M., Gbadebo, A. M., Aromoro, A. O. (2005).Waste disposal and pollution management in urban areas. A workable remedy for the environment in developing contries. *American Journal of Environmental Science,* 6(1), 260–263.

Ayodele J.T., Gaya, U.M. (1998). Chromium, Manganese and zinc in Kano Municipality Street Dust. *Journal of Chemical Society of Nigeria*, 23, 24–31.

Ayodele J.T., Beyero, A.S. (2009). Lead and Zinc Concentration in Hair and Nails of some Kano inhabitants. *African Journal of Environmantal Science and Technol*ogy, 3 (3), 164–170

Babalola, O.O., Okonji, R.E., Atoyobi, J.O., Sennuga, T.F., Raimi, M.M., Ejim-Eze, E.E., Adeniran, O.A., Akinsiku, O.T., Areola, J.O., John, O.O. and Odebunmi, S.O. (2010). Distribution of Lead in Selected Organs and Tissues of albino rats exposed to acute lead toxicity. *Scientific Research and Essay*, 5 (9), 845–848

Back, I. A. (1947). An examination of the Detjare method for determining soil organic matter and a proposed modification of the chronic acid titration. *Soil Sci*ence, 37, 29-36.

Bäckströrm, M., Nilson, U., Karsten, Bert, A. and Stelan, K. (2003). Speciation of heavy metals in road run-off and roadside total deposition. *Water, Air and soil Pollution*, 147, 343–366.

Bacud, L., Sioco, F. and Majain, J. (1994). A descriptive study of the water quality of drinking wells around payatas dumpsite. *Unpublished BSc. Thesis, University of Phillipens college of public health.*

Baeyens, W., Goeyens, L., Monteny, F. and Elskens, M. (1998). Effect of organic complexation on the behavior of dissolved Cd, Cu and Zn in Scheldt estuary. *Hydrobiologia*, 366, 81-90

Baldo, M.A., Daniele, S. and Bragato. C. (2003). Bismuth micr-electrodes for heavy metals monitoring by anodic stripping voltammetry. *Journal of Physics*, (4), 103 – 107.

Bambgose, O. Arowolo, T.O.A. and Odukoya, O. (2000). Earthworms as bio-indicators of metal pollution in dumpsites of Abeokuta. *Nigeria. Revista Biologica Tropica, 48, 1*

Baron, J. M. and Legret, M. (1990). Study of interactions between heavy metals and sewage sludge. Determination of stability constants and complexation capacities of complexes formed with Cu and Cd. *Env. Techno*l., 11, 151–162

Baykov, B.D., Staynor M.P. and Gyugova M.L. (1996). Cadmium and lead bioaccumulation in male chickens for high food concentrations. *Toxicology and Environmental Chem*istry, 54, 155–159.

Belton, P. S. (1998). Trace element analysis of food and diet RSC food analysis monographs. *Royal Society of Chemistry*, Thomas Graham House Science park, Milton Road, Cambridge, CB4 0WF, UK

Benson, N. U. (2004). *The distribution of some heavy metals in floodplain soils around cross river in Itu, Nigeria*. M.Sc. Thesis, University of Uyo, Uyo, Nigeria.

Black C. A. (1965). *Methods of Soil Analysis*. American Society of Agronomy, Maduson,Wisconsin, U.S.A. Vol. 1, Pp.19.

Bolan, N.S. and Duraisamy, V.P. (2003). Role of inorganic and organic soil amendments on immobilization and phyto-availability of heavy metals. A review involving specific case studies. *Australian Journal of Soil Research*, 41, 533–555

Boulding, J. R. (1994). *Description and sampling of contaminated soils*. In F.L. Boca raton(ed), Alfeid Guide (2nd edition), Lewis publishers. Pp.30

Boris, A. R. (1994). Lead in hair and urine of children and adults from industrialized areas. Arch. Environ. Health, 49 (1), 59–62

Bouyocos, G. H. (1951). A re-calibaration of the hydrometer for making mechanical analysis of soils. *Agronomy Journal*, 43, 434–438

Brady, N.C. and Weil, R..R (1999). *The Nature and Properties of Soils.* 12th ed. Practice Hall inc. N. J. Pp. 890.

Brew, G. J. ( 2010 ). Copper toxicity in the general population. *Clinical neurophysiol*. 12 (14), 459-60

Buffle, J. and Tercier, W. (2005). Voltammetric environmental trace metal analysis and speciation; from laboratory to *in situ* measurements. *Analytical Chemistry*, 24 (3), 172-190

Burt, R., Wilson, M. A., Keck, T. J., Doughert, Y., Storn, D.E., Lindhal, J.A. (2003). Trace elements speciation selected smelter-contaminated soils in anaconda and Deer Lodge Valley, Montana, USA. *Advance Environmental Research*, 8(1), 51-67,

Caplat, C., Texier, H., Barrillier, D., Lelieure, C. (2005). Heavy metals mobility in harbor contaminated sediments. The case of Port-en-Bessin. *Marine Pollution Bulletin*, 50, 504-511

Carlson, C.W. (1976). Land application of waste material soil conservation. *soil America Ankeny, IOWA,* Pp. 3-7.

Casey, C. E., Hambidge, K. M. (1980). *Trace element deficiencies in man. Advances in Nutrition Res*. Draper, H. H., ed Plenum Publication, 3, 55

Chapel, A. (1986). Foliar fertilization. In Matinis Nijhoff Dordrechi, A. Alexander ed. Stittgart, Pp. 16–86

Chapman (1992). Water Quality Assessment. World Health Organisation Published by E and FN Spon an Imprint of Chapman Hall, *1st edn conference on water and the Environment* held in January, 1992, in Dublin.

Che Fauziah, I., Rasazlin, A., Rosenani, A.B., Zauyah, S. (2007). Domestic sewage sludge application to an acid tropical soil, part III. Fractionation study of heavy metals in sewage sludge. *Malaysian Journal of Soil Sci*ence, 11, 81-95

Chen, H.J., Wang, S.Y., Tang, C.W. (2010). Re-use of incineration fly ashes and reaction ashes for manufacturing light-weight aggregate. *Journal of Construction Building Material*, 24 (1), 46–55

Chlopecka, A.J.R., Bacon, M.J., Wilson, J.K. (1993). Form of Cd, Pb and Zn in soils from south-west Poland. Journal of Environmental Quality, 25, 69-79

Chojnecka, K., Gorecka, H., Gorecki, H. (2006). The influence of living habits and family relationships on elemental concentration in human hair. *Science Total Environment*, 366, 612-620

Ciba, J. Korlewicz, T., Turek, M. (1999). The ocuurrence of metals in composted municipal wastes and their removal. *Water, Air, Soil Pollut*ion,111, 159–170

Codex (1998). Metal limits in poultry. Codex alimentarum of the Slovak republic no. 981/1996.

