CHAPTER ONE
INTRODUCTION

1.1 Background of Study

The problem of the human environment to which attention is increasingly drawn are mainly the event and the obvious consequences of the over exploitation of the earth's resources, some of which are already recognized to have a very limited lifetime (Park, 1997).

These effects on the environment include the worst features of urbanization, with industrial and mining operations causing gross problems of pollution by their products and wastes such as oil spillages in the oceans, chemical waste discharges into rivers and unsightly slag heaps (Park, 1997).

An average Nigerian throws away nearly a ton of solid waste each year and it has been difficult to dispose of this ever increasing amount of solid waste which causes air, water or soil pollution.

Waste can be defined as any substance which includes scrap material or effluent or unwanted surplus substance arising from the application of any process, and any substance or article which requires to be disposed off as being broken, worn out, contaminated or otherwise spoiled (Park, 1997).

A pollutant may be defined as a substance or effect which adversely alters the environment by changing the growth rate of species, interferes with the health, comfort, amenities or property values of the people (Park, 1997).

Solid waste is a term used to discribe non – liquid refuse. In some developing cities of Nigeria, one rarely plies about 4km without seeing solid waste dumps. It has been a culture among the citizenry to heap these waste materials along the major roads, within the streets or inadvertently drop them in sacks at close environments (Brock and Stopford, 2003).

These refuse dumps comprise of wastes like clothing materials, women weavons, beverage and food cans, polythene bags, glasses, worn-out tyres, plastics, papers, corn residues, carcasses, batteries, exhaust pipes, water pipes, chemical containers, tobacco sticks and packets, pharmaceuticals, cow dungs, human faeces (Scheper, 2002).

Apart from the eyesore or the despoliation of urban and rural scene they cause pollution of the soil, air and water. These wastes contain many toxic substances like acids, alkalis, phenols, cyanides and heavy metals. Metals especially are non-biodegradable and in the ecosystem are persistent (Jakko, 1991).

Heavy Metals

Heavy metals pose serious concern to the society at large because of the deleterious effect to environment and humans. In this research, our investigation centres on the concentration of Lead in solid waste dumps from a battery manufacturing industry in Nnewi and possible remediation of the environment contaminated by this waste. Industries have the ability to pollute the environment. They discharge industrial wastes often fairly treated and consequently pollute their environment.

It is evident that by the activities of battery manufacturing industry both the soil, air and water in and around this industry may have been seriously contaminated. The remediation of this environment from lead therefore is important. Remediation processes have been proposed by researcher (Kumar *et al*., 1995). These remediation processes may be broadly stated as chemical, biological or physical. However, what ever processes of remediation that is available, the management of waste is important to avoid high accumulation of toxic substances in the environment.

1.2 Statement of the Problem

Automotive battery manufacturing industry has been known to pollute the environment with Lead, a component of automotive battery. Work on an automotive battery in question indicated the pollution of the environment with Lead. Hence the remediation of this environment is important for cleaning the environment of this lead pollutant. Hence the work on phytoremediation of the environment using non-edible flowering plants. Other remediation processes such as Chemical extraction, Bioremediation, Dehalogenation, Solar detoxification, Soil washing exist but the most current and eco-friendly process is phytoremediation.

Literature had it that some edible plants such as, *Abelmoschus esculentus, Talinum* triangulare and *Vigna unguiculata* have been used in the past to treat heavy metal pollution of the soil. This practice was not recommendable as both humans and animals are at high health risk should they consume such plants (vegetables) thus choice of non-edible flowering plants such as *Duranta erecta*, *Aloe barbadensis*, *Hibiscus*

rosasinensis,*Ficus benjamina*, *Ageratum houstonianum*,*Gaillardiax grandiflora*,*Euphorbia milivarspendens* and *Ixora coccinea* to clean up lead polluted soil.

1.3 Aim and Objectives of the Study

The aim of this study is to assess lead concentrations in soil around an automotive Battery manufacturing site and remediate the polluted soil using flowering plants.

The objectives of this study therefore include:

I. Determination of lead concentration in soil around battery manufacturing industry in Nnewi.
II. Determination of the amount of lead sequestrated by the plants used in remediation.
III. Determination of the amount of lead in different parts of the plants such as root, stem and leaves.
IV. Determination of the most useful plant for phytoremediation.

1.4 Significance of Study

I. To portray phytoremediation as one of the good remediation processes in controlling land pollution.
II. To offer low capital and operating cost of pollution control unlike other methods such as chemical extraction and solar detoxification.
III. To offer the additional advantage of making contaminated soil/sites more aesthetically appealing, a bonus that is likely to garner future interest and support for phytoremediation.

IV. To offer an environmental friendly method of remediation since it utilizes plants.

1.5 Scope of Study

A total of one hundred and sixty (160} soil samples collected from the North, Northeast, East, Southeast, South, Southwest, West and Northwest at top soil, 5 cm, 10 cm, 15 cm and 20 cm from the Ibeto battery manufacturing site located at Otolo Nnewi in Anambra State. In each location, five soil samples were collected. The soil samples were digested and in triplicates for lead using Atomic Absorption Spectrophotometer (Buck scientific, AA220FS). The same triplicates analysis was made with pH meter (Searchtech,PHS- 7010) to check the level of acidity of the soil. The sampling were done during rainy and dry seasons. The control sample was collected from a distance of about 500 m away from the industrial location to validate the pollution status of the industry.

The following flowering plants; duranta, hibiscus, aloe vera, yellow bush, blue horizons, blanket, pinkixora and crown of thorns were planted on these polluted soil samples to monitor the level / degree of adsorption of the lead by these plants.

After a period of 3 months, these plants were harvested, air dried, digested and analyzed using atomic absorption spectrophotometer (AAS) for the residual heavy metal (Lead).

CHAPTER TWO

LITERATURE REVIEW

2.1 Waste Management Techniques

Ex situ (as well as *in situ*) remediation option can be grouped into categories based on their treatment mechanism: physical, chemical, electrical, thermal and biological. In the digest, physical, chemical and electrical mechanisms have been abridged into one group, called physico-chemical. Due to the complex nature of many polluted soils and the fact that pollution, in many situations, is due to the presence of a cocktail of different types of contaminants, it is frequently necessary to apply more than one remediation technique (treatment train) to reduce the concentrations of pollutants to acceptance levels (Anderson, 1999).

2.1.1 Chemical extraction

This is a process that separates contaminant from soils, thereby reducing the volume of the contaminant that must be treated. The two major chemical extraction processes which are based on the type of contaminants present in the soil are:

i. **Acid extraction:** This method uses acid to extract contaminants from the soils. Heavy metals are potentially suitable for recovery. Clean soils are devastated and mixed with lime and fertilizer to neutralize any residual acid.

ii. **Base Extraction:** This method uses base solvents to remove metals and mixtures of metal and organic compounds from the soil.

Physical separation is generally used before chemical extraction on the assumption that major part of the contamination is from the smaller particles (Wallinga *et al.,* 1995).

Chemical extraction is used to treat soils containing contaminants such as semi volatile organic compounds (SVOCs), explosives, inorganic materials, fuels and heavy metals (Wallinga *et al.,* 1995).

The advantage of this process lies in the fact that it can be used to extract a wide range of target contaminant and high concentrations of pollutants.

However, the limitations of the process indicate that it is generally less effective on high molecular weight organics or on hydrophilic substances. Certain solvents will be ineffective in some soil types or where excessive moisture is present. After acid extraction, any residual acid in treated soil needs to be neutralized. Further, the toxicity of the solvent is an important consideration as traces may remain in the treated soil (Temminghoff et *al.,* 1990).

2.1.2 Biopiles (Biological Treatments)

Biopiles, also known as biocells or bio mounds are engineered system in which excavated soils are combined with soil amendments, formed into compost piles and enclosed for treatment. They are commonly provided with an air distribution system by blowers or vacuum pumps. Several properties of the process such as nutrients and oxygen can be controlled in order to enhance the remediation procedure (Roger and John, 1994). This technology is generally used to reduce concentrations of petroleum constituent in excavated soils. The treatment is generally covered or contained with an

impermeable liner to minimize the risk of contaminants loading into uncontaminated soil. The leachate must be collected and treated (Roger and John, 1994).

This has been applied for the treatment of non-halogenated volatile organic compounds (VOCs) and fuel hydrocarbons, halogenate VOCs, SVOCs and pesticide can be treated (Anderson, 1999).

The technology is a very simple technology to design and implement; cost competitive and can be designed to be a closed system. Further, it can be engineered to be potentially effective for any combination of site conditions and petroleum products (Anderson, 1999).

However, the limitations of this technology shows that concentration reduction > 95% and constituent concentration <0.1ppm are very difficult to achieve. Also the presence of significant heavy metal concentration may inhibit microbial growth and vapour generation during aeration may require treatment prior to discharge. Contaminated soils must be excavated and dust and noise must be controlled. Further, static treatment processes may result in less uniform treatment than processes that involve periodic mixing (Cheng and Zheng, 2000).

2.1.3 Bioreactors

A bio-reactor is a generic term from an engineering system in which contaminants are degraded in a specific media, with micro organism (Cook and John, 1995). This technique also referred to as slurry phase bioremediation, varies considerably in its operating conditions. The principal emphasis is on stimulating the biological degradation

rate by choosing the optimum temperature, pollutant concentration, degree of aeration and other factors.

Experience has shown that bioreactors are effective and capable of adapting to differing process/environmental conditions. Typically, the soil is mixed with water and any prescribed additives are placed in a batch reactor vessel. This slurry is kept at controlled operating conditions, with oxygen and nutrient supplied as required, until the remediation is complete. Typically, slurry contains from 10 to 30% solids by weight. The soil is then dewatered and the resulting liquid reused, discarded or treated as required. Aerobic system are effective on the target contaminants while anaerobic bioreactors have been applied more effectively to halogenated hydrocarbons, to effect dehalogenation prior to break down of the hydrocarbon itself. This technology has been successfully implemented to remediate organic compounds at leaking underground storage tank and industrial sites (Cook and John, 1995).

The bioreactor techniques have been successfully used to remediate soil contaminated with petroleum hydrocarbons, petrochemicals, solvents, pesticides, wood preservatives, SVOCs VOCs and other organic chemicals. Bioreactors are more suitable for heterogeneous soils, soils with low permeability, soil belonging to area where ground water would be hard to capture or scenarios requiring relatively short treatment times (Weesner & Bleam, 1998).

The technology is rapid when compared to other bioremediation methods and is widely available and can be particularly effective on contaminated clays.

However, it is highly dependent on the soil type and chemical properties of the contaminated media. Also the process control is complex, more so than solid phase bioremediation techniques. Contaminated ground water is often too dilute in nutrients to support an adequate microbial population. At the other extreme, very high concentration may be toxic to micro organisms. Finally, residual contaminant may require further treatment or disposal (Weesner and Bleam, 1998).

2.1.4 Land farming

Land farming also known as land treatment or land application, is an above-ground remediation technology for soils. It reduces concentration of contaminants through biodegradation. In the *ex-situ* process, the contaminated soil is first excavated, mixed with soil amendments such as soil bulking agents and nutrients and then tilled into the earth. The soil is spread over an area and periodically turned to improve aeration.

Turning the soil also avoids the disadvantages of having heterogeneous degradation. Soil conditions are controlled to optimize the rate of contaminant degradation. The enhanced microbial activity results in degradation of adsorbed petroleum product constituents through microbial respiration. The petroleum industry has used land farming for many years (Vanstraalen and Lokke, 1999).

Land farming has been proven most successful in treating petroleum hydrocarbon and other less volatile biodegradable contaminants. It can also be applied to certain halogenated volatile, semi-volatile and non-halogenated semi volatile organic compounds and pesticides. Diesel fuel, oily sludge, wood-preserving wastes have also been successfully treated (Van Gestel, 1999).

The technology is extremely simple rather inexpensive and requires no process controls. Also relative unskilled personnel can handle the technique. Certain pollutants such as oil sludge, diesel fuel and wood preserving waste can be completely removed from the soils

However, it requires extensive space and time; pollutants cannot be reduced to sufficiently low level. Run off must be collected and may require further treatment. Again, it can incorporate contaminated soil into uncontaminated soil thus, creating a larger volume of contaminated material. Conditions affecting biological degradation of contaminant (e.g temperature and rainfall) are largely uncontrolled. This may increase the time to complete remediation (Van Gestel, 1999).

2.1.5 Dehalogenation

Dehalogenation, also known as dechlorination is a technology in which the chlorine in organic compounds is displaced by hydrogen or a reducing radical containing a hydrogen donor. This process is achieved by either the replacement of the halogen molecules or the decomposition and partial volatilization of the contaminants. Contaminated soil is screened, processed with a crusher, mixed with chemical reagents and the mixture is heated in a reactor (Tye *et al.*, 1999).

There are two dehalogenation processes, namely;

i. **Base-Catalysed Decomposition (BCD)-** In this process the contaminated soil is screened, processed with a crusher and pug mill and mixed with

sodium bicarbonate. The mixture is heated to above 330^0C (630^0f) in a reactor to partially decompose and volatilize the contaminants and the volatilized contaminate are captured, condensed and treated separately.

ii. **Glycolate/Alkaline polyethylene Glycol Application**: This is a process in which an alkaline polyethylene glycol (APEG) reagent is used. In this process, the reaction causes the polyethylene glycol to dehalogenate to form glycol ether and / or a hydroxylated compound and an alkali metal salt which are water soluble by-products (Tye *et al.,*1999).

Contaminants that can be treated are halogenated SVOCs and pesticides in salts. APEG dehalogenation can be used but may be less effective against selected halogenated VOCs. The technology is amenable to small scale applications. The BCD can also be used to treat halogenated VOCs but will generally be more expensive than other technologies (Tye *et al.*, 1999).

This technique has been used successfully to eliminate polychlorinated biphenyls (PCBs).The technique uses low-cost reagents that do not need to be recovered and reused.

However, this process is generally not cost effective for large volumes of contaminated soil. Soils with elevated concentration of chlorinated contaminants require large volumes of reagent to be treated. Some glycol ethers are very toxic and persistent. It is still not completely clear what by-products the APEG technology produces and how they are captured and treated (Tye *et al.*, 1999).

2.1.6 Separation

Separation techniques reduce the volume of contaminated soil through physical and chemical processes by selectively removing the portion containing the contaminants (Twiss, 1989). There are several types of separation techniques;

i. **Gravity separation**: This is used to separate solid from soil based on the density difference between contaminants and soil e.g., when the metal-contaminated soil is suspended in water, denser materials such as metals sink and are removed.

ii. **Sieving/ physical separation:** This technique is based on separation according to size of the particles

iii. **Magnetic separation:** This technique is used to separate slightly magnetic particles from soil. All uranium and plutonium compounds are slightly magnetic while most soil is non-magnetic.

iv. **Chemical leaching processes:** Chemical leaching uses weak acids such as acetic acid to dissolve and wash the metals from the soil. The metal recovered by the processes can possibly be recycled (Twiss, 1989).

This technology is applied in the treatment of fuel, inorganic, heavy metals, some SVOCs and VOCs (Stumm and Morgan, 1992).

Also it reduces the volume of contaminated soil considerably and it has been successfully demonstrated in municipal waste treatment.

However, this technology does not work well when the undesirable material homogenously are distributed in the soil; also the segregated soil is not at all cleaned by this techniques thus, subsequent process is required to actually remove the pollutants from the soil particles.

Further, special measures may be required to mitigate odour problems resulting from organic sludge that undergoes septic conditions and magnetic separation may leave small suspension of contaminated materials in the slurry, which may be more difficult to remediate than the original soil contamination (Stumm and Morgan, 1992).

2.1.7 Solar Detoxification

Solar detoxification, otherwise known as photolysis, is an emerging remedial technology which is used for the destruction of a wide range of hazardous organic chemicals in soil and /or water by photo catalytic oxidation or direct thermal decomposition (Schmidt, *et al.,* 2000). In this process, vacuum extraction is used to remove contaminants from soils. After condensation, contaminants are mixed with a semi-conductor catalyst and fed through a reactor illuminated from electric lamps. The light activates the catalyst and this result in the generation of radicals which oxidize the contaminants into non-toxic by-product such as carbon dioxide and inorganic salts.

This is used for destruction of VOCs, SVOCs solvents, pesticides, fuels and explosives, some applications of removing heavy metals from water have been done with this technique. Also, this system completely destroys the toxic compounds instead of just removing them. The solar process has no atmospheric emissions, hence effective

technology for reducing different pollutants to minimum concentrations (Schmidt *et al.,* 2000).

This technology cannot be used in full scale application and no adequate information about costing is known. Biological or physical fouling with suspended solid or precipitates could limit its effectiveness. It can only be effectively used during the day time with normal intensity of sunlight. Large spaces are required for the reactor in other words the larger the reactor, the more efficient the process (Schmidt *et al.,* 2000).

2.1.8 Chemical Reduction / Oxidation

Chemical reduction /oxidation, also known as redox reactions, convert hazardous contaminants to non-hazardous or less toxic compounds that are more stable, less mobile and / or inert (Vande Ven, 1990). Redox reactions involve the transfer of electrons from one compound to another (Vande Ven, 1990). One compound oxidized (loss electrons) and the other is reduced (gain electrons). The oxidizing agents most commonly used are ozone, hydrogen peroxide, hypochlorite, chlorine and chlorine dioxide. A mixture of these reagents or combining them with ultraviolet oxidation makes the process more effective. In the reduction process, sodium borohydride or metals with low oxidation potential are generally used for unsaturated organic contaminants or high oxidation state metals e.g. (Cr, V) (Vande Ven, 1990).

The redox method treats metal and inorganic in soil. Redox processes, have also been applied for the treatment of pesticides, cyanides, triazines and formaldehyde contamination (Heimstra and Vanriemsdijk, 1996).

Also technique is well established and has been used for decades in related chemical processes.

However, excessive oil and grease compete with the contaminants during chemical reactions and may need to be removed prior to treatment. Also the decontamination may be incomplete or results in the formation of intermediate contaminants for certain pollutants or process conditions.

Finally, this process is not cost effective for high contaminant concentration due to the excessive amounts of reagents required (Heimstra and Vanriemsdijk, 1996).

2.1.9 Soil Washing

Soil washing is a technique in which contaminants sorbed on to fine particles are separated from bulk soil in an aqueous-based system on the basis of particle size (Cheng and Zheng, 2000). Contaminants are removed from the soil in one of two ways:

By dissolving or suspending them in the wash solution and by concentrating them into a smaller volume of soil through particle size separation, gravity separation and attrition scrubbing (Cheng and Zheng, 2000). The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically to clay, silt and organic soil particles. Most silt and clay are stuck to larger particles like sand and gravel. Washing separates the small particles from the large ones by breaking adhesive bonds / the separated material is smaller in volume and is more easily disposed off (Cheng and Zheng, 2000).

This method is used to treat contaminants such as SVOCs, fuels, explosive and heavy metals. This technology can be used on selected VOCs and pesticides and it offers the ability for recovery of metals and can clean a wide range of organic and inorganic contaminants from coarse grained soils (Cheng & Zheng, 2000).

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It is also a well-established and versatile techniques and it provides a cost effective and environmental proactive alternative to stabilization and land filling.

However, this technique is not always effective on all soil types and works better on coarse particle and sandy soils and high levels of organic matter inhibit soil washing. Also the aqueous stream will require treatment at demobilization and complex mixture of pollutant may be difficult to remediate with a single wash regime.

2.1.10 Solidification / Stabilization (S/S)

In *ex-site* solidification / stabilization (S/S), contaminants are physically bound or enclosed within a low permeability mass (solidification) or chemical reactions are induced between a stabilization agent and contaminants to reduce their mobility (stabilizing). Ex situ S/S, however, typically requires disposal of the resultant materials. This technique is also applicable in in-site interventions with a different technological set up (Tye *et al.,* 1999).

This is used in treating inorganic contaminants including radionuclide. This technique is a relatively inexpensive method for treating soil contaminated with inorganic and can be extremely simple to apply.

However, the pollutants are neither removed nor made less toxic, only rendered less mobile; the volume of the final mass is generally higher than that of the original contaminated soil (when using solidification), the resulting mass may still need to be controlled as a hazardous waste for stabilization. Treatability studies may be required to determine application and organic contaminants are generally not immobile (Tye *et al.,* 1999).

2.1.11 Soil Vapour Extraction

Soil Vapour Extraction (SVE), also known as soil venting, is a technology which in principle, is similar to in-site SVE. However, in the *ex-situ* process, the contaminated soil is excavated. A vacuum is applied to a network of above ground piping to encourage volatilization of organic from the excavated media. The soil piles may be covered with a geomembrane to prevent volatile emissions and to prevent the soil from becoming saturated by precipitation. The process includes a system for handling of gases (De Haan, 199 7).

Contaminants that are treated with this technique are VOCs, volatile metal and fuels contaminants. SVE works only on compounds that readily vapourize under process condition.

Further, this design is simple and easily implemented and can prove to be productive in area where access to the contaminated site is very limited.

The excavation process forms an increased number of passage ways, leachate collection is possible and treatment is more uniform and easily monitored. Also the

equipment requires relatively little control during operation and pollutants are under vacuum conditions, thus there is little chance of an environmental release during the application of this technique (De Haan, 1997).

However, there is an increased excavation cost and materials handling may pose hazardous emissions to the surrounding. Also the application is limited to contaminants that will partition into the vapour phase. High moisture content, high humic content or compact soil inhibits volatilization.

More so, field-pilot study is necessary to establish the feasibility of the method, the best process conditions, as well as, to obtain information necessary to design and configure the system (De Haan, 1997).

2.1.12 Hot gas Decontamination

Hot gas decontamination is essentially a low temperature thermal adsorption process. The process raises the temperature of the contaminated soil to approximately 260^0C for a specified period of time by exposing it to hot gases (i.e. heated air), volatilizing the contaminations and destroy them in an after burner (Weng and Burau 1994). This technology can be used to decontaminate equipment and structures that have been contaminated with explosive residues.

It is applied for equipment requiring decontamination for reuse, for explosive item, such as mines and shell being demilitarized (after removal of explosives) or scrap material contaminated with explosive such as TNT. It can also be used for buildings or structures associated with ammunition plants, arsenals and depots involved in the manufacture

and processing of explosive and propellants (Weng and Burau 1994). Also in this technique, contaminates are completely destroyed.

However hot gas decontamination has the problem of atmospheric emission from the thermal oxidizer; the furnace design must take into consideration possible explosion and the cost of this method is higher than open burning.

2.1.13 Open Burning

Open burning, also known as open detonation is a techniques used to destroy excess, obsolete, or unserviceable ammunition and explosive materials. These materials are destroyed by self-sustained combustion, which is ignited by an external source. An auxiliary fuel may be added to initiate and sustain the combustion of materials. In the past, open burning generally occurred in the surface of the land or in pits. Burn trays and blast boxes have been used to control and contain resulting emissions (Weng and Burau, 1994). This technology is used to destroy explosives and ammunition.

However, emissions of hydrocarbons, metals and other substances from operations are extremely difficult to capture and may not be permitted in many areas; also sub-surface processes may minimize release of emission. Substantial space is required for open processes in order to maintain minimum distance requirements for safety purposes and this is a process that can lead to toxic releases and exposure of gaseous substance (Macnicol and Beckett, 1990).

2.1.14 Thermal Desorption

Thermal desorption is a physical separation process in which water and organic contaminants in contaminated soil are volatilized by heating the soil to moderately high temperatures (100^0-55^0C) (William and Anderson 1997). A carrier gas or vacuum systems transport the volatilized water and organics to the gas treatment system. The bed temperatures and residence times designed into these systems volatilize selected contaminants but do not degrade them.

Based on the operating temperature of the desorber, thermal desorption processes can be categorized into two groups:

i. High temperature thermal desorption (HTTD): In this process, contaminants are heated from 320^0 to 560^0C.

ii. Low temperature thermal desorption (LTTD): Also contaminants are heated between 90^0 and 320^0C.

There are also two common thermal desorption designs, namely the rotary dryer and thermal screen. Rotary dryers are horizontal cylinders that can be indirect or direct-fired. The dryer is normally inclined and rotated. For the thermal screw units, screw conveyors or hollow augers are used to transport the medium through an enclosed trough. Hot air or steam circulates through the auger to indirectly heat the medium. All thermal desorption system require treatment of the off-gas to remove particulates and contaminants. Particulates are removed by convectional particulate removal equipment such as wet scrubbers or fabric filters (Rahuman, 2000).

Contaminants treated in LTTD systems are SVOCs VOCs, and fuels. For HTTD, the groups are SVOCs, PAHs, PCBs and pesticides. VOCs and fuels may be treated but treatment may be less cost- effective. Volatile metal may be removed by HTTD (Jerome, 1998).

Also the cost is typically less than that of incineration and is applicable to a wide range of pollutants

Thermal desorption has some limitations with heavy metals which may remain in the solid residue and may form toxic by-product during treatment. There are specific particle size and materials handling requirements that can impact applicability or cost at specific sites (Jerome, 1998).

2.1.15 Plasma Arc

Plasma arc technology is a pyrolysis process. It uses a plasma arc device to create extremely high temperatures (10000^0C or even higher) for destruction of toxic substances in contaminated soil.

In plasma arc treatment, an electric current is directed through a low-pressure gas stream to create a thermal plasma field. Plasma arc fields can reach 5000 to 15000^0C (Staley, 1992).

Energy is transferred to contaminants exposed to the plasma and contaminants are then atomized, ionized, pyrolysed and finally destroyed as they interact with the decaying plasma species (Staley, 1992).

It is applied for the treatment of organic substances. Initial test results have shown it is a promising alternative for destruction of “difficult to treat” wastes such as dioxin contaminated sludge (Staley, 1992).

It is an effective technology to safely destroy PCBs, dioxins, furans and pesticides plasma. A plasma system has very intense radioactive power and therefore is capable of transferring its heat much faster than a conventional flame.

Since it is a pyrolysis process, it does not need the energy to heat excess air required by conventional incinerators; it needs a smaller capacity of downstream cleanup systems, because no excess air is involved and because of its compactness, the system has potential for use as a mobile treatment system. The process has a very short on-off cycle (Huffman and Lee, 1994).

However, this uses electricity as an energy source and so is more expensive when compared to using oil to fire incinerators. It requires a separate extraction process such as solvent extraction or thermal desorption to remove the contaminants from bulk solid media.

Also solid must be first converted to liquid or gas prior to treatment.

Metal may impede treatment and must be separated for the techniques in order to be effective.

Also because the temperatures are so high, the durability of the arc and the refractory materials could be a potential problem (Huffman and Lee, 1994).

2.1.16 Incineration

Incineration is a technology which uses high temperature 850^0-1200^0C and oxygen, to volatilize and combust different kinds of hazardous contaminants (Mouvet and Bourg, 1998). Auxiliary fuels are used to initiate and sustain combustion. Proper incinerator design and operation are essential to ensuring adequate destruction of undesirable combustion gases. A proper operated incinerator can meet the stringent requirements for all gaseous emissions. Air pollution control systems are employed to remove particulates and to neutralize and remove acids (Mouvet and Bourg, 1998).

Incineration is different from other thermal technologies in that it oxidizes bulk quantities of contaminants that may be in liquid and solid phase. Four common incinerator types are rotary kiln, liquid injection, fluidized bed and infrared kiln.

It is used to remediate soils contaminated with hazardous substances (VOCs, SVOCs), particularly halogenated and organic compounds, fuels and explosives (Edinger, 1995).