Cointreau, S.J. (1982). *"Environmental Management of Urban Solid Wastes in Developing Countries, a project guide".* Urban Development Department, World Bank. Retrieved on 5 march, 2012 from http://www.worldbank.org/html/fpd/urban//solidwm/techpaper 5.pdf

Cooper, C.D., Reinhart, D.R., Ragh, F., Seligman, D., Reely, D. (1992). Landfill gas emission report 92 , 2, *Civil and Environmental Engineering Dept. University of Central Florida,* 134.

Dantas, T.N.C., Neto, A.A.D., Moura, M.C.P., Neto, E.L.B., Forte, K.R., Leite, R.H. (2003). Heavy metal extraction by micro-emulsion. *Water Resources*, 37 (11), 2709–2717

Dara, S.S. (2008). *Environmental chemistry and pollution control*. S. Chard and company limited,Vol.15, Pp. 41-42.

Davies, B. E. (1983). A graphical estimation of the normal lead content of some British soils. *Geoderma*, 29, 67-75.

DeAntanio, S. M., Katz, S. A., Scheimar, D. M. and Wood, J. D. (1982). Anatomically related variation in trace metal concentration in hair. Clin. Chem. Acta, 71, 501 – 510

Doan, P. L. (1998). "Institutionalizing household waste collection: The Urban Environmental Management Project, Cote D'Ivoire". *Habitat International*, 22 (1), 27 - 39

Duffus (Department of Health and Social Security) (1989). Lead and Health: *Report of a DHSS working party on lead in the environment*. London, HMSO

Duruibe, J.O. Ogugwuegbu, M.O.C., Egwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sci*ence, 2(5), 112–118

Ebong, G.A., Etuk, H.S. and Johnson, A.S. (2007). Heavy metals accumulation by *Talinum triangulare* grown on waste dumpsites in Uyo Metropolis, *Journal of Applied Sciences*, 7 (10), 1404-1409.

Eddy, N.O., Odoemelem, S.A. and Mbaba, A. (2006). Elemental Composition of Soil in Some Dumpsites. *Electronic J. Environm. Agric. and Foof Chemistry*, 5 (3), 1349 - 1365.

Egila, J.N. and Nimyeh, A.D.N. (2002). Determination of trace metal speciation in sediments from some dams. *Journal of Chemical Society of Nigeria*, 27 (10), 71–74

Eisler, R. (1988). Load hazards to fish, wildlife, and invertebrates: a synoptic review. *US fish and wild life service*, Washington, DC.

Eja, M.E., O.R., Ogri and G.E., Arikpo (2003).Bioconcentration of heavy metals in Surface Sediments from the Great Kwa River Estuary, Calabar, South Eastern Nigeria. *Journal of Nigerian Environmental Soc*iety, 1, 247-256.

Elaigwu, S.E., Ajibola, V.O. and Folaranmi, F.M. (2007). Studies on the impact of municipal waste dumps on the surrounding soil and air quality of two cities in northern Nigeria. *Journal of Applied Science*, 7 (3), 421–425

EPA (1979). *Toxic metals in mammalian and human hir and nails*. EPA. 6004.049. United States Environmental Protection Agency, Research and Development.

EPA (1980). *Environ. Protection Agency. Biol. Monitoring of trace metals.* EPA 600/3 – 80 – 089

Esakku, S., Palanivelu, K., Kurian, J. (2003). Assessment of heavy metals in a municipal solid waste dumpsite. Workshop on sustainable landfill management. *Chennai India.Proceeding Booklet,* 139–145.

Esimai, O.A., Awoleye, O.O. (2009). Estimation of lead in urine of school children in south western Nigeria and effect of ascorbic acid intervention. *African Journal of Science and Technology,* 3 (11), 370–375.

Etekpo, E.I. (1999). Generation and management of solid wastes in Eket, Nigeria. A seminar paper submitted to the Department of Chemistry/Biochemistry, University of Uyo, Nigeria.

European Union (2002). *Heavy metal in wastes European commission on environment.* http://ec.europa.en/environment/waste/studies/pdf/heavy_metals retrieved on 14th january, 2012.

Evans, L. J. (1989). Chemistry of metal relation soils. *Environmental Science and Technology*, 23, 1046-1056.

Falex (2005). Definition: environment, the free dictionary, Felex Inc publishing, USA. Retrieved *from www.the free dictionary.com* on 1st January, 2010

FEPA (1991). *Federal Environmental Protection Agency. National Interim Guidelines and Standards for Environmental Pollution Control in Nigeria*. Federal Ministry of Environment.

Fergusson, J. E. (1990). The heavy metals : *Chemical Environmental Impact and health effects* Pergamon Press, Oxford, Pp. 478.

Fernendes, H. M. (1997). Heavy metals distributions in sediments and ecological risk assessments. The role of the Digenetic processes in reducing metal toxicity in bottom sediments. *Environmental Pollution*, 97, 317–325

Ferner D. J. (2001). Toxicity, heavy metals . Bio*med Journal*, 2(5), 1, retrieved from www.cockatiels.org /diseases/metals.html on 14th January, 2012.

Finzgar, N.P. and Thistos L.D. (2007). Relationship of soil properties to fractionation bioavailability and mobility of lead and zinc in soil. *Plant, Soil, Environ*ment, 53(5), 225–238.

Fuge, R., Laidlaw, I.M.S., Perkins, W.T. and Rogers, K.P. (1991). The influence of acidic mine and spoil drainage on water-quality in the mid-wales area. *Environmental Geochemistry and Health,* 13 (2), 70-75.

Fytianos, K. and Lourantou, A. (2004). Heavy metal distribution in sediments samples collected at lakes Volvi and Koronia, N. Greece. *Environmental Int*ernational, 30, 11–17

Gale, N.L., Adams, C.D., Wixson, B.G., Loftin, K.A. and Huang, Y. (2002). Lead concentrations in fish and river sediments in the old lead belt of missouris. *Environmental Science Technology,* 36, 4262-4268.

Garbarino, J. R., Hayes, H., Roth, D., Antweida, R., Brinton, T. C., Taylor, H. (1995). Contaminants in the Misissipi River, U.S. Geological Survey Circular, 1133, Virginia, USA.

Gasu M. B. and Ntemuse, U. E. (2011). Physicochemical properties of soils under municipal solid waste dumpsites in Ife East local government area, Osun State, Nigeria *Syllabus Review*, 2(3), 106–113

Glenn, L. S. (2008). Assessing the effect philippians to groundwater quality in Payatas, Phillipines. *American Journal of Environmental Sci*ence, 4(4), 276– 280.

Gratani, L.S., Taglini, Grescente, M.F. (1992). The accumulation of lead in agricultural soil and vegetation along high way. *Chemisphere*, 24, 94-940.

Gupta, S. K., Chen, K. Y. (1975). Partitioning of trace metals in selective chemical fractions of near shore sediments. *Environmental Science Technol*ogy, 15, 1378-1383.

Gworek, B., Mocek, A. (2003). Comparison of sequential extraction methods with reference to zinc fractions in contaminated soils. *Polish Journal of Environmental Studies,* 12, 41.

Habashi, F. (1992). Environmental issues in the metallurgical industry, progress and problems, environmental issues and waste management in energy and mineral productions. *Balkama, Rotterdam,* Pp. 1143-1153

Hambidge, K.M., Casey, C. W., Krebs, N. F. (1987). Zinc: In W. Mertz (ed). Trace elements in human and anim. *I Nutr. 5th ed. Academic press Inc., San Diego*, 2, 50-51,

Han, F.X.,m Banin, A., Kingery, W.L., Tripetti, G.B., Zho, U.L.X., Zheng, S.J. and Ding, .X. (2003). New approach to studies of heavy metal redistribution in soil. *Advance Environmental Research*, 8, 113.

Harada, M. (1995). Methylmercury poisoning in Japan by environmental pollut. *Critical Review on Toxicology*, 25, 1–24

Harrison, R.M. (1981). Chemical association of lead, cadmium, copper and zinc, in street Dusts and Roadside Soils. *Environmental Science Technol*ogy, 15, 1378-1383.

Harrison, R.M., Chirgawi, M.B. (1989). The assessment of air, soil as contributes of some trace metals to vegetable plants. *Science Total Environmental,* 83, 13-34.

He, M., Wang, Z. and Tang, H. (1997). Spatial and temporal patterns of acidity and heavy metals in predicting the potential for ecological impact on the Le An river polluted by acid mine drainage. *Science Total Environment*, 206 (1), 67-77.

Heathwaite, L. (1994). Eutrophication. *Geography Review*, Vol. 7. No. 4. Pp. 31–37.

Holum, J. R. (1983). Elements of general and biological chemistry, *6th edition, John Wiley and Sons*, Pp. 324–469.

Hoonweg, D. and Thomas, L. (1999). What a waste, solid waste management in Asia. *World bank, Washington D.C*., Pp.1-7.

Hopps, H.C. (1977). The Biol. Bases for using hair and nail for analysis of trace elements. *Science Total Environment*, 7, 71–89.

Horsfall, M.N. and Spiff, A.L. (1999). Speciation of heavy metals in intertidal sediments of the okrika river system (Nigeria). *Bulletin of Chemical Society Ethiopia*, 13 (1), 1-9

Huan–Jung, F., Hung–yee, S., Hsin–Shin, Y., Wen–Chin, C. (2005). Characterization of Landfill Leachates in Central Taiwan. *Science Total Environ*ment, 361, 25– 37.

Hutton, E.A., Hocever, S.B., Mauko, L. and Ogoreve, B. (2006). Electrochemical stripping analysis os selected heavy metals. *Analytical Chim-Acta*, 580, 244.

IAEA (1980). Elemental analysis of biological materials. *Technical report series no*. 197, `IAEA, Vienna.

IITA. (1979). Selected Methods for Soil and Plant Analysis. *International Institute of Tropical Agriculture*, Ibadan, Nigeria, Pp. 42

Ikem, A., Osibanjo, O., Shridhar, M. K. and Sobande, A. (2002). Evaluation of Groundwater characteristics near two waste sites in Ibadan and Lagos, Nigeria. *Water, Air and Soil Pollution*, 140 (1-4), 307-333

Inyengar, G.V. (1984). Preservation and preparation of biological matter for trace element analysis. Quality assurance in Biomedical Neutron Activation Analysis. IAEA Tedoc. 323, *International Atomic Energy Agency*, Vienna. Pp89.

Iwagbue, C. M. A., Nwajei, G.E. and Iyoha, E.N. (2008). Heavy metal residues of chicken meat and gizzard and turkey meat consumed in southern Nigeria. *Bulgerian. Journal Veterinary Medicine*, 11 (4), 275–280

Jaiswal, P.C. (2004). *Soil Plant and Water Analysis*, Kalyani publishers, New Delhi. Pp 403

Jung, M.C. (2001). Heavy metal contamination of soils and waters in and around the Imcheon Au-Ag mine, Korea. *Applied Geochemistry*, 16 (11-12), 1369-1375.

Juste, C. and Mench, M. (1992). Long term application of sewage sludge and its effects on metal uptake by crops: In Biogeochemistry of trace metals, D.C. Adriano (ed), CRC Press, *Broca*. Pp . 159–194

Kabala, C. and Singh, B.R. (2001). Distribution and forms of cadmium in soils near a copper smelter polish. *Journal of Environmental Studies*, 15 (29), 90-97

Kabata–Pendias, A. and A. Pendias (1984). *Trace elements in plants and soils*. CRC Press inc. Boca Raton Florida, Pp. 321-337.

Kallip, S., Kasuk, H., Grozovski, V., Mollar, P. and Lust, E. (2008).Adsorption of camphor and 2'-biphyridine on Bi (111) electrode surface. *Electrochimica Acta*, 53 (8), 3337-3349

Kallip, S. and Lust, E. (2005). In situ studies of Bi(111) electrodes in aqueous electrolyte. *Electrochemistry Communications*, 7 (8), 863–867

Kapoor, A., and Viraraghavan, T. (1998). Removal of heavy metals from aqueous solutions using immobilized fungal biomass in continuous mode. *Water Resources*, 36(6), 1968-1977

Keller, C. and Vedy, J.C. (1994). Distribution of copper and cadmium fractions in two forest soils. *Journal of Environmental Quality*, 23, 987

Kiekens, L. (1983). Behaviour of heavy metals in soils: In Berghund, S., R. D., Davis and Fermite, P. (eds). Utilisation of sewage sludge on land.: Rates of application and long term effects of metals. Dordrecht : D. Reidel publishing. In : Oviasogie, P.O. and Ndiokwere, C.L. (2008). Fractionation of lead and cadmium in refuse dump-soil treated with cassava mill effluent. *Journal of Agriculture and Environment*, 9, 10–15

Kim, J., Park, S.K., Koo, T.H. (2007). Trace elements and pollutants concentrations in shorebirds from Yeonghong Island, Korea in the eastsin-Australian migration flyways. *Ecotoxicology*, 16, 403-410

Kim, N.D. and Fergusson, J.E. (1991). Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soils. *Science Total Environment,* 105:191

Krolicka, A., Bobrowski, A., and Kowai, A. (2006). Effects of electroplating variables on the voltammetric properties of bismuth deposits plated potentiostatically. *Electroanalysis*, 18 (17), 1649–1657.