It is also one of the most mature and well-known treatment technologies and at high temperatures it is fast and very effective (99%).
It is also highly effective for a wide range of contaminants in high concentrations (Edinger, 1995).

However, it is a costly technique; Pre-treatment to remove heavy metals may be required because they remain in the solid residue or may possibly leave with the flue gases. It may release toxic chemicals from their stacks and when chlorinated hydrocarbons are incinerated, products of incomplete combustion can be formed; these

may include dioxins and furans. Finally wastes with heavy metals can produce a bottom ash of high concentration (Edinger, 1995)

2.1.17 Pyrolysis

Pyrolysis also known as plasma pyrolysis is the thermal degradation of organic species in the absence of oxygen or other reactant gases (Roy *et al.,* 1995). In practice, it is not possible to achieve a completely oxygen-free atmosphere, actual pyrolytic system are operated with less than stoichiometric quantities of oxygen (Roy *et al.,* 1995).

This thermal technology is a form of incineration at operating temperature above 430^0C. Organic materials are transformed into gases, small quantities of liquid and solid residue (coke) containing carbon and ash (Roy *et al*., 1995). The off-gases may also be treated in a secondary thermal oxidation unit. Particulate removal equipment is also required. Conventional thermal treatment methods such as rotary kiln, rotary hearth furnaces or fluidized bed furnaces are used for waste pyrolysis.

This technique treats and destroys SVOCs, fuel and pesticides. The process is applicable for the separation of organic from refinery waste, coal tar wastes, wood-treating wastes, creosote-contaminated soils, hydrocarbon-contaminated soils mixed (radioactive and hazardous) wastes, synthetic rubber processing waste and paint waste (Roy *et al*., 1995).

Also, the reactions are thermal, making it possible to control pyrolysis temperature by regulating heat addition.

Heavy metal volatilization and emissions are greatly reduced because the waste stream is only exposed to mild temperatures and caustic can be added during pyrolysis of halogenated contaminants to trap halogens such as sodium halides, thus reducing exhaust gas scrubber loads. Solid produced in this process can be high-value product such as adsorbents, electrodes and catalyst supports.

This technology requires drying of the soil prior to treatment; there is concern that systems that destroy chlorinated organic molecules by heat have the potential to create product of incomplete combustion, including dioxins and furans. Also, pyrolysis is not effective in either destroying or physically separating inorganic from the contaminated medium; by-products containing heavy metals may require stabilization before final disposal (Roy *et al.,* 1995).

2.1.18 Vitrification

This ex-technology is much like *in-situ* vitrifcation, except that it is done inside a chamber. Heating devices include plasma torches and electric arc furnaces. With plasma torch technology, contaminated soil is fed into a rotating hearth; the contaminants and molten material are held against the side by centrifugal force. During the rotation, the contaminants move through plasma generated by a station torch. To remove the molten material from the furnace, the hearth's rotation slows and the slags flow through a bottom opening. Effluent gases are generally kept in a separate container where high temperature combust / oxidize the contents. The arc furnace contains carbon electrode, cooled sidewalls, a continuous fed system, and an off gas treatment system. In this process, contaminated soil is fed into a chamber where it is

heated to temperature greater than 1500^0C. The melt exits the vitrification unit and cools to form a glassy solid that immobilizes inorganics (Marn and Marcus, 2002).

It is applicable for the treatment of organics, inorganics and radionuclide. It is an effective technology to immobilize heavy metals (Marn and Marcus, 2002).

However, there is increase in cost due to high moisture content. Excavation of radioactively contaminated soil could cause radiation exposure to workers from fugitive gas and dust emissions, and it may also increase the risk to nearby population. There is potential for the accumulation of volatile radionuclide in the smelter off gas system.

2.2.0 Heavy Metals as pollutant in the environment

Heavy metals are defined as metals having density greater than $5g/cm^3$ (Pearce, 2007). This classification includes transition metals and higher atomic weight metals of group (iii) to (v) of the periodic table.

The heavy metals include Pb, Hg, As, Cr, Ni, Se, Fe, Cd. These metals constitute some forms of pollution when present in the environment at lethal concentrations. In practice, heavy metal pollution implies any metal exposure which is clinically undesirable and which constitutes potential hazards to human health and environment (Pearce, 2007). The study of these heavy metals pollutants has led to a branch of science called toxicology. Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage and even deaths. (Neddleman, 2004). Although some of them have some important uses, caution has to be applied in handling processes involving them to minimize their toxicological effects (Neddleman, 2004).

These metals pollute the air, water, soil and food. In the air, they occur as solid particulate matters for example lead gets into the atmosphere during smelting process in industries and also by motorized vehicles during exhaust emission (Pearce, 2007). Lead (Pb) particulates finally gains its way into human beings, animals, and vegetation, soil and water bodies through food chain. A metal and its compound in the soil are absorbed by root hairs of plants, then to the branches and finally to the fruits they bear. Man, animals and birds partake of the fruits. Some flora and fauna breed mostly in refuse dump sand, feeding on them poses some danger as result of likelihood of bioaccumulation of the metals (Pearce, 2007)

Lead (Pb)

Lead poisoning can cause a variety of symptoms and signs which vary depending on the individual and the duration of lead exposure (Grant, 1998). Symptoms are non-specific and may be subtle, and someone with elevated lead levels may have no symptoms.

Symptoms usually develop over weeks to months as lead builds up in the body during a chronic exposure, but acute symptoms from brief intense exposure also occur (Ross, 2008). Symptoms from exposure to organic lead, which is probably more toxic than inorganic lead due to its liquid solubility, occur rapidly. Poisoning by organic lead compound has symptoms predominantly in the central nervous system, such as insomnia, delirium, cognitive deficits, tremor, hallucinations, and convulsion (Patrick, 2006). Symptoms may be different in adults and children, the main symptoms may be

different in abdominal pain, memory loss, kidney failure, male reproductive problems and weakness, pain or tingling in the extremities (Needleman, 2004).

Early symptoms of lead poisoning in adults are commonly non-specific and include depression, loss of appetite, intermittent abdominal pain, nausea, diarrhea, constipation and muscle pain. Other early signs in adults include malaise, fatigue, decreased libido and problems with sleep (Hu *et al.,* 2007). An unusual taste in the mouth and personality change is also early signs. In adults, symptoms can occur at levels above 40µg/dL (Hu *et al.*, 2007). Symptoms begin to appear in children generally at around 60µg/dL However, the lead levels at which symptoms appear vary widely depending on unknown characteristics of each individual. At blood lead levels between 25 and 60µg/dL, neuropsychiatric effects such as delayed reaction times, irritability and memory loss, as well as slowed motor nerve condition and headache can occur (Hu *et al.,* 2007). Anaemia may appear at blood lead level higher than 50µg/dL. In adults, abdominal colic involving paroxysms of pain may appear at blood lead levels greater than 80µg/dL. Signs that occur in adults at blood lead levels exceeding 100µg/dL include wrist drop and foot drop and signs of encephalopathy (a condition characterized by brain swelling), such as those that accompany increased pressure within the skull, delirium, coma, seizures and headache (Hu *et al.,* 2007). In children, signs of encephalopathy such as bizarre behaviour, disco-ordination, and apathy occur at lead level exceeding 70µg/dL. For both adults and children, it is rare to be asymptomatic if blood lead levels exceed 100µg/dL (Pearson & Schonfeld, 2011).

In acute poisoning, typical neurological signs are pain, muscle weakness, paraesthesia and rarely, symptoms association with encephalitic. Abdominal pain, nausea, vomiting,

diarrhea and constipation are other acute symptoms (Hu *et al.,* 2007). Lead's effects on the mouth include astringency and a metallic taste gastrointestinal problem, such as constipation, diarrhea, poor appetite, or weight loss is common in acute poisoning. Absorption of large amounts of lead over a short time induce can shock (in sufficient fluid in the circulating system) due to loss of water from the gastrointestinal tract (Pearce, 2007). Hemolysis (the rupture of red blood cells) due to acute poisoning can cause anaemia and haemoglobin in the urine. Damage to kidney can cause changes in urination such as decreased urine output. People who survive acute poisoning often go on to display symptoms of chronic poisoning (Timbrell, 2008).

Chronic poisoning usually presents with symptoms affecting multiple systems but is associated with three main types of symptoms, via: Gastrointestinal, neuromuscular and neurological (Needleman, 2004).Central nervous system and neuromuscular symptoms usually result from intense exposure while gastrointestinal symptoms usually result from exposure over long periods. Signs of chronic exposure include loss of short-term memory or concentration depression, nausea, abdominal pain, loss of coordination and numbness and tingling in the extremities (Patrick, 2006). Fatigues, problem with sleep, headache, stupor, slurred speech, and anaemia are also found in chronic lead poisoning. A 'lead hue' of the skin with pallor is another feature (James *et al.,* 2005). A blue line along the gum, with bluish black edging to the teeth, known as Burton line is another indication of chronic lead poisoning. Children with chronic poisoning may refuse to play or may have hyperkinetic or aggressive behaviour disorders (Chisolm and Harrison, 1996).

Infants developing in the womb of the women with elevated blood lead level are also susceptible to lead poisoning. There is also a risk as the baby comes closer to full terms, as the women is more likely to have a premature, or with low birth weight (Bellinger, 2004).

Children are more at risk of lead poisoning because their smaller bodies are in a continuous state of growth and development (Bellinger, 2004). Lead is absorbed at a faster rate in them compared to adults which causes more physical harm than to older people. Furthermore, children especially as they are learning to crawl and walk are constantly on the floor and therefore more prone to ingesting and inhaling dust that is contaminated with lead (Bellinger, 2004).

The classic signs and symptoms in children are loss of appetite, abdominal pain, vomiting, weight loss, constipation, anemia, kidney failure, irritability, lethargy, learning disabilities and behaviours, such as talking and use of word and permanent mental retardation are both commonly seen (Bellinger, 2004).

Lead has no known physiologically relevant role in the body (Sanborn *et al.,* 2002) and its harmful effects are myriad. Lead and other heavy metal create reactive radicals which damage cell structures including DNA and cell membrane (Jacobs *et al.,* 2002). Lead also interferes with DNA transcription, enzymes that help in the synthesis of vitamin D and enzymes that maintain the integrity of the cell membrane. Anemia may result when the cell membranes of red blood cells become more fragile as a result of damage to their membranes (Jacobs *et al.,* 2002). Lead interferes with metabolism of bones and teeth (Brudevold and Steadman, 1986) and alters the permeability of blood vessels and collagen synthesis (Dimaio *et al.,* 1983). Lead may also be harmful to the

developing immune system causing production of excessive inflammatory proteins. This mechanism may mean that lead exposure is a risk factor for asthma in children (Landrigen *et al.,* 2002). Lead exposure has also been associated with a decrease in activity if immune cells such as polymorph nuclear leukocytes. Lead also interferes with the normal metabolism of calcium in cells and causes it to build up within them (Billings *et al.,* 2004).

The primary effect of lead toxicity is its interference with a variety of enzymes because it binds to sulfhydryl groups found on many enzymes (Shih *et al.,* 2007). Part of lead toxicity results from the ability to mimic other metals that take part in biological processes, which act as co-factors in many enzymatic reactions, displacing them at the enzymes on which they act (Meyer *et al.,* 2003). Lead is able to bind to and interact with many of the same enzymes as other metals but, due to its differing chemistry does not properly function as a cofactor thus interfering with the enzyme's ability to catalyse its normal reaction or reactions. Among the essential metal with which lead interacts are calcium, iron and zinc (Brudevold & Steadman, 1986).

One of the main causes for the pathology of lead is that it interferes with the activity of essential enzyme called delta aminolevulinic acid dehydratase or ALAD, which is important in the biosynthesis of heme, the co-factor found in haemoglobin (Shadick *et al.,* 2000). Lead also inhibits the enzyme ferrochelatase, another enzyme involved in the formation of heme. Ferrochelatase catalyses the joining of portoprophyrin and fezt to form heme (Lin and Hang, 1994). Lead's interference with heme synthesis results in production of zinc portoporphyrin and the development of anemia. Another effect of

lead's interference with heme synthesis is the buildup of heme precursor, such as aminolevulinic acid, which may be directly or indirectly harmful to neurons (Park *et al.,* 2008).

Lead interferes with the releases of neurotransmitters, chemicals used by neurons to send signals to other cells. It interferes with the release of glutamate, a neurotransmitter important in many functions including learning, by blocking N-Methyl-D-aspartate (NMDA) receptor. The targeting NMDA reception is thought to be one of the main causes of lead toxicity to neurons (Wright *et al.,* 1984). A John Hopkins report found that in addition there is an inhibition of NMDA receptor in part of the brain (Lanphear *et al.,* 2005). In additional, lead has been found in animal studies to causes programmed cell death in brain cells.

Lead affects every one of the body's organ systems, especially the nervous system. It also affects the bones and teeth, the kidney and the cardiovascular, immune and reproductive system (White *et al.,* 2007). Hearing loss and tooth decay have been linked to lead exposure as have cataracts (Pearce, 2007). Intrauterine and neonatal lead exposure promotes tooth decay (Manay *et al.,* 2008). Apart from the developmental effects unique to young children, the health effects experienced by adults are similar to those in children though the thresholds are generally higher (Woolf *et al.,* 2007).

Kidney damage occurs with expose to high level of lead, and evidence suggests that lower levels can damage kidney as well (Mass *et al.,* 2005). The toxic effect of lead causes nephropathy and may cause fanconi syndrome, during which the proximal tubular function of the kidney, is impaired (Spitz *et al.,* 2008). Long-term exposure at

levels lower than those that cause lead nephropathy has also been reported as nephrotoxic in patients from developed countries that had chronic kidney disease or were at risk because of hypertension or diabetes mellitus (Fugita *et* al., 2002). Lead poisoning inhibits excretion of the waste product urate and causes a predisposition for gout, in which urate build. This condition is known as saturnine gout (Fujita *et al.,* 2002).