Kronvang, B., Jeppesen, E., Conley, D.J., Sondergaard, M., Larsen, S.E., Ovesen, N.B. and Castensen, J. (2005). Nutrient pressures and ecological responses to nutrient loading reductions in Danish Streams Lakes and coastal Waters *Journal of Hydrol*ogy, 304, 274–288

Kucera, J., Lener, J., Soukal, H., Horakova, J. (1996). Air pollution and biological monitoring of environmental exposure to Vandavin short time neutron activation analysis. *Trace Microprobe Teclin,* 141 (1), 193.

Kuo, S., Heilman P. E. and Baker,A.S. (1983). Distribution and forms of Cu, Zn, Cd, Fe and, Mn in Soil near a Copper Smelter. *Soil Sci*ence, 135, 10–109.

Lee, G.J., Lee, H.M., Uhm, Y.R., Lee, M.K. and Rhee, C.K. (2008). Square wave voltammetric determination of thallium using surface modified thick-film graphite electrode with Bi nanopowder. *Electrochim communications*, 10 (12), 1920–1923

Lenntech (2004). *Water treatment and air purification published by Lenntech, Rotterdams.* Sewage, Netherlands, In; Jothivel, S. Pillai. http://www.lenntech.com/index.htm retrieved on the 1 February, 2005

Lenntech, B.V. (2013). *Water Treatment Solutions*. http://www.lenntech.com/index.htm retrieved on the 1 February, 2013

Lewis, W.J., Foster, S.S.D., Drasar, B.S. (1982). *The risk of groundwater pollution by on-site sanitation in developing countries*. IRCWD report 01/82, IRCWD, Duebendorf, Pp.79

Li., Y.H., Lui, X.Y., Zeng, X.D., Liu, Y., Liu., X.T., Wei, W.Z., Luo, S., L. (2009). Recent advances in the field of biotechnology. *Journal Sensors and Actuators*, 139, 604.

Lin, L. Lawrence, N.S., Thongngamdee, S. J. Wang, Y.-H. Lin (2005).Catalytic adsorptive stripping determination of trace chromium (VI) as bismuth film electrodes. *Talanta,* 65 (1), 144–148

Lombi, E., Gerzabek, M.H. (1998). Deter mination of mobile heavy metals in soil, result of a plot experiment with sewage sludge. *Communication in Soil Science and Plant Analysis*, 29, 2545–2556

Long, J.-J. and Nagaosa, Y. (2007). Determination of selenium (IV) by catalytic stripping voltammetry with in-situ plated bismuth-film electrode. *Analytical Science,* 23, 1343

Loredo, J. Ordonez, C., S. and De-miquel, K. (2003). Influence of industry on the geochemical urban environment of Miers (Spain) and associated health Risk. *Environmental Geochemistry and Health*, 25, 307–323.

Luke B. (2008). *Waste disposal* www.umich.edu/gs265/society/wastedisposal.html 27/5/2009

Ma, L.Q. and Rao, G.N. (1997). Chemical fractionations of cadmium, copper, Zinc and Nickel in contaminated soils . *Journal of Environmental Qual*ity, 26, 259 – 264.

Mahmud, A.S. (2013). *Electrochemical and Kinetic Studies of Iron in Abandoned mine water at Newcastle, United Kingdom. Unpublished PhD Thesis,University of Newcastle, UK.*

Maize, I., Esnaola, M.V. and Millon, E. (1997). Evaluation of heavy metal availability in contaminated soils. *Journal of Environmental Qual*ity, 26, 259–264

Mandil, A., and Amine, A. (2009). Scree-printed electrodes modified by bismuth film for the determination of released lead in Moroccan ceramics. *Analytical Lett*ers, 42 (9), 1245-1257

Mapanda, F., Nyamadzawo, G. Nyamangara, J. and Wuta, M. (2007). Effects of discharging acid mine drainage evaporation pond limed with day on chemical quality of the surrounding soil and water. *Journal of Physical chemistry and Earth*, 32, 1366–1375.

Margaret, I., and Guy, H. (1999). Developing realistic water quality standards integrated development for water supply and sanitation. *25th UEDC conference held in Addis Ababa, Ethiopia.*

Mariam, I., Iqbal, S. and Nagra, S.A. (2004). Distribution of some trace and macro-minerals in beef, mutton and poultry. International Journal of Agricultural Biology, 6, 816-820.

Martin, R.R., Kempson, I.M., Naften, S.J. and Skinner, W.M. (2005). Preliminary synchrotron analysis of lead in hair from a lead smelter worker. *Chemosphere*, 58, 1385-1390.

Matsuo, N., Suzuki, T. and Akagi, H. (1989). Mercury concentrations in organs of contemporary Japanese. *Archives of Environmental Health*, 44, 298–303

Maugh, H. T. (1978). Hair : Diagnostic tool to compliment serum and urine. *Science*, 202, 1271–1277

Mcbean, E. A., Rovers, F. A. and Farqular, G. J. (1995). Solid waste landfill engineering and design. *Prentice Hall.* PTR, USA, 52

McBean, E.A., Rovas, F.A. and Ferguhar, G.J. (1995). *Solid waste landfill engineering and design prentice-hall*, PTR, USA, 521.

McCarthy, G.J and Walsh, A. (2012). *"Walsh, Alan-Biographical entry". Encyclopedia of Australian Science, Retrieved 22 May 2012*

McCluggage, D. (1991). Heavy metal poisoning, NCS, magazine, published by the bird hospital, Co. USA. In: Seasonal variations of heavy metal concentrations in abbatoir dumping site soil in Nigeria. *Journal of Applied Science and Environmental Management*, 13 (4), 9-13

Mclaren, R.G. and Crawford, D.V. (1973). Studies on soil copper: the fractionation of copper in soils. *Journal of Soil Science*, 24, 172-181

Meghasi, A.T. Halshell, H.B. Heineman, W.R. and Rilo., H.L.R. (2004). *Analytical Biochem*istry, 326, 183

Mehra, R. and Juneja, M. (2005). Fingernails as boil indices of metal exposure. J. Biosci., 30 (2), 101–105

Melese, T. (1998). *Solid waste management and the role of community participation in Addis Ababa, with reference to two kebeles in the slums of markato, area* as retrieved from etd.aau.edu.et/dspace/bitstream/123456789/1755/1/Ermias Seyoum.pdf on 1 January, 2012.

Merian, E. (1991). *Metals and their compounds in the environments,occurrence, analysis and biological relevancy* .UCH, Weinheim, New York. P.45.