Evidence also suggests that lead exposure is associated with high blood pressure and studies have also found connections between lead exposure coronary heart disease, heart rate variability and death from stroke (Campbell *et al.,* 2000). People who have been exposed to higher concentrations of lead may be at a higher risk of cardiac autonomic dysfunction on days when ozone and fine particles are higher (Sander *et al.,* 2009). Lead affect both the male and female reproductive system in men, when blood lead levels exceed 40µg/dL sperm count is reduced and changes occur in volume of sperm, their modality and their morphology (Cecil *et al.,* 2008). A pregnant woman's elevated blood lead level can lead to miscarriage, prematurely, low birth weight and problems with development during childhood (Bellinger, 2008). Lead is able to pass through the placenta and into breast milk resulting in similar blood lead level in mothers and infant (Bellinger, 2008). A Fetus may be poisoned in uterus if lead from the mother's bones is subsequently mobilized by the changes in metabolism due to pregnancy; increases calcium intake pregnancy may help mitigate this phenomenon (Needleman *et al.,* 1990).

Lead affects the peripheral nervous system (especially motor nervous) and the central nervous system (Fred, 2009). Peripheral nervous system effects are more prominent in

adults and central nervous system effects are more prominent in children (Cleveland *et al.,* 2008). Lead causes the axons of nervous cells to degenerate and lose their myelin coats. The brain is the organ most sensitive to lead exposure (Ross, 2008). Lead poisoning interferes with the normal development of a child's brain and nervous system therefore children are at greater risk of lead neurotoxicity than adults (Ragan and Turner, 2009). In a child's developing brain, lead interferes with synapse formation in the cerebral cortex, neuro chemical development (including that of neurotransmitters) and organization of ion channels (Guidotti and Regain, 2007). It causes loss of neurons' myelin sheaths, reduces number of neurons, interferes with neuro transmission and decreases neuronal growth (Gilbert and Weiss, 2006). Lead exposure in young children has been linked to learning disabilities and children with blood lead level greater than 10µg/dL are in danger of developmental disabilities (Gilbert and Weiss, 2006). Increased blood lead level in children has been correlated with decreases in intelligence, non-verbal reasoning, short-term memory, attention, reading and arithmetic ability, fine motor skills, emotional regulation and social engagement (Woolf *et al.,* 2007). The effect of lead on children's cognitive abilities takes place at very low levels (Woolf *et al.,* 2007). There is apparently no lower threshold to the dose-response relationship (unlike other heavy metal such as mercury (Brodkin *et al.,* 2007). Reduced academic performance has been associated with lead exposure even at blood lead levels lower than 5µg/dL (Mass *et al.,* 2005). Blood lead levels below 10µg/dL have been reported to be associated with lower lQ and behaviour problems such as aggression, in proportion with blood lead levels. Between the Blood lead levels of 5 and

35µg/dL, an lQ decrease of 2-4 points of each µg/dL increase is reported in children (Gilbert and Weiss, 2006).

High blood lead levels in adults are also associated with decrease in cognitive performance and with psychiatric symptoms such as depression and anxiety (Lin and Huang, 1994). Increase in blood lead levels from about 50 to about 100µg/dL in adults have been found to be associated with persistent, and possibly permanent, impairment of central nervous system function (Hu *et al.,* 2007).

Lead exposure in children is also correlated with neuropysiatric disorders such as attention deficit hyperactivity disorder and antisocial behaviour (Chisolm and Harrison, 1996). Elevated lead level in children is correlated with higher scores on aggression and delinquency measures (Chisolm and Harrison, 1996). A correlation has also been found between prenatal and early childhood lead exposure and violent crime in adulthood. Countries with the higher air lead levels have also been found to have the highest murder rates, after adjusting for confounding factors (Shadick *et al.,* 2000).

Cadmium (Cd)

Cadmium is an extremely toxic metal commonly found in industrial workplaces. Due to its low permissible exposure limit, over exposure may occur even in situation where trace quantities of cadmium are found. Cadmium is used extensively in electroplating, although the native of the operation does not generally lead to over exposure. Cadmium is also found in some industrial paints and may represent a hazard when sprayed. Operation involving removal of cadmium paints by scalping or blasting may pose a significant hazard. Cadmium is also present in the manufacturing of some types of

batteries. Exposures to cadmium are addressed in specific standards for the general industry, ship year employment, construction industry and the agricultural industry (Jarup, 1998).

Sources of exposure of cadmium

In the 1950s and 1960s industrial exposure of cadmium was high, but as the toxic effects of cadmium became apparent, industrial limits on cadmium exposure have been reduced in most industrialized nations and many policy makers agree on the need to reduce exposure further. While working with cadmium, it is important to do so under a fume hood for protection against dangerous fumes. Silver solder, for example which contains cadmium should be handled with care. Serious toxicity problem have resulted from long-term exposure to cadmium plating baths.

Building of cadmium levels in the water, air and soil has been occurring particularly in industrial areas (Taylor, 1997). Environmental exposure to cadmium has been particularly problematic in Japan where many people have consumed rice that was grown in cadmium contaminated irrigation water (Jarup, 1998). This phenomenon is known under the name itai-itai disease. Food is another source of cadmium. Plants may only contain small or moderate amount in non-industrial areas, but high level may be found in the liver and kidney of adult animals (Shannon, 1998). Cigarettes are also a significant source of cadmium exposure. Although there is generally less cadmium in tobacco than in food, the lungs absorb cadmium more efficiently than the stomach. Apart from tobacco smokers, people who live near hazardous waste sites or factories that release cadmium into the air have the potential for exposure to cadmium in air

(Basalt, 2008). However, numerous state and federal regulation control the amount of cadmium that can be released to the air from waste sites and incinerators so that properly regulated sites are not hazardous. The general population and people living near hazardous waste sites may be exposed to cadmium in contaminated food, dust or water from unregulated release or accidental release. Numerous regulation and use of pollution controls are enforced to prevent such releases. Workers can be exposed to cadmium in air from the smelting and refining of metals, or from the air in plants that make cadmium products such as batteries coating or plastics. Workers can be exposed when soldering or welding metals that contain cadmium (Basalt, 2008).

Artists who work with cadmium pigments can easily and accidentally ingest dangerous amount, particularly if they use the pigments in dry form, as with chalk pastes or in mixing their own paints. Phosphate fertilizer contains cadmium in amount of up to 100mg/kg which can lead to an increase in the concentration of cadmium in soil.
Nickel cadmium batteries are one of the most popular and most common cadmium-based products. An experiment during the early 1960s involving the spraying of cadmium over Norwich has recently been declassified by the UK government, as documented in a BBC News article.

Acute exposure to cadmium fumes may cause flu-like symptoms including chills, fever and muscle ache sometime referred to as “the cadmium blues” symptoms (Jarup, 1998). More severe exposure can cause tracheobrochitis, preumonitis and pulmonary edema. Symptom of inflammation may start hours after the exposure and include

cough, dryness, irritation of the nose and throat, headache, dizziness, weakness, fever chills and chest pain (Jarup, 1998).

Inhaling cadmium-laden dust quickly leads to respiratory tract and kidney problems which can be fatal (often from renal failure). Ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver and the kidneys. Compounds containing cadmium are also carcinogenic (Shannon, 1998). The bones become soft (Osteomalacia), lose bone mineral density (Osteoporosis) and become weaker. This causes the pain in the joints and the back, and also increases the risk of fractures. The kidney loses their function to remove acids from the blood in proximal renal tubular dysfunction, (Jarup, 1998). The kidney damage inflicted by cadmium poisoning is irreversible. The proximal renal tubular dysfunction creates low phosphates levels in the blood (hypophosphatemia), causing muscle weakness and sometime coma (Shannon, 1998).

The dysfunction also causes gout, a form of arthritis due to the accumulation of uric acid crystals in the joints because of high acidity of the blood (hyperuricemia). Another side effect is increase level of chloride in the blood (hyperchloremia). The kidney can also shrink up to 30% (Taylor, 1997).

Arsenic (As)

Arsenic poisoning is a medical condition caused by elevated levels of the element arsenic. The dominant basis of arsenic poisoning is from ground water that naturally contains high concentrations of arsenic. A 2007 study found that over 137 million people in more than 70 countries are probably affected by arsenic poisoning of drinking water (Smedley and Kinniburgh, 2002).

Symptoms of arsenic poisoning begin with headache, confusion, severe diarrhea and drowsiness. As the poisoning develops, convulsion and changes in fingernail pigmentation called leukonychia may occur. When the poisoning becomes acute, symptoms may include diarrhea, vomiting, blood in the urine, cramping muscles, hair loss, stomach pain and more convulsions. The organs of the body that are usually affected by arsenic poisoning are the lungs, skin, kidneys, and liver. The final result of arsenic poisoning is coma or death (Tseng *et al.,* 2003).

Arsenic is related to heart disease (hypertension related cardiovascular), cancer, stroke (cerebrovascular disease), chronic lower respiratory diseases and diabetes (Smith *et al.,* 1994).

Long-term exposure to arsenic is related to vitamin A deficiency which is related to heart disease and night blindness (Chiou *et al.,* 1997). Research has shown that the inorganic arsenates (trivalent forms) in drinking water have much higher acute toxicity than the organic arsenates (pentavalent form) (Hendyx, 2009). The acute minimal lethal dose of arsenic in adult is estimated to be 70 to 200mg or 1mg/kg/day (Navas-Acien *et al.,* 2008). Most reported arsenic poisoning is caused by one of arsenic's compound, also found in drinking waters, (arsenic trioxide which is 500times more toxic than pure arsenic). Chronic arsenic poisoning results from drinking contaminated well water over a long period of time. Many aquifers contain high concentration of arsenic salt (Hsueh *et al.,* 1998). The World Health Organization recommends a limit of 0.01mg/L (10ppb) of arsenic in drinking water (Kile and Christian, 2008) This recommendation was established based on the limit of detection of available testing equipment at the time of publication of the WHO water quality guidelines (Kile and Christian, 2008). More recent

findings show that consumption of water with levels as low as 0.00017mg/l (0.17ppb) over long periods of time can lead to arsenicosis (Dart, 2004). Industries that use inorganic arsenic and its compounds include wood preservation, glass production, nonferrous metal alloy, and electronic semi-conductor. Industrial inorganic arsenic is also found in coke oven emission associated with the smelter industry. (Kingston *et al.,* 1993)

Zinc

Zinc is a silvery white metal which is fairly soft, properly connected with its low melting point (419^0C). Its boiling point is 908^0C and is more volatile than other transition metals. It is not attacked by air or water at ordinary temperatures, but the hot metal burns in air and decomposes steam to form white oxide Zn0 (Fosmire, 1990).

The metal is mainly used for galvanizing iron and in alloys especially brass. Its most important compound Zn0, is used as a pigment, as a filler for rubber and as an emollient in zinc ointment. Considerably quantities of zinc are also employed in the production of chemicals such as the sulphates, oxides, sulphide, chlorides and chromate.

Zinc is equally essential to living organisms. It stabilizers coiled ribosome, plays important role in sexual maturation and reproduction (Bothwell *et al.,* 2003).

Apart from its uses, it is slightly toxic to human health, causing vomiting. Pollution from industrial smoke may cause lung disease and continuous uses of zinc promote zinc pollution.

Zinc deficiency affects about two billion people in the developing countries and is associated with many diseases (Barceloux *et al.,* 1999). In children, it cause growth

retardation, infection susceptibility and diarrhea, contributing to death of about 800,000 children worldwide per year, Enzymes with a zinc atom in the reactive Centre are widespread in biochemistry, such as alcohol dehydrogense in humans consumption of excess zinc can cause ataxia, lethargy and copper deficiency (Feranbach and Tucker 1996).

Nickel (Ni)

Nickel is a trace element that occurs in the environment only at very low concentrations. It is released into the air by power plants and rash incinerators. It will then settle to the ground or fall down after reaction with raindrops. It usually takes a long time for nickel to be removed from air (McNeil and Lan, 1990). Nickel can also end up in surface waters when it is part of waste water streams. The larger part of all nickel compounds that are released to the environment will adsorb to sediment or soil particles and become immobile (Carnes *et al.,* 2009). In acidic soil however, it becomes mobile and will often rinse out to the ground water. Other sources of nickel may include foodstuffs such as fats and chocolate. Nickel is applied in different processes such as an ingredient of steel and other metal products. It stabilizes coiled ribosome and acts as active metal in several hydrogenases and plant ureases. Nickel is essential in chicks and rats and its absence shows some impaired liver functions and morphology (Derek, 2005).

Nickel toxicity sets in when people eat large quantities of vegetables from polluted soils. Smokers have a higher Nickel uptake through their lungs. Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes (stellman *et al*., 1998). Its consequence include higher chances of development of lung cancer, nose

cancer, larynx cancer and postulate cancer, sickness and dizziness after exposure to nickel gas, lung embolism, respiratory failure, birth defects, asthma and chronic bronchitis (Barceloux *et al*., 1999).

High nickel concentrations on sandy soil and surface waters can clearly damage plants and diminish the growth rates of algae respectively.

Nickel is essential but can be dangerous when the maximum tolerable amounts are exceeded.

Iron (Fe)

Iron is a transition metal that exists in two oxidation states, +2 and +3. It is by far the most widespread and important transition metal with a functional role in living systems. Iron has two chemical properties of higher affinity for oxygen and redox potential.

The redox potential between the two common oxidation states of iron is such that oxidation processes centered on the iron atom can be readily coupled to metabolic reactions. Iron also possesses high affinity for oxygen atoms.

These two properties also endow iron with the potential of being toxic.

Iron contained in proteins (Heme proteins) participates in two main processes; oxygen transport and electron transfer (Longmore *et al.,* 2004).

Iron also occurs in conjunction with molybdenum in enzymes that catalyses nitrogen fixation. Iron affects human health in a lot of ways; iron deficiency leads to low hemoglobin and anaemia in women because of loss by menstruation and children because an enhanced requirement for growth are susceptible to iron deficiency (Wander *et al.,* 2008). Symptoms of iron deficiency are not unique to iron deficiency (i.e.

not pathogononomic). Iron is needed for many enzymes to function normally, so a wide range of symptom may eventually emerge, either as the secondary result of the anemia, or as other primary results of iron deficiency. Symptoms of iron deficiency include, fatigue, pallor, hair loss, instability, weakness, pica, brittle or grooved nails, Plummer Vinson syndrome, painful atrophy of the nocuous membrane covering the tongue, the pharynx and the esophagus, impaired immune function, pagophagia, restless legs syndrome (Weinberg, 1984)

Too much iron occurs so rarely but when occurred, it leads to primary heamochromatosis (a genetic effect) or secondary heamochromatosis in severe cases and thalassaemia (Kluger and Rotherburg, 1979). In such cases, the only treatment available is the application of chelating therapy.

2.2.1 Chelation Treatment of Heavy Metals

A chelating agent is a molecule with at least two negatively charged groups that allow it to form complexes with metal ions having multiple positive charges, such as lead (Flora and Paschauri, 2010). The chelate that is thus formed is non-toxic and can be excreted in the urine, initially up to 50 times the normal rate. The chelating agent used for the treatment of lead poison are edentate disodium calcium ($CaNa_2$ EDTA), dimercaprol (BAL) which are injected and succimer and depenicillamine, which are administered orally (Chisholm, 2000). Chelation therapy is used in cases of acute lead poisoning (Chisholm, 2000). Severe poisoning and encephalopathy is considered for people with blood lead level above 25µg/dl (Thompson, 2007). While the use of chelation for people with symptoms of lead poisoning is widely supported, use in asymptomatic people with

high blood lead level is more controversial (Thompson, 2007). Chelation therapy is of limited value for cases of chronic exposure to low levels of lead (Susan *et al.*, 2008). Chelation therapy is usually stopped when symptoms resolve or when blood lead level return to premorbid levels. When lead exposure has taken place over a long period, blood lead levels may rise after chelation is stopped because lead is leached into blood from stores in the bone (Knudtson *et al.,* 2002). Thus repeated treatments are often necessary.

People receiving dimercaprol need to be assessed for peanut allergies since the commercial formulation contains peanut oil. Calcium EDTA is also effective if administered four hours after the administration of dimercaprol. Administering dimercaprol prior to calcium EDTA is necessary to prevent the redistribution of lead into the central nervous system (Seely *et al.,* 2008). An adverse side effect of calcium EDTA is renal toxicity. Succimer is the preferred agent in mild lead poisoning cases. This may be the case in instances where children have a blood lead level > 25µg/dL. The most reported adverse side effect for succimer is gastrointestinal disturbances (Brown *et al.,* 2006). It is also important to note that chelation therapy only lower blood lead levels and may not present the lead–induced cognitive problems associated with lower lead level in tissue. This may be because of the inability of this agent to remove sufficient amounts of lead from tissue or inability to reverse pre-existing damage (Atwood *et al.,* 2008). Chelating agents can have adverse effects for example, chelation therapy can lower the body's level of necessary nutrient like zinc (Stokstad, 2008). Chelating agents taken orally can increase the body absorption of lead through the intestine (Weber & Newmark, 2007).

Chelation challenges, also known as provocation testing, is used to indicate an elevated and mobilizable body burden of heavy metals including lead (Kalia & Flora, 2005). This testing involves collecting urine before and after administering a one-off dose of chelating agent to mobilize heavy metals into the heavy metals, from this analysis overall body burden is inferred. Chelation challenge mainly measures the burden of lead in soft tissues and may not accurately reflect long-term exposure or the amount of lead stored in bone (Ernst, 2000). Although the technique has been used to determine whether chelation therapy is indicated and to diagnose heavy metal exposure, evidence does not support either of these uses as blood levels after chelation are not comparable to the reference range typically used to diagnose heavy metal poisoning (Bernard, 2000). The single chelation dose could also redistribute the heavy metal to more sensitive areas such as central nervous system tissue (Weber & Newmark, 2007).

2.2.2 Soil Processes and the Behaviour of Metals in Soil

The soil is a key component of terrestrial ecosystems, both natural and agricultural, being essential for the growth of plant and the degradation and re-cycling of dead biomass. It is a complex heterogeneous medium comprising mineral and organic solids and gaseous components. The minerals present are usually weathering (chemically decomposing) rock fragments and secondary minerals such as phyllo-silicates or clay minerals oxides of Fe, Al and Mn and sometimes carbonates (usually C_aCO_3) (Alloway, 1998). The organic matter comprises living organisms (meso fauna and micro – organism), plant material (litter) and colloidal humus formed by the action of micro-organisms on plant litter. The solid components are usually clustered together in the

form of aggregates thus creating a system of interconnected voids (pores) of various sizes formed with either water or air. The solid components have the ability to adsorb ions, but this differs between materials and is strongly influenced by the prevailing pH and redox conditions and the relative concentrations of the ions present in the aqueous soil solution (Alloway, 1998).

This structured heterogeneous mixture of organic and mineral components is the habitat for many organisms as well as the medium in which plant root grows, extracting water, oxygen and ions. Roots also release $C0_2$ and exude organic compounds which are responsible for the intense microbial activity in the inter facial zone between the root and the soil called the “rhizosphere”. Plant roots modify the chemical and physical properties of the soil around them and thus influence the bio-availability of some chemical elements

The soil is a dynamic system, subject to short-term fluctuations, such as variations in moisture status, pH and redox conditions and also undergoing gradual alterations in response to changes in management and environmental factors. These changes in soil properties affect the form and bio availability of metals and need to be considered in decisions on the management of polluted soils or the use of soils for disposal of waste materials. Soils can show marked spatial variability in physical and chemical properties at the micro- and macro scales, thus emphasizing the need for thorough sampling to include the range of parameters at any site investigated.

The soil reaction is the pre-eminent factor controlling the chemical behaviour of metals and many other important processes in the soil. However, the pH concept is not as

precise for solid as it is for solutions in vitro because of heterogeneity of soils, the relatively small portion of solution present in the pores of the solid soil and the adsorption of (cationic) H^+ (ions) on to solid surfaces. The pH of a soil applies to the H^+ (ion) concentration in the solution present in soil pores which is in dynamic equilibrium with the predominantly negatively charged surfaces of the soil particles. Hydrogen ions are strongly attracted to the surface negative charges, and they have the power to replace most other cations (Ure & Alloway, 1995).

The diffused layer close to a negatively charged surface therefore has a higher concentration of H^+ ions than the bulk soil solution. When the soil solution is diluted the diffuse layer expands causing the pH of the bulk solution to increase. This has important implications for the measurement of soil pH in the laboratory. This normally involves mixing dry soil with 2-2.5 times its weight of water, shaking and then measuring the pH in the supernatant solution after 30 minutes. The pH value obtained is about 1 to 1.5 units higher than that of the soil solution near to the solid surfaces where the reactions take place. This dilution effects is usually overcome by measuring the pH in a suspension of a solution of a neutral salt, such as $CaCl_2$ solution (Alloway, 1995).
Normally, pH is measured in suspensions of soil with either distilled water or a dilute solution of a neutral salt such as $CaCl_2$ or KCl. pH values are usually expressed together with the soil solution ration and the solvent used. It is assumed that if the solvent is not measured the pH was measured in distilled water.

Soil pH is affected by the changes in redox potential which occur in soils that become water logged periodically. Reducing conditions generally cause a pH increase and

oxidation brings about a decrease. Variations up to 2 units can occur over a year in gley soils prone to water logging. Oxidation of pyrite (FeS_2) in a soil parent material can cause a marked decrease in pH.

Soils have several mechanisms which serve to buffer pH to varying extents, including hydroxyaluminium ions, CO_2 carbonates and cation exchange reactions (Alloway, 1995).

Soil pH usually increases with depth in humid regions where bases are leached down the profile and can decrease with depth in environments where evaporation causes salt to accumulate in the surface horizon. As a result of the variations which can occur, it is not necessarily meaningful to express soil pH measurements more accurately than to the nearest 0.2 division of a unit (Alloway, 1995).

In general, heavy metal cations are most mobile under acid conditions and increasing the pH by liming usually reduces the bio availability. However, molydate anions become more available with increasing pH (Nouri *et al.*, 2008).

Soils generally have pH values within the range 4 – 8.5, owing to the buffering action of Aļ at the lower end and by $CaCO_3$ at the upper end of the range. Brady states that the normal pH is 5 – 7 in soil of humid regions and pH 7 – 9 in the soils of clay regions (Nouri *et al.,* 2008).

In a typical temperate environment, such as the UK, soils normally have a pH in the range 4-8; the optimum pH for most available crops is 6.5 on mineral soils and 5.5 on peaty soils.

Soil pH can be raised by liming but it is impracticable to acidify agricultural soils more alkaline than the acidic soil (Nouri *et al.,* 2008).

The main feature which distinguished soil from regolith (decomposed rock) is the presence of living organisms, organic debris and humus. All soils contain organic matter although the amount and type may vary considerably. Colloidal soil organic matter has a major influence on the chemical properties of soils and can be divided into 'non - humic' and 'humic' substances. The non-humic substances comprise unaltered biochemical such as amino acids, carbohydrates, organic acids, fats and waxes that have not changed from the form in which they were synthesized by living organisms. Humic substances are series of acidic yellow to black coloured poly electrolytes of moderately high molecular weight. They are formed by secondary microorganisms and have characteristics which are dissimilar to any compounds in living organisms. They have a wide variety of functional groups, including carboxyl, phenotic hydroxyl, carbonyl, ester and possibly quinine and methoxy groups. The elemental composition of humus is typically (on an ash-free basis): 44 – 53% C, 3.6 – 5.4% H 1.8 – 3.6% N and 40 – 47%.0 (Jackson, 1991).

Soils are subject to variations in oxidation reduction (redox) status and this mainly affects the elements C, N, O, S, Fe and Mn. Ag, As, Cr, Cu, Hg and Pb can also be affected. Redox equilibrium sometime controls the bioavailability of metals in soil. Hence metal can be fractionated into different forms such as carbonate bound, oxidizable, Fe-Mn oxide bound, reducible and residual bound.

The most important chemical processes that affect the behaviour and bioavailability of metals in soils are those concerned with the adsorption of metals from the liquid phase

on the solid phase (Alloway, 1995). The processes control the concentration of metal ions and complexes in the soil solution and thus exert a major influence on their uptake by plant roots. Several different mechanisms can be involved in the adsorption of metal ions, including cation exchange (or non-specific adsorption), specific adsorption, co-precipitation and organic complexation (Alloway, 1998). However, although the extent of adsorption can be measured and isotherm derived, it is frequently difficult to be precise about which particular process is responsible for the retention of metals in any particular soil.

Most heavy metals (with certain exceptions) including the metalloids, (As and Se) and the metals (M_O and V) exist mainly as cations in the soil solution, and their adsorption depends on the density of negative charges on the surface of the soil colloids. In order to maintain electroneutrality, the surface negative charge is balanced by an equal quantity of cations. Ion exchange refers to the exchange between the counter ions balancing the surface charge on the colloids and the ions in the soil solution (Merrinton & Alloway, 1994). It has the following characteristics: It is reversible, diffusion controlled and stochiometric and in most cases, there is some selectivity or preference for one ion over another by the adsorbent. This selectivity gives rise to a replacing order amongst the cations determined by their valency and degree of hydration. The higher the valency of an ion, the greater its replacing power; H^+ ions behave like polyvalent ions and the greater the degree of hydration, the lower its replacing power, other things being equal. Adsorption by cation exchange can also be described as the formation of outer-sphere complexes with the surface functional groups to which they are bound electrostratically. The cation exchange capacity (CEC) of mineral soils can range from a few to 60

Mols/kg but in organic soils it may exceed 200Mols/ kg (Smith *et al.,* 1996). The cation exchange capacity of soils is far larger than their anion exchange capacity.

Specific adsorption involves the exchange of heavy metal cations and most anions with surface ligands to form partly covalent bonds with lattice ions. It results in metal ions being adsorbed to a far greater extent than would be expected from the CEC of a soil. For example, Brummer showed that the sorptive capacities of amorphous Fe and Al oxides for Zn were 7 and 26 times greater respectively than their CECs at pH 7.6 (Smith *et al.,* 1996).

Specific adsorption is strongly pH dependent and is related to the hydrolysis of the heavy metal ions. The metals most capable of forming hydroxyl complexes are specifically adsorbed to the greatest extent. The equilibrium constant (P_k) values of the reaction $m^2 + H_2O = mOH^+ + H^+$ determine the adsorption behavior of the different metals. Specific adsorption increases with decreasing P_k values. In the case of Cu and Pb which have the same P_k value,Pb with the greater ionic size is more strongly adsorbed (Smith *et al.,* 1996). Brummer gives the order for increasing specific adsorption as: Cd (P_k = 10.1) < Ni (P_k = 9.9) < C0 (P_k = 9.7) <Zn (P_k = 9.0) < < Cu (P_k = 7.7) < Pb (P_k = 7.7 < Hg (P_k = 3.4).

The hydrous oxides of Al, Fe and Mn are thought to be the main soil constituents involved in the specific adsorption reaction.

In addition to being adsorbed on mineral surfaces, heavy metal ions can also diffuse into minerals such as goethite, Mn oxides, Illites, and some other minerals. The relative rate of diffusion of the metal ions into minerals increase with pH up to a maximum which

is equal to the P_K value for the situation when M^{2+} = mOH^+ on the mineral surface. Above this pH the $MOA^+ > M^{2+}$ and the relative diffusion rate increases for Cd, Ni and Zn decrease in the order Ni> Zn > Cd and can be related to their ionic diameters (Ni = 0.69nm, Zn = 0.74 nm and Cd = 0.97nm. Adsorption of metals by goethite therefore comprises three different steps: first, surface adsorption: second diffusion into goethite particle and third, adsorption and fixation at positions within the mineral particles.

Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with their elements by any mechanism and at any rate (Smith *et al.,* 1996).

Insoluble Precipitates of Heavy Metals in Soils

When the physio – chemical conditions and concentrations of appropriate ions are sufficiently high, metals can form insoluble precipitates (solid phases) which could play a role in controlling their solubility in the soil solution. The following summarized information for selected metals is taken from Lindsay (Selinus *et al.,* 1997).

Cadmium – Octavite ($CdC0_3$) could be a major factor controlling the solubility of Cd soils. In strongly gleved soils (with reducing conditions) the sulphide minerals greenockite (CdS) can be formed. This explains the low solubility of Cd in flooded paddy soils and a return to oxidizing conditions results in Cd^{2+} and $S0_4^{2-}$ being formed along with a marked decrease in pH which results in an increase in the mobility and bioavailability of Cd (Merrington & Alloway, 1995) .

Copper:- Under most physio – chemical conditions encountered in soils the adsorbed forms of Cu (soil – Cu) are more stable than soil Cu.

Lead:- Several Pb phosphates can occur in soils including

Pb_5 $(P0_4)_3$ OH, Pb_3 $(P0_4)_2$ and Pb_5 $(P0_4)_3$ Cl. The latter form chloropyromorphite is the most insoluble of the Pb phosphate minerals and could control the solubility of Pb^{2+} throughout a wide pH range especially in soils of high pH status such as sewage sludge amended soils.

Manganese: - Under well oxidised conditions the most stable Mn mineral is pyrolusite B($Mn0_2$). Manganese generally forms hydrous oxides with mixed valence state but under strong reducing conditions manganite is formed (Jackson, 1991).

Mercury: - The halide complexes Hg_2 I_2, Hg_2 Cl_2 and Hg_2Br_2 are possible mineral forms in soils if the respective anion concentrations are sufficiently high. In reducing, Allen has reviewed recent literature concerned with the speciation of metals in sediments and more briefly, their application to soils of particular interest is references to work by Lec *et al*., who used K_d values of soil to determine safe maximum concentrations rising above the drinking water standards (Lec *et al.,* 1995). They determined the K_d values of soils for Cd at a range of pH values and then established a soil quality criteria value, in mg / kg (soil Qc) using the drinking water standard for the metal (DWS) and the porosity (n), particle density (D_s) and degree of water saturation (P) of the soil investigates.

SFor a range of new jersey (USA) soils with pHs between 3.9 and 6.2 organic matter contents up to 2.98, clay contents up to 37% and CEC values between 0.9 and 9.5 (mols/kg they obtain soil Qc concentrations of Cd of between 0.09 and 4.5 mg / kg) (Lec *et al.*, 1995).

2.2.3 Biological Methylation of Heavy Metals

Some elements including Hg, As, Sc, Te, Ti and Zn can undergo methylation by micro – organisms to form volatile molecules, such as CH_3 Hg^+, CH_3Se and CH_3 As and this can be a major route for losses of these elements from soils. Methylation is known to be brought about by both aerobic and anaerobic segments in aqueous environments. All biological methylation involves methyl cobalamin, a methylated derivative of B_{12} which contains CO. The rate at which biological methylation occurs depends on the condition, including temperature, redox and pH, but non – biological methylation can also occur (Davies, 1990).

The methylated forms of Hg are $(CH_3)_2$ Hg (most stable in alkaline conditions) and CH_3 Hg+ (stable in neutral to acid soils). Lead is also thought to be methylated in the environment by both biological and abiotic mechanisms but the evidence is not conclusive. However, most organic-Pb compounds in the environment are probably derived from additions in petrol (Davies, 1990).

A soil plant relation of heavy metals is the major interrelationship affecting the dynamics of heavy metals between the soil and the plant. The soil-plant system is an open system subject to such, as contaminants, pesticides, and to losses such as the removal of metals in harvested plant material, leaching, erosion and volatilization (Davies, 1990).

2.2.4 Plant Uptake of Metals

The factors affecting the amounts of metal adsorbed by a plant are those controlling. (i) The concentrations and speciation of the metal in the soil solution (ii) the transport of the metal from the root surface into the root and (iii) its translocation from the root to the

shoot. Plant uptake of mobile ions present in the soil solution is largely determined by the total quantity of this ion in the soil. In the case of strongly adsorbed ions, adsorption is more dependent upon the amount of root produced. Mycorrhizae are symbiotic fungi which effectively increase the adsorptive area of the root and can assist in the uptake of nutrient ions, such as orthophosphates and micronutrients. Roots possess a significant CEC, due largely to the presence of carboxyl groups, and this may form part of the mechanism of moving ions through the outer part of the root to the plasmalem where active absorption occurs. Absorption of metals by plant roots can be by both passive and active (metabolic) processes. Passive (non-metabolic) uptake involves diffusion of ions in the soil solution into the root endodermis. On the other hand, active up-take place against a concentration gradient but requires metabolic energy and can therefore be inhibited by toxins. The mechanisms appear to differ between metals (Alloway, 1995).

Pb uptake is generally considered to be passive while that of Cu, Mo and Zn, is thought to be either active metabolic uptake or a combination of both active and passive uptake. Absorption mechanism can vary for different metal ions, but ions which are absorbed into the root by the same mechanisms are likely to complete with each other. For example, Zn absorption is inhibited by Cu and H^+ but not by Fe and Mn. Cu absorption is inhibited by Zn, NH^{4+}, Ca and K (Alloway, 1996).

The rhizosphere is the zone about 1 -2mm wide between plant roots and the surrounding soil. It receives appreciable amounts of organic materials, mucilage, sloughed off cells and their lyocites (Alloway & Gala, 1984). These organic compounds give rise to intense microbiological and biochemical activity in the rhizosphere which

enables roots to mobilize some of the metals which are strongly adsorbed in the soil, by acidification, redox changes, or the formation of organic complexes.

Phenolic compounds and certain amino acids are known to be involved in the solubilisation of Fe^{3+} and M_n^{4+}

Cereal deficiency in micronutrients such as Fe and Zn appear to have root exudates containing substances such as phytosiderophere-2-deoxymugineic acid which are effective in mobilizing these and other metals from sorption sites in the vicinity of the root. Mench and Martin (1990) showed that exudates with identical carbon contents from maize and tobacco extracted amounts of Mn, Cu, Cd and Fe which differ with the plant species (Mench & Martin, 1990).

Tobacco root exudates increased the extraction of Cd but decreased that of Fe. Those of maize did not affect the concentrations of either of these metals. The uptake of metal from soils is greater in plants grown in pots of soil in the green house than from the same soil in the field. Devries and Tiller found the uptake of Cd by lettuce and onion bulbs grown in pots to be 6 and 25 times greater, respectively, than when grown in the same soil. This is probably due to differences in microclimate and soil moisture and to the roots of container grown, plants growing solely in contaminated soil; whereas those of field grown plant may reach down to less contaminated soil (Davies & Tiller, 1982).

Relative differences in the uptake of metal ions between plant species is genetically controlled and can be due various factors including surface area of evapo-transpiration. The latter mechanism affects the mass flow of the soil solution in the vicinity of the root and the movement of the ions to the root absorbing surface.

E. Cal gave the general order of the transfer coefficients for most of the biologically important heavy metals. The transfer co efficient is the metal concentration in plant tissue above ground divided by the total metal concentration in the soil (Nickolson *et al.*, 1998).

Although numerous soil and plant factors can affect the accumulation of metals in plants, the values given are intended guides to the order of magnitude of the transfer coefficients and root precise values.

2.3.0 Phytoextraction Process

Phytoextraction is the removal of inorganic contaminants from the subsurface through plant uptake (Scheper, 2014). These include heavy metals, metalloids, radionuclide and salts. Phytoextraction utilizes the root of plants to absorb, translocate and concentrate toxic metals from the soil to the harvestable plant tissues. The concentration processes results in a reduction of contaminated mass and also transfer of the metal from an aluminosiliate – based matrix (soil) to a carbon – based matrix (plant) (Scheper, 2014). The two special classes of plant species that have been investigated for their uptake capabilities for a wide range of inorganic minerals are hyper accumulators and halophytes (Llya & Burt, 2000).

Hyper accumulator is one that can concentrate specific metal to at least 1000mg / kg (0.1%) depending on the specific inorganic. Halophytes are species that can tolerate or accumulate salinity level present in the form of sodium, calcium or magnesium chloride, or as free chloride ions between 3 and 7 times normal concentrations (less than 10,000

parts per million (ppm) 1% total salts). Not all halophytes are accumulators (Llya & Burt, 2000).

Phytoextraction is a technology that leaves a much smaller mass to be disposed off when compared to excavation and land filling. A key to the success of metal phytoextration is to increase and maintain metal concentrations in the soil solution. Chelates and other chemical compounds have been used to increase the solubility of metals in plant growth media, and could significantly increase Metal accumulation in plants (Nancy *et al.*, 2002).

2.3.1 Phytostabilization of Metals (Phytorestoration)

In this process, chemical compounds produced by the plant immobilize contaminants rather than degrade them (Scheper, 2014). Phytostabilization is a site stabilization technique that reduces the risk of soil contaminants through the use of soil amendments that induce the formation of insoluble contaminant species. Less soluble forms of metal contaminants are less likely to leach through the soil profile, and are less likely to interact biological with humans, animals, or plants (Scheper, 2014).

Phytostabilization is similar to establishing a pasture using agricultural equipment, planting schemes and soil remediation practices (Leon, 2012).

Phytostabilization is an adaptable technique that can help minimize various hazards and eliminate exposure pathways to organism of soil metal contaminant, although the most effective amendments and application rates may vary for individual metal contaminants (Scheper, 2014).

2.3.2 Phytofiltration of Metals

Pollution of surface water and ground water with heavy metals and radionuclide is problem humanity cannot afford to ignore. Enormous amounts of heavy metals have been mobilized in the past century as a result of global industrial and in particular metalliferous mining as well as smelting, agriculture and waste disposal activities (Scheper, 2014).

The presence of toxic metals (heavy metals and radionuclide) in water often jeopardizes the ecosystem stability and poses serious danger to human health. A variety of methods to remove toxic metals from water base on ion exchange or chemical and micro biological precipitation has been developed and used with some success (Nancy, 2015).

2.3.3 Rhizofiltration

Rhizofiltration is the use of plant root to absorb, concentrate, and precipitate heavy metals from water (Nancy, 2015). Rhizofiltration is similar to phytoaccumation (extraction), but the plants used for cleanup are raised in green houses with their roots in water. The system can be used for, ex-situ ground water treatment. That is, ground water is pumped to the surface to irrigate these plants. As the roots become saturated with contaminants, they are harvested and disposed off (Nancy, 2015). Rhizofiltration has been used to remove uranium from groundwater on sites at Ashrabula (Nancy *et al.*, 2002).

2.3.4 Phytodegradation

In this process, plants actually metabolize and destroy contaminants within plant tissue. Phytodegradation is the ability of plants to produce the enzymes or co-factors necessary to degrade organic contaminants (Fiegl *et al.*, 2010).

2.3.5 Phytovolatization

Volatilization or transpiration involves the mass transfer of a compound from a liquid or solid phase into the gaseous phase (Nancy *et al.*, 2002). It is controlled by vapour pressure, which is the pressure of the gas in equilibrium with the liquid or solid at a given temperature. In this process, plants actually take up water containing organic contaminants and release the contaminants into the air through their leaves. The process depends heavily on the physical characteristics of the contaminants itself. In order to get into the plant, the contaminant should have the proper chemistry to pass through the root membrane.

In addition to volatile organic, certain metalloid organics such Hg and Se are susceptible to this phytotechnology mechanism as well.

2.4.0 Phytoremediation of Some Heavy Metals

Lead rarely occurs in its elemental state. The most common ore is the sulfide (gelena). Though lead in form of lead silicates and carbonate is very useful as heat and light stabilizer for polyvinylchloride plastics, lead Azide ($Pb(N_3)_2$) is a standard detonator for explosive, litharge (head oxide) is widely employed at a level of approximately 2% lead to improve the magnetic properties of barium Ferrite ceramic magnets. Lead silicates

are used for the manufacture of glass and ceramics. Lead arsenate are used in large quantities as insecticides for crop protection, a calcined mixture of lead zirconate and lead titanate is used as a piezoelectric material, the most important application is in ultrasonic cleaning equipment. Lead is used for the manufacture of storage battheries, tetra ethyl Lead, cable covering soldier, pigments, construction and ammunition (Christian, 2009). In human, exposure to lead can result in a wide range biological effect depending on the level and duration.

Average daily lead intake for adults is estimated at 1.6µg from air, 20µg from drinking water, although mist people receive the bulk of the lead intake from food (Burris & Means, 2005).

Lead in the environment arises from both natural and anthropogenic sources (Christian, 2009). Lead affects the kidney and has neurological and hematological effect on mammals. Naturally, weathering moves 11,000 tons of lead annually to the oceans, the anthropogenic addition from agriculture and land construction to this is 33,000 tons annually. The mining industry produces 4 million tons of lead annually. The effluent of lead from industry to water is 140, 000 (Christian, 2009).

2.4.1 Phytoremediation of Lead

Lead is known to be “molecularly sticky” since it readily forms a precipitate within the soil matrix, has low aqueous solubility and in many cases, is not readily bioavailability. In most soil capable of supporting plant growth, the soluble Pb^{2+} levels are relatively low and will not promote substantial uptake by the plant even if it has the genetic capability of accumulate the metal. The second limitation of lead phytoextraction is the poor

translocation of the metal from the roots to the harvestable shoots. In plants that do translocate lead, translocations is less than 30% (Christian, 2009).