Miller, W.P. and Mcfee, W.W. (1983). Distribution of Cd, Zn, Cu and Pb in soils of industrial north-western indiana. *Journal of Environmental Qual*ity, 12, 29 - 33.

Mor. S. Ravindra, K. Dahiya, R. and Chandra, P. (2006). Leachate Characterization and Assessment of Groundwater Pollution near Municipal Solid Waste Landfill Site. *Environmental Monitoring Assessment*, 118, 435 – 456.

Morfobos, M. A. and Economou, A. (2004). Voulgaropoulos. Simultaneous determination of nickel (II) by square wave adsorptive stripping voltammetry on a rotating disc bismuth –film electrode. *Analytical Chim. Acta*, 519,57

Mosley, A. L. and Ozcan, S. (2004). Glucose regulation of insulin gene expression requires the recruitment of p300 by the beta-cell specific transcription factor, pdx-1. *Molecular Endocrinology*, 18 (9), 2279 - 2290

Murhekar, G.H. (2011). Determination of physicochemical parameters of surface water samples in and around Akot city. *International Journal of Research in Chemistry and Environment*, 1(2), 547 – 551

Musa, A., Garba, M., Yakasai, I.A. and Odunola, M. T. (2011). Determination of blood levels of cadmium in humans from zaria, Nigeria. *New Clues in Sciences*, 2, 49- 54

Nayak, L. (2000). Heavy metal concentrations in some catfishes from from Gopalpur Coast, *East Coast of India*, Pp. 77 – 79

Neil,O. P. (1993). *Environmental Chemistry*. Chapman and Hall, London. Pp.193.

Nick, C.O, Leo, C.O., and Uche, I.O. (2012). Assessment of heavy metal pollution in muscles and internal organs of chickens raised in rivers state, Nigeria. *Journal of Emerging Trends in Enginering and Applied Sciences (JETEAS)*, 3(3), 406- 411.

NIS (2007). Nigerian standard for drinking water quality. *NIS*, 554, 14

Njoroge, G. N., Busman, R.W. (2007). Ethnotherapeutic management of skin diseases among kikuyu of central Kenya. *J. Ethnopharm*, 111, 303–307

Nnorom, I.E., Igwe, J.C. and Ejimme, J.C. (2005). Multi-element analysis of human scalp hair samples from three distant towns in south eastern Nigeria. *African Journal of Biotechnology*, 4, 1124-1127.

Nolan, K.R. (2003). Copper toxicity syndrome. *Journal of Orthomology and Psychiatry*, 12, 270–282

Norvell, W.A. (1984). Comparison of Chelating Agents for metals in diverse soil materials. *Soil Science Society American Journal*, 48, 1285–1292.

Nowak, B. (1998). Contens and relationships of elements in human hair for a non-industrial population in poland. *Science of the Total Environment*, 209, 59-68

Nriagu, J.O. (1989). A global assessment of natural source of atmospheric trace metals. *Nature*, 338, 47–49

NSDWQ (2007). *National Standard for Drinking Water Quality.Approved by SON Governing Council*, NIS 554. Pp.16-17

Nuonamo, L., Yemefack M., Techienkwa, M. and Njomgang, R. (2000). Impact of Natural Follow Duration Cameron. *Nigerian Journal of Soil Resource*, 3, 52-57.

Nyle, C.B. and Ray, R.N. (1999). *The nature and properties of soils*. 12th edition. United States of America, Pp.743-785.

Obuli, P., Karthikeyan, S., Mumgesan, K.J and Lizy, P. (2011). Characterization of particulate matters and volatile organic compounds in the ambient environment of open dumpsites.*Universal Journal of Environmental Research and Technol*ogy, 1(2), 140 – 150

Odukoya, O. O., Bamgbose, O., and Arowolo, T.A. (2000). Heavy metals in top-soil of Abeokuta dumpsites. *Global Journal of Pure Applied Sci*ence 7, 467- 472.

Ogwuegbu, M.O.C., Muhanga, W. (2003). Effects of certain heavy metals on the population due to mineral exploitation. In: International conference on scientific and environmental issues in the population. *Environment and Sustainable Development in Nigeria*. University of Ado-Ekiti, Ekiti State, Nigeria. Pp.8 - 10

Okafor, P.C., Ekpe, U. J., Ibok, U.J., Ekpo, P. O., Ebenso, E.E. and Obadimu, C.O. (2009). Atmospheric pollution of mild steel in Niger Delta region of Nigeria, Part 1. Characterisation of Calabar, Cross River State Environment. *Global Journal of Environmental Science*, 8(1), 9,18

Okoronkwo, N.E.I Odemelaon, S.A. and Ano, O.A. (2005). Risk and health implication of polluted soils for crops production. *African Journal of Biotechnology*, 4(13), 1521-1524.

Okoronkwo, N.E.I., Odemelaon, S.A. and Ano, O.A. (2006). Levels of toxic elements in soils of abandoned waste dumpsite. *African Journal of Biotechnol*ogy, 5 (13), 1241 – 1244.

Okunola, O., J., Uzairu, A., Gimba, C. E. and Kagbu, J. A. (2011). Metals in roadside soils of different grain sizes from traffic roads in Kano Metropolis,Nigeria. *Toxicological and Environmental Chemistry*, 93 (8 ), 1572 - 1590

Onibokun, A., G. and Kumuyi, A. J. (2003). The urbanization process in Africa. *International Development Research Centre (IDRC), Spain.* Andrews mcmeel publishers, 3rd edition, Pp.12.

Onyeka, S.O. (1987). Environmental pollution in Onitsha: Problems and Solution: *Unpublished BURP Dissertation, University of Nigeria, Nsukka, Nigeria*, Pp. 20-21

Onyeri, J., Muohi, A.W.., Omondi, G. and Maruti, K.M. (2000). Heavy metals in sediments from Makura and Port-Reitz systems, Kenya. Env. Int.m 28, 639–647.

Onyeri, J.M., Wandiga, S.O., Njenga, G.K., and Nyatabe, J.O. (1991). Lead contamination in street of Nairobi City and Mombase Island, Kenya. *Environmenmtal Contamination Toxicology*, 46, 782-789.

Oskarson, A.L., Jorchem, L., Sundberg J, Nilson, N. and Albanus L. (1992). Lead poisoning in cattle. Transfer of lead to milk. *Science Total Environment,*111, 83-94

Osuji, L. C. (1998). Some environmental effects of oil spillage in two sites in Rivers State. *PhD thesis, University of Ibadan*

Oyedele, D.J., Gasu, M.B. and Awoleye, O.O. (2008). Changes in soil properties and plant uptake of heavy metals on selected municipal solid waste dumpsites in Ile-Ife, Nigeria. *African Journal of Environmental Science and Technol*ogy, 5, 107 – 115

Pardo, R., Barado, E., Perez, L. and Vega, M. (1990). Determination and speciation of copper and lead in sediments of mediterranean river (Riverteen, Catalonia, Spain. *Water Resource*, 22, 449-455.