The mobilization of metal contaminants, both in the soil and the plant is another important factor influencing the success of phytoremediation.

Soil pH is a significant parameter in the uptake of metal contaminants. This is a result of the fact that the soil pH value is one of the principal soil factors controlling metal availability. It was found by (Chlopecka *et al.*, 2014) that soil sample of pH less than 5.6 contained relatively more of all metals.

2.4.2 Phytoremediation of Zinc

Zinc is a very common substance that occurs naturally. Many food stuffs contain concentration of zinc (Fosmire, 1990). Zinc is important contractor for enzymes that are essential for normal metabolism. Drinking water also contains certain amount of zinc, which may be higher when it is stored in metal tanks. Industrial sources or toxic sites may cause health problems (Burris, 2000).

Although zinc is a trace element that is essential for human health (lack of zinc can cause loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores and even birth defects), too much zinc intake can still cause eminent health problems, such as stomach cramps, irritation, vomiting, nausea and anemia, very high levels of zinc can damage the pancreas and disturb the protein metabolism and cause arterioclerosis, reproductive effect, growth retardation, expiratory disorder (Barceloux *et al.*, 1999) .

Zinc can be a danger to unborn and new born children when the mothers have absorbed large concentrations of zinc, the children may be exposed to it through blood or milk of their mothers.

Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing (Fosmire, 1990).

The world's zinc production is still rising. This basically means that more and more zinc ends up in the environment.

Water is polluted with zinc, due to the presence of large qualities of zinc in the waste water of industrial plants. If this waste water is not purified satisfactory, one of the consequences is that rivers will deposit zinc polluted sludge on the banks Zinc may also increase the acidity of water (Burris, 2000).

Some fish can accumulate zinc in their bodies, when they live in zinc contaminated water ways. When zinc enters the bodies of these fish, it is able to biomagnified up the food chain.

Large quantities of zinc can be found in soils when the soils of farmland are polluted with zinc, animal will absorb concentrations that are damaging to their health. Water soluble zinc that is located in soils can contaminate ground water (Burris, 2000). Zinc cannot be only threat to cattle, but also to plant species. Plants often have zinc uptake that their systems cannot handle. On zinc-rich soils, only a limited number of plants has

a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. But to the effect upon plants zinc is a serious threat to the production of farmlands. Despite this zinc containing manures are still applied.

Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of micro-organism and earthworms. The breakdown of organic matter may seriously slow down because of this.

The toxicity of zinc and copper in three species of brassica has been reported (Barkay & Scheafer, 2001). The plant was examined to determine if they show sufficient tolerance and metal accumulation to be used to phytoremediate a site contaminated with these two heavy metals. It was observed that the presence of 6.5mg/L Zn or 0.32mg/L Cu or a mixture of the two, inhibited growth of the various species. Cu inhibited lateral root elongation. While Zn tended to decrease only lateral root diameter (Chen & Zhen, 2000). There was also inhibition of the Fe and Mn uptake which may have a significant role to play in the reduction of plant growth.

In terms of heavy metal removal, the Brassica Spp, were more effective at removing Zn from the nutrient solution than Cu. The extent of Zn and Cu removal was reduced in the presence of both metals as compared to the single heavy metal treatments.

It has been indicated that rag weed and thlapi rotundifolium are better Lead removers from polluted environment than other plants even though they are slow in comparison with the removal of Zn and Cd by Alpine Pennycress. Pennycress is a wild herb found on zinc and nickel-rich soil in many countries (Chen & Zhen, 2000). Of the species tested at Pig's Eye landfill in St Paul Minnesota, penny cress was the best at taking in cadmium, zinc, and lead Penny Cress has proven especially good at removing zinc and

cadmium, accumulating up to 30000 parts per million (ppm) of zinc in its leaves without yield reduction. Most plants experiences zinc toxicity by the time they reach 500ppm (Blaylock *et al.*, 1997).

Pennycress can take in zinc at the rate of 125kg per hectare (kg/ha) per year (108 pounds / acre), if fertilized and managed carefully.

2.4.3 Phytoremediation of Cobalt

Cobalt is an element that occurs naturally in the environment, in air, water, soil, rocks, plants and animals. It may also enter air and water and settle on land through wind-blown dust, and enter surface water through run-off when rainwater runs through soil and rock containing cobalt (Burris, 2000).

As cobalt is widely dispersed in the environment, humans may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Skin contact with soil or water that contains cobalt may also enhance exposure (Park, 1997).

Cobalt is not often freely available in the environment, but when cobalt particles are not bound to soil or sediment particles, the uptake by plants and animals may occur.

Cobalt is beneficial for humans because it is a part of vitamin B_{12}, which is essential for human health. Cobalt is used to treat anaemia with pregnant women, because it stimulates the production of red blood cells (Brock & Stopford, 2003).

However, too high concentration of cobalt may damage human health. When we breathe in too high concentration of cobalt through air, we experience Lung effects, such as asthma and pneumonia.

This mainly occurs with people that work with cobalt. Cobalt also causes benign dermatoses, either in people new to handling them or after prolonged exposures (Schirrmatcher, 1967).

But in parts of the world where soil and plants are deficient in cobalt, trace amounts of cobalt salts for example the chloride and nitrate of CO (II) are added to livestock feeds and fertilizers to prevent serious wasting disease of cattle and sheep, such as pining, a debilitating disease especially common in sheep (Bardgett & Saggar, 1994).

When plants grow on contaminated soil they will accumulate very small particles of cobalt, especially in the parts of the plant we eat, such as fruits and seeds. Soils near mining and smelting facilities may contain high amounts of cobalt so that uptake by humans may be through eating. Health effects that are a result of the uptake high concentration of cobalt are; vomiting and nausea, vision problems, heart problems and thyroid damage (Tower, 2010).

Health effect may also be caused by radioactive cobalt isotopes. This can cause sterility, hair loss, vomiting, bleeding, diarrhea, coma and even death. This radiation is sometimes used with cancer patient to destroy tumors (Bardgett & Saggar, 2005).

Exposure to cobalt may also cause cough, shortness of breath, nodular fibrosis, loss of weight, dermatitis, respiratory hypersensitivity, permanent disability and death (Bardgett & Saggar, 2005).

International Agency for research on cancer (IARC) has listed cobalt and cobalt compounds within group 2B (agents which are possibly carcinogenic to humans).

Cobalt has been classified to be carcinogenic to experimental animals by the Federal Republic of Germany (Engh *et al.*, 2009).

Humans add cobalt by releasing small amounts into the atmosphere from coal combustion and mining, processing of cobalt containing ores and the production and use of cobalt chemicals. The radioactive isotopes of cobalt are not present naturally in the environment but are introduced through nuclear power plant operations and nuclear accidents (Tower, 2010).

Cobalt cannot be destroyed once it has entered the environment. It may react with other particles or absorb soil particles or water sediments. Cobalt will only mobilize under acidic conditions.

Also soil near mining and smelting, facilities may contain very high amounts of cobalt, so that the uptake by animals through eating plant can cause health effects. Cobalt can accumulate in plants and in the majority of food chain (Brock & Stopford, 2003).

Limitations of Phytoremediation

Although phytoremediation offers many advantages over conventional soil remediation techniques, a realistic look at phytoremediation points to some serious limitations. Hyper accumulating plants often accumulate a specific element only, indicating a limited applicability to sites with multiple of mixed contaminants (Scheper, 2014).

The toxicity and bioavailability of biodegradation products is not always known (Llay & Burt, 2000). High metal concentration or other contaminants may be toxic to the plant. If contaminant concentrations are too high, plants may die.

The depth of the treatment zone is determined by the plants used in phytoremediation (Mac Donald & Scriluawondha, 2008). Root contact is a primary limitation on phytoremediation applicability. Remediation with plants requires that the contaminants be in contact with the root zone of the plants. Either the plants must be able to extend roots to the contaminants, or the contaminated media must be moved to within range of the plants. In most cases, phytoremediation is limited to shallow soils (surface soils) (Llay & Burt, 2000). Phytoremediation is also limited by the growth rate of the plant (Nancy *et al*., 2002). Phytoremediation is frequently slower than traditional physical, chemical or thermal technique, requiring several growing seasons for site up. In addition to the general relevance on the life cycle of plants and the seed to coordinate plantings with ordinary growing seasons, many naturally occurring hyper accumulator plants are extremely slow growers – it has been estimated that natural hyper accumulators might take 13 – 16years to clean a typical site (Nancy *et al*., 2002).

So more time may be required to phytoremediate a site as compared with other traditional cleanup technologies (Scheper, 2014).

Phytoremediation may also require that the site be large enough to accommodate traditional agricultural cropping techniques. The terrain of the site and instability of slopes and surface materials will affect efficacy or cost. Phytoremediation may also require considerable input costs such as pretreating waste material or the sites on which the waste is deposited. Also some ecological exposure may occur whenever plants are used to interact with contaminants from the soil. The fate of the metals in the biomass is a concern. At one site, sun flower plants that extracted Ceasium (Cs) and

strontium (Sr) from surface water were disposed of as radioactive waste (Nancy *et al*., 2002).

Threat of bioaccumulation of contaminants such as heavy metals from primary to secondary consumers in the food chain is another limitation of phytoremediation. Phytoremediation can transfer contaminant across media, e.g. from soil to air. Products may be mobilized into groundwater or bio accumulated in animals (Leon, 2012). Additional research is needed to determine the fate of various compounds in the plant metabolic cycle to ensure that plant droppings and products do not contribute toxic or harmful chemicals into the food chain (Caltane, 2002).

Phytoremediation is seasonally dependent, the location and the plant are the determining factor (Diane, 1996). Many hyper accumulator plants are relatively rare, with small population.

As with any clean up technology, the difficulties associated with waste characterization and the effects of heterogeneous site conditions also apply to phytoremediation. The soil texture, contaminated level, pH, salinity, and toxicity levels must all be within the limits of plant tolerance. Highly soluble contaminants may leach outside the root zone rendering plant uptake less effective (Scheper, 2014).

The success of phytoremediation depends on establishing a selected plant community. Introducing new plants species can have widespread ecological ramifications (Caltana, 2002).

Also phytoremediation is unfamiliar to regulator while phytoremediation appears to be a very cost effective approach to clean up contaminated sites, further validation under

actual field conditions and cost comparisons are needed in order to allow effective estimated of project cost and process viability on a site specific basis study of the economics, performance capabilities and comparison to competing technologies are still very much required in order to determine the potential share of phytoremediation in the remediation market as well as the potential for commercialization (Diane, 1996).

Among the strategies being used to overcome the disadvantages are; the use of genetic engineering to introduce genes into fast growing cultivars, to regulate root growth, or to increase production of selected plant enzymes may address the problem of growth rate, uses of chelators to enhance metal solubility in soils (Blaylock *et al*., 1997). Also use of irrigation and insecticides may be required to effectively remediate the site; combining phytoremediation with other in-situ technologies, using classical genetics or advanced molecular biology tools (Llya & Burt, 2000).

2.5.1 Hibiscus flower (*Hibiscus rosasinensis*)

This flowering plant is believed to be native to southernmost china and produces flower with blood red petals. It has a botanical name of *Hibiscus rosasinensis*. It is a woody plant, often described as beings either small tree or large shrub. A mature plant usually develops a rounded shape with an oral upright habit. It matures 5 to 15 feet fall with hundreds of extant cultivars. The mature tropical hibiscus can grow with a densely branched, rounded silhouette or with a low, moulded but spreading shape. The bark is grayish brown to grey and becomes almost corky on large, old plant.

The evergreen foliage on topical plant resembles pointed orals. The leaf blade is a wide, tapering oval with a pointed tip. The base of the leaf where it attaches to the petiole

stem is either rounded or wedge-shaped. Each leaf measures, on average 3 to 4 inches long and 2 to 3 inches wide (Philip, 1993).

Plate 2.1: structure of *Hibiscus rosasinensis*

2.5.2 Aloe barbadensis

The botanical name is *Aloe barbadensis* and belongs to the family of Aloeceae. Aloe Vera is a clump forming perennial with rosettes of thick, fleshy, spiky, gray-yellow waves young specimens being red spotted and the plants bears yellow tubular flower in summer. It is a bitter herb with anti-inflammatory astringent emollient, antifungal, anti-bacterial and antiviral properties and is useful in the uterus. It consists of 95% water, they are extremely frost tender. They should be planted in full sunlight shade. It is also noted that the established plants will survive a drought quite well but the benefit of the plant, water should be provided. Older specimens may even bloom producing a tall stock covered with bright coloured coral flower (Bindler & Renberg, 1988).

Plate 2.2: Structure of *Aloe barbadensis*

2.5.3 Euphorbia milivarpendens

It is commonly known as crown of thorns, Christ plant, Chris torn having botanical name as *Euphorbia milivarspendens*. It belongs to the family Euphorbia cease. It is treated like a cactus, provision of plant of sunlight to maintain leaves and flower is needed. It is a dicotyledonous and the leaves are not parallel veined. Leaves are roundish, up to two inches long, and steams are thorny. Flowers occur in pairs on leafless stems held above leaves up to one inch wide. Its flower does not have fragrance. It is available throughout the year. Flowered colour is red. Its growth habit is woody perennial to 4 feet (102m). Occasional watering is needed in the dry season which helps it retain its leaves. Its sap is poisonous and it irritates the skin (Andrew *et al*., 2001).

Plate 2.3: Structure of *Euphorbia milivarspendens*

2.5.4 Ficus benjamina

It is commonly known as weeping fig; benjamina fig, a ficus tree. Its botanical is *Ficus benjamina* having a decorative life of weeks, months to years depending on its use. For post-harvest care, it does best under bright sunlight conditions but will tolerate moderate amount of watering during dry season. It is a specie of fig tree and is classed as a dicotyledonous. It is a topiary tree reaching 50m (98ft) tall in natural condition with gracefully dropping branch lets and glossy leaves 6-13cm (2-5ich) long. It has an oval and acuminate tip (Eusley, 2005).