Pardo, R., Barrado, E., Castrillego, Y., Velasco, M.A., and Vega, M. (1993). Study of the contents and speciation of heavy metals in river sediments by factor analysis. *Analytical Letters*, 26, 1719–1739

Paulikaite, R.Metelka,R. Svancara,I. Krolicka, A. Bobrowski, A. Yytras, K. E. Nornus and Kalcher, K. (2002). *Analytical Bio-analytical Chemistry*, 374, 1155

Pempkowiak, J. , Sikora, A., and Biernacka, E. (1999). Speciation of heavy metals in marine sediments versus their bioaccumulation by nussels. *Chemosphere*, 39 (2) : 313–321

Pickering, W. F. (1986). Metal ion speciation –soils and sediments. *Ore Geol. Rev*., 1, 83–146

Pierangel, M.A.P., Madison, C.R.G., Guilherme, L.R., Oliveira, N.C. and Silva, M.L.N. (2003). Efieto da Forca ionica da solucao de equilirio na adsorcao de cadmio em latossols Brasileiros. *Pesquisa Agropecuaria Brasileira*, 38, 737 – 745

Porteus, A. (1985). *Hazardous Waste Management Handbook.* Butternorths Publication Sevenoaks, Kent, UK and distributed by Chichester, Pp. 25.

Potter, J.L., Timmons, G.D., West, R., Sividi, A. (1974). Arginino succinicacidenia. *The hair abnormalily.* American Journal Dis Child 1, 27

Rabinove, C.J., Long, F. and Brookhent, J.W. (1958). Saline water resource of North Dakota. U.S. *Geological Survey of Water Supply Paper*, 1428, 72

Ramos, L., Hernandez, L. M. and Gonzatez, M.J. (1994). Sequential fractionation of copper, lead, cadmium, and zinc in soils from or near Donana national park . *Journal of Environmental Qual*ity, 23, 50-57.

Rapin, F., Membraine, G.P., Forstner, U. and Gracia, J. L. (1983). Heavy metals in marine sediments phases determined by sequential chemical extraction and their interaction with interstitial water. *Environmental Technology Letters*, 4, 387-396

Rashad, M. and Shalaby, E.A. (2007). Dispersion and deposition of heavy metals around two municipal solid waste (MSW) dumpsites. Alexandria, Egypt. *American-Eurasian Journal of Agricultural and Environmental Science*, 2 (3), 204–212

Rodriguez, G.L.A., Varas-Lorenzo, C., Maguire, A., Ganza L.A. (2004). Nonsteroidal anti-inflammatory drugs and the risk of myocardial infarction in the general population. *Circulation*, 109, 3000–3006

Romann, T., Kallip, S., Sammelseq, V. and Lust, E. (2008). Bismuth micro-electrode system with in-situ renewable surface for electro-analysis and adsorption studies. *Electrochemistry communications*, 10 (7), 1008–1011

Rothstein, H.A.L. (1960). The metabolism of mercury in the rat studied by isotope techniques. *Journal of Pharmacological Experiment*,130, 166–176

Ryabukin, Y. S. (1978). Activation analysis of hair as an indicator of contamination of man by environm. Trace elements pollutants. *IJAEA report, Vienna, Introduction to Atomic Energy Agency, IAEA/RL/50*

Ryan, J.A., D'more, J.J., Al–Abed, S. R. and Schekel, K. G. (2005). *Methods for separation of metals in soils: Alliance of crop, soil and environmental science societies.Pp.200*

Sahuquillo, A., Rigol, A. and Rauret, G. (2003). Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *Trends in Analytical Chem*istry, 22, 152–159.

Salam, A. (2010). Environmental and health impact of solid wastes at Mangwanemi dumpsite in Manzini, Swaziland. *Journal of Sustainable Development in Africa*, 12 (7), 1-7

Salwa, A. Abduljaleel, M. Shuhaimi, O. and Abdulssalam, B. (2012). Assessment of trace contents in chicken (*Gallus gallus domesticus*) and Quail (*Coturnix coturnix*

*japonica*) Tissues from Selangor, Malaysia. Journal of Environmental Science and Technology, 5, 441-451

Salwa, A., Abduljaleel, M., Shuhaimi, O. and Abdulsalam, B. (2012). Assessment of trace metal contents in chicken (*Gallus gallus domesticus*) and quail (*Cotunix japonica*) Tissues from Selangor (Malaysia). *Journal of Environmental Science and Technology*, 5 (6), 441-451.

Sandra, C., Alcides, S. D., Margarida, M., Rejane, S., Solange, M. M., Severino, F. and Patrick,K. (2002). Parametrs for the evaluation of Zn Nutri. Status. Comparison between Zn hair and serum alakaline phosphates in pre–scholars of the municipality of Jaoao pessoa, Paraiba, Paraiba, Rev. Bras. Sande Mater Infant, 2(3), 275-282

Schonfeldt, H.C. and Gibson, N. (2008). Changes in the nutrient quality of meat in an obesity context. *Meat Sci*ence, 80, 20-27

Schwartz, J. I. Ballester, F;. Saez, M. Perez–Hoyos, S. Bellido, J. Cambra, K., Arribas, F. and Canada, A. Rerez-Boillos, M. and Sunyer, J. (2001). The Concentration response relation between air pollution and daily death. *Journal of Environmental Health Persp*ective, 109 (10), 1001–1006.

Shrivastava, D., Sujeet, K. and Banerjee, K. (2004). Speciation of metals in sewage sludge and sludge amended Soil. *Water, Air, and Soil Pollution,* 152, 219-232.

Shu'aibu, U.O and J.T. Ayodele (2002). Bioacummulaton of four heavy metals in Leaves of Calastropis Procera. *Journal of Chemical Society of Nigeria*, 27, 26-27.

Shuman, L. M. (1985). Fractionation method for soil micro-elements. *Soil Science*, 140, 11-22.

Sia-Su, L. G. ( 2008). Assessing the effects of a dumpsite to ground water quality in Payatas, Philiphines. *American Journal Environmental Sci*ence, 4 (4 ), 276–280

Smith C. J. Hopmans, P. and Cook, F. J. (1996). Accumulation of Cr, Pb, Cu, Ni, Zn and Cd in soil following irrigation with untreated urban effluents in Australia. *Environmental Pollution,* 94 (3), 317–323.

Sposito, R. C. (1982). Trace metal chemistry in arid zone field soils amended with sewage sludge. Fractionation of Ni, Cu, and Zn in Kaduna, Solid Phases. *Soil Science Society of America,* 46, 260-264

Stephen, W. (2004). *Municipal solid waste management in developing countries*. Pp.1 - 14

Stover, R.C., Sommers, L.E. and Silviea, D.J. (1976). Evaluation of metal in waste water sludge. *Journal of Water Pollution Control Federation*, 48, 2165 - 2175

Strain, W. H. S., Pories, W. J., Flynn, A., and Hill, O.A. (1972). Trace element nutriture through head hair analysis. In: Hemphil, D.D. (ed). Trace substances in Environ. Health Univ of Missouri. Press, Columbia, Pp. 383.

Stumm, W. and Morgan, J. J. (1981). Aquatic: *An introduction emphasizing chemical equilibria in natural air, soil pollution water*. 2nd ed. John Wiley and Sons, New York, Pp130.

Sukumar, A., and Subraanian, R. (2003). Elements in the hair of non-mining workers of a lignite open urine in Neyveli. Industrial Health, 41, 63-68

Suleiman, I. M., Fayer, R., Bern, C., Gilman, R. H., Trout, J. M., Schautz, P. M., Das, P., Lai, A. A. and Xiao, L. (2003). Triosephosposition Paper Against Mining In Rapu–Rapu. retrieved from www.adnu.edu.ph/institutes/inecar/paper1.asp on 1st December, 2010.

Suman, M. Khaiwal, R., Dahiya, R.I. P. and Chamdra, A. (2011). Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental Monitoring and Assessment*, 118, 435-456

Sutherland, R. A. and Verloo, M. G. (2000). Operationally defined metal fractions on road deposited sediments. Honolulu, Hawaii. *Journal of Environmetal Qual*ity, 29, 1431- 1439

Svancara, I., Chad, P., Samo, B.H. and Joseph, W. (2010). A decade with bismuth based electrodes in electroanalysis. *Electro-analytical Chem*istry, 22 (13), 1405–1420

Taiwo, A.M., Adeogn, A.O., Olatunde, K.I. (1998). Analysis of groundwater quality. *Science of the Total Environment*, 128, 69–81

Takahata, H. and Watanabe, S. (1970). Accumulation of mercury in the brains of two autopsy cases with chronic inorganic mercury poisoning. *Folia Psychiatrica et Neurologica Japanica*. 24, 59–69

Tavo , R., Silver, K., Vaino, S. and Enn, L. (2008). Bismuth microelectrode system with *insitu* Renewable Surface for Electroanalysis and Adsorption Studies. *Electrochemistry communication*, 10, 1008-1011

Tchobanoglous, G., Theisen, H. and Vigil, S. M. (1993). Integrated solid waste management engineering principles and management issues. Mcgraw-Hill, New York, Pp45-50

Teleghani, G. and Shabani–kia, A. (2005). Technical economical analysis of saveh biogas power plant, *Renewable energy*, 30, 441–446.

Tessier, A., Campbell, P.G.C. and Bisson, N. (1979). Sequantial extraction procedure for the speciation of particulate trace metals. *Analytical Chem*istry, 51(7), 844–861.

Todorovi, Z., Poli. P., Djordjevi, D. and Antoni jevi, S. (2001]) Lead Distribution in Water and it's Association with Sediment Constituents of the Barje Lake [Leskovae, Yugoslavia]. *Journal of Serbian Chemical Society,* 66 (1), 697-708.

Torma, F., Grun, A., Bitter, I. and Toth, K. (2009). Calixaene/Nafion modified bismuth-film electrode for adsorptive stripping voltammetric determination of lead. *Electroanalysis*, 21(17-18), 1961–1969.

Trivedi, R. K. and Goel, P. K. (1986). Chemical and biological methods for water pollution studies. *Environmental Publication, India*, Pp. 49-59.

Uba, S. Uzairu, A., Harrison, G. F. S., Balarabe, M.L. and Okunola, O. J. (2008). Assessment of Heavy Metals Bioavailabilty in Dumpsites of Zaria Metropolis. *Journal of African Biotechnol*ogy, 7 (2), 122-130.

Uba, S., Uzairu, A. and Okunola, O. J. (2009). Contents of Heavy metals in *lumbricus terrestris* and associated soils in dumpsites. *International Journal of Environmental Research*, 3 (3), 353–358.

Udedi, S. S. (2003). From guinea worm scourge to metal toxicity in Ebonyi State. Chemistry in Nigeria as the New Millennium Unfolds, 2, 13-14. In: Heavy metal contents in soil medicinal plants in high traffic urban area. *Pakistan Journal of Nutrition*, 10 (7), 618 – 624

Udosen, E.D., Udoessien, E. I. and Ibok, U. J. (1990). Evaluation of Some Metals in the Industrial wastes from a Point Industry and their Environmental Pollution Implications. *Nigeria Journal Technology Res*ources, 12, 71-77.

Ulouzlu, O.D., Tuzen, M., Mendil, D., Kahveci, B. and Soyak, M. (2009). 3-ethyl-4-(p-chlorobenzylidenamin-4-4,5-dihydro-1H-1,2,4-triazol-5-one(EPHBAT) as precipitant for carrier element free co-precipitation and speciation of chromium (III) and Cr (VI). *Journal of Hazardous Matter*, 172, 395–399.

Ulvi, H., Yigita, R., Yoldas, T., Dolu, Y., Var., A. and Mungen, B. (2002). Mn, Zn and Cu contents in hair and their serum concentration in patients with epilepsy. *Eastern Journal of Med*icine, 7 (2), 3–5

Umeakuka, J. M. and Mba, H. C. (1999). Solid waste management practices: A case study of Anambra State. *Journal of Nigerian Institute of Town Planners*, 12, 12–45.

UN–Habitat (2009). UN–habitat annual report. Retrieved from unhabitat.org/un-habitat-annual-report-2009 on 1st December, 2009

UNEP (2005). Annual report. Environment for a secure future and protecting nature's capital. ISBN. No. 92-807-2682-X, retrieved from www.unep.org on 17.04.2012

UNEP (2008). United nations environmental programme. Issued by WHO department of food safety, *Zoonorses and foodborne diseases, Geneva, Switzerland*. UNEP chemicals. 11-13, C H-1219

UN-Habiat (2009). *Solid waste management in the world cities*: publication series, UN-HABITAT, Nairobi, Kenya, retrieved from www.un.org/esa/dsd/susdevtopics/sdt_pdfs on 1 January, 2014

USEPA (1986). *Safe Drinking water Act Ammendment of 1986 public law 99 -339. United state congress, 99th congress,United states government printing office, Washington D.C.* http: //www,epa.gov/3056/2000 report. Retrieved on the 20 February, 2011. *In: Research needs in drinking water :* A basis in regulations in the united states. *Journal of water and health. 4, 1-9.*

USEPA (2000). *United states environmental protection agency, national water quality inventory*, http: //www,epa.gov/3056/2000 report. Retrieved on 20 February, 2011

USEPA (2003). *National water quality inventory*.http://www.epa.gov. Retrieved on the 19, February, 2011

Uzairu, A. (2006). *Basic statistical tools for a chemist.* Department of Chemistry, Ahmadu Bello University, Zaria. Pp.13.

Uwakwe, V. (2012). Solid waste management: A case study of Eneka, Portharcourt, Rivers state. *Retrieved from hyattractions.wordpress.com/2012/05/19/solidwaste – management-a-case-study-of-eneka-portharcourt-rivers-state, retrieved on the 12 June 2012.*

Vasuki, N.C. (2001). *International Perspective on Solid Waste. www.forester.net/msw.0011/international.html. 27/5/2009*

Vision 2010 Committee(2003). *"Ecology and the environment:Protect our environment for the unborn children".* http://wwwvision2010.org/vision2010/ecology.html. 27/5/2009

Vivoli, G. F., Fantuzzi, G., Bergomi, M., Tonelli, E., Gatto, M. R. A., Zanetti, F. and Del, D. M. (1990). Relationship between Zn in serum and hair and some hormones during sexual maturation in human. *Science Total Env*ironment, 95, 29–40.

Vytras, K. Baldrianova, L. Krolicka, A. Svancara, I., Bobrowski, A. Vytras, K. *(*2005*). In sensing in electroanalysis* (Eds. K.Vytras, K.. Kalcher). University of Perdubice, Czech Republic. Pp.75-87

Wang, J. (2006). *Analytical Chemistry*. third edition, New Jersey: John Wiley. Pp.250

Wang, J., Chen, C. (2009). Biosorption of heavy metals by saccaromyces cerevisiae: *A review*, 31, 2154 – 2156

Watanabe, A., Ochara, A., Tarima, N., Yoneki, S. and Hosoya, Y. (2003). PSA application for PCBs Detoxification *Plant. J. Material Cycle and Waste Management*, 5(1), 39 - 48.

WEF (1995). *Standard methods for the examination of water and waste water*. 19th edn. Washington, D. C. American Public Health Association/American Water Works Association/Water and Environemtal Federation, Washington, DC.

WHO (1993). *World Health Organization Guidelines for Technologies for Water Supply Systems in Small Communities*. Geneva recommendations, Vol. 1

WHO (1997). World health organization guidelines for drinking water quality 2nd edition vol. 2. *In Health Criteria and other supporting information, WHO, Geneva*. Pp. 940 - 949

WHO (1998). *Environmental health criteria, IPCS. International Program of Chemical Society*. A guide for managers and addendum to Vol. 1.

WHO (1999). *Guideline for drinking water quality 2nd edition recommendation*.World health organization. geneva.Vol.1. Pp. 30-113.

Wikipedia (2011). *Sampling and data collection*, the free encylopaedia. Retrieved from en.wikipedia.org/wiki/statistical theory on 14th February, 2011.

WHO (2006). Guidelines for drinking water quality 2nd edition recommendations. *World Health Organization*. Geneva. 1, 30–113

WHO (2011). Lead in drinking water. Background document for development of WHO guidelines for drinking water quality. WHO/SDE/WSH/03.04/09/Rev/1

Wilcox, L.V. (1950). Electrical Conductivity. *American Water Works Association Journal,* 42, 775-776.

Wilhelm, M., Hafner, D., Lombeck, I. and Ohnesorge, F. K. (1991). Monitoring of Cd, Cu, Pb and Zn status in young children using toenails. Comparison with scalp hair. Science Total Environment 103 (2–3), 199–207

Williams C.H. and Steinbergs A. (1964). The evaluation of plant available sulphur in soil. The availability of adsorbed and insoluble sulphate. *Plant Soil*, 2, 50.

World Bank (2002).“*Restoring Urban Infrastructure and Services in Nigeria*”.http://www.worldbank.org/agr/findings/english/62.html.27/ 5/2008

World Bank Nigeria (2000): *Community based urban development project, NGPE 69901, 1818H Street, N.W. Washington.* 20433.www.forester.net/msw.0011/international. html. 27/5/2008

Xian, X. (1989). Effect of chemical forms of cadmium, zinc and lead in polluted soil and their Uptake by cabbage plants and soil. *Journal of Environmental Science and Health*,113, 257-264.

Yeung, Z.L.L, Kwok, R.C.W., Yu, K.N. (2003). Determination of multi – elements profiles of street dust using energy dispersive X – ray fluorescence (EDXRE). *Appl. Radiation and Isotopes*, 58 : 339-346.

Yisa, J., Gawa, P.J., Jimoh, T.O. and Visa, D. (2011). Underground water quality assessment in our community, Niger State, Nigeria. *Journal of Emerging trends in Engineering and Applied Science (JETEAS*), 3 (2) : 383 – 286

Yogendra, K. and Puttaiah, E.T. (2008). Determination of water quality index and suitability of an urban water body in Shimoga Town, Town, Karnataka. *Proceeding of Taal2007, the 12 world lake conference*, 342-346.

Young, R.A. (2005). *Toxicity Profiles. Toxicity summary for cadmium, risk assessment information system*. University of Tennessee, Neshville, USA.

Yu, K.C., Tsai, L.G., Chen, S.H., Hu, S.T. (2001). Correlation Analyses on binding behavior of heavy metals with sediments matrices. *Water Research*, 35 (10), 2417–2428

Yusuf, A.A., Arowolo, T.A. and Bamgbose, O. (2003). Cadmium, copper and nickel levels in Vegetables from Industrial and Residential Areas of Lagos City, Nigeria. *Food Chemstry and Toxicol*ogy, 41, 375-378.

Yusuf, K. A. (2006). Evaluation of the three stage BCR (European Community Bureau of Reference). Sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in roadside soils. *Pakistan Journal of Science and Industrial Resource*. 49, 181-188

Zauyah, S.B., Juliana, R. Noorhafizah, C.I., Fauziah and A.B. Rosenmi (2004). Concentration and speciation of heavy metals in some cultivated and uncultivated

utisol and inceptisols in peninsular, Malaysia. *3rd Australian New Zealand Soil Conference held in University of Sydney, Australia.*

Zong, P. and Nagosa, Y. (2009). Determination of an antimony (III) and (V) in natural water by cathodic, stripping voltammetry with *in-situ* plated bismuth bismuth film electrode. *Microchim Acta*, 166 : 139–144.