Plate 2.4: Structure of *Ficus benjamina*

2.5.5 Ixora coccinea

It is also called pink flower and its botanical name is *Ixora coccine*a. This is a genius of more than 400 species with handful cultivated as ornamental plants. It is a low growing evergreen perennial shrub or small tree of moderate growth rate ranging in height from 3-8ft (1-2.5). lxora's growth habit is multibranched, upright, rounded and compact. The colour, size and shape vary depending on the species and cultivars. This plant spread from Africa to India to southern Asia. It is used as a hedge and the propagation of this plant is done from stem cuttings. It requires temperature of about 12^0C (Charlotte, 1996).

Plate 2.5: Structure of *Ixora coccinea*

2.5.6 Ageratum houstorinumn

This belongs to the family of Asteraceae, a hybrid derived from plants native to Mexico and Central America. It has a botanical name of *Ageratum houstonianum.* The plant grows as an evergreen sub shrub with a dense, bushy habit; it can self-sow and is potentially weedy in frost free region. The foliage is an attractive green, heart shaped and has scalloped edges. Throughout the season, it produces numerous clusters of fluffy, light blue to pale blue violet flower. It is easily grown from seed and needs sites with full and average moist soil with good drainage (Zagury, 2001).

Plate 2.6: Structure of *Ageratum houstonianum*

2.5.7 Gaillardiax grandiflora

This is also called try of tough or tough flower. Its brightly beauty colour blossoms resembles those of Native American blanket patterns, thus the name. Its botanical name is *Gaillardiax grandiflora.* The plant is a tough flower also and has its size from 2 to 5 feet wide. It is a perennial plant and the leaves are not parallel veined. The plant is a dicotyledonous and has no fragrance (Carlos, 1990).

Plate 2.7: Structure of *Gaillardiax grandiflora*

2.5.8 Duranta erecta

This is a Brazilian sky flower. Its botanical name is *Duranta erecta.* This a species of flowering shrub in the verbena family verbenacea, native from Mexico to South America and the Caribbean. It is considered an invasive species in Australia, China, and South Africa and on several pacific Islands. It has small glossy leaves and a profusion of pendulous racemes of small flowers with colours varying from light blue to purple. It is partly perennial and partly annual depending on location. Its height ranges from 12 to 15 feet, a growth rate is medium and it has a wide soil pH range (does well in acid or alkaline). It requires medium to high light exposure and a hardness zone from sub-tropical to tropical. The plant has medium salt tolerance and drought tolerance and can be chlorotic in poor fertility sites (Joyce, 1999).

Plate 2.8: structure of *Duranta erecta*

2.6 Principle of Atomic Absorption Spectrophotometer (AAS)

Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state (Walsh, 1995). 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 seventy (70) different elements in solution or directly in solid samples (Broekaert 1998). 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 Gustar Robert Kirchhoff, both professors at the university of Heideling Germany.

This technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It required 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 orbital (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e. wavelength is specific to a particular electron transition in a particular element (Harnly, 1986).

In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few Pico meters (pm), which gives the technique its elemental selectivity (Skoog and Douglas 2007). The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ration between the two values (the absorbance) is convened to analyte concentration or mass giving the Beer-Lambert law.

In order to analyse for its atomic constraints. It has to be atomized. The atomizer most commonly used nowadays are flames and electro thermal (graphite tube) atomize. The atoms should then be irradiated by optical radiation, and then radiation source could be an element-specific line radiation source or a continuum radiation source. The radiation then passes through a monochromatic in order to separate the element- specific

radiation from any other radiation emitted by the radiation sources, which is finally measured by a detector (Welz *et al*., 2005).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The following materials were used during the analysis, Analytical weighing balance (Model CS200), Atomic Absorption spectrophotometer (Buck scientific, AA 220FS), pH meter (Searchtech,PHS- 7010) and Stuart scientific model Rh 12 NB furnace.

3.2 Reagents

Nitric Acid (BDH Chemicals Ltd. Poole England. Tel. (01202) 669700)

Tartaric acid

Distilled water

3.3 Methods

3.3.1 Collection of Plastic Containers and Soil Sample

A total of 200 plastic containers of capacity 3 liters were purchased from Nkwo Nnewi market washed and allowed to dry. Soil samples were collected from the compound of Ibeto Battery Manufacturing Industry at Nnewi from top soil, 5 cm, 10 cm, 15 cm and 20 cm along the North, North East, East, South East, South, South West, West and North West direction of the industry and were analyzed for lead (Pb). The soil samples were collected twice in dry seasons, (Jan/Feb and March/April) and also twice in rainy seasons (June /July and Sept/Oct). Control sample was taken from a distance about

500 m away from the industry to validate the pollution status of the industry. The soil samples were digested and analyzed using AAS (model AA200FS). The acidity of the soil samples was also determined.

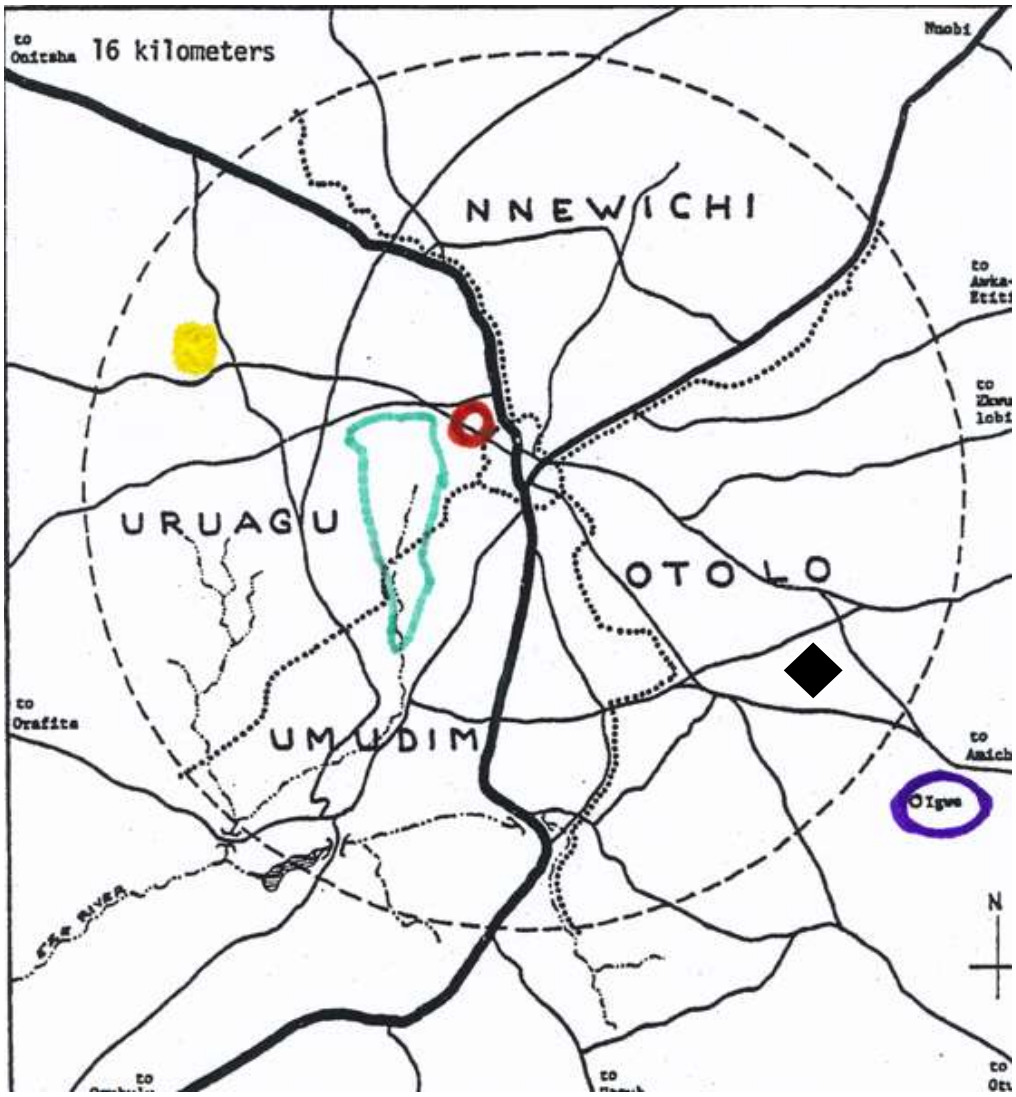

Fig 3.1: Map of Nnewi North

KEY

◆ Sampling Location

Source: http://www.amightytree.org

3.3.2 Determination of the pH of the Soil Sample

The pH determination was calculated using buffer 7 solution. Then the pH meter was adjusted with known pH of buffer solutions 4.0 and 7.0. Soil sample (20g) was weighed and transferred into 100 ml beaker and distilled water (40 mL) was added and stirred well with a glass rod. This was allowed to stand for an hour with intermittent stirring. To the soil-water-suspension in the beaker, the electrode was immersed and pH value was determined from automatic display of the pH meter.

3.3.3 Digestion of Soil Samples

One gram of each soil Samples was digested using 10 ml vol. each of mixture of Nitric and tartaric acid in the ratio of (1:1).The concentration of lead (Pb) in each soil sample was obtained using AAS (model AA220FS).Then process of obtaining this concentration is by obtaining an equivalent absorbance of a control solution produced by BDH laboratory supplies, poole.BH15 ltd. England. To obtain the concentration of the control, 1ml of the control solution (Lead) was aspirated into the AAS (AA 220FS).

3.3.4 Collection of the Plant Seedlings

The seedlings of *Hibiscus rosasinenses, Ixora coccinea, Euphorbia milivarspendens, Ficus benjamina, Ageratum houstonianum,Gaillardiax grandiflora*, *Aloe* barbadenses and *Duranta erecta* were collected from Nnewi Horticulture.

3.3.5 Method of Planting

A total of 400 grams of the soil from each depth (top soil, 5 cm, 10 cm, 15 cm and 20 cm) from the same location was mixed homogeneously to obtain 2 kg of soil for planting. This was repeated for each location (North, Northeast, East, Southeast, South, Southwest, West and Northwest). The plants were then monitored and harvested after a period of 3 months.

3.3.6 Air-drying of the Plant Biomass

The plants harvested were washed properly with distilled water to ensure that sand / contaminants adhering in the roots were washed off. The roots, stems and leaves of each plant were cut off and dried in a room with separate labeled tray. This was done for a period of 6-8 weeks.

3.3.7 Weighing of the Sample

The weight of root, stem and leaf were taken with analytical weighing balance and labeled and stored in polythene bags.

3.3.8 Determination of Lead (Pb) in the Sample

Each of the root, stem and leaf were ashed in a muffle furnace at a temperature of 300^0C. This was cooled and then moistened with 10 ml conc. HNO_3. The moist sample was then diluted with 20 ml distilled water and left to boil on a hot plate at about 100^0C until the content evaporated to 10 ml. It was then filtered through a hardened filter paper into a 100ml volumetric flask and made up to the mark with distilled water. The heavy metal Lead (Pb) was analyzed using AAS instrument.

3.3.9 The Statistical Method of Analysis (ANOVA)

The statistical method of analysis of variance (ANOVA) was used.

The hypotheses tested are as follows:

H_{01} : The lead concentration in the soil is the same for the different soil depths.

H_{02} : The lead concentration in the soil is the same for seasons.

Versus

H_{11} : The lead concentration in the soil is not the same for the different soil depths.

H_{12} : The lead concentration in the soil is not the same for the seasons

The Decision Rule is to accept H_{0i} if the Pvalues > 0.05 (α),

Otherwise accept H_{1i}. i = 1, 2

CHAPTER FOUR

RESULTS AND DISCUSSIONS

The results of the pH and concentration of lead in soil samples from the different locations of the industry are shown in Tables (4.1-4.10) and Figs (4.1-4.9)

4.1.1 Variation in pH of different soil sample at different seasons of the year.

Bioavailability of metals is controlled generally by the soil pH. According to Chlopecka, *et al,* 2014, soil sample with pH of 5.6 or less than 5.6 contain relatively more of all metals. Thus, the pH values of different soil samples analysed are shown in table 4.1 below. The average of 5.6 indicated that lead contained in the soil would be available for plants uptake or extraction. Thus the possibility of using phytoextraction method is viable.

Table 4.1: pH values of soil sample at different cardinal points

Location	Jan/Feb	March/April	June/July	Sept/Oct
North	5.6	5.5	5.6	5.5
North East	5.5	5.6	5.5	5.6
East	5.5	5.6	5.6	5.6
South East	5.6	5.5	5.7	5.6
South	5.7	5.4	5.6	5.5
South West	5.6	5.7	5.7	5.7
West	5.6	5.7	5.4	5.7
North West	5.6	5.6	5.5	5.7
Mean	5.6	5.6	5.5	5.7

Control Sample: Below Detectable Limit (BDL)

4.1.2 Concentration of lead in soil samples at the Northern location of the industry at different period of the year

Table 4.2, Fig, 4.1 showed the concentration of lead in the soil sample of the Northern location of the waste dump area industry, during the two seasons of the year (Rainy and Dry seasons).

The results showed that generally, on average the concentration of lead in the different soil samples was higher in the dry season than in rainy season. This could be attributed to the fact that during rainy season, the water aids the lead in percolating down the soil and leaching could also be another factor that contributed to the lower concentration of lead recorded during the rainy season.

Furthermore, the results of lead concentration on the different depths of the soil analysed showed that the concentration of lead was highest in the top soil, followed by 5 cm depth, 10 cm depth, 15 cm depth and 20 cm depth. This showed that the pollution is still at the primary stage and also confirmed the fact that lead is highly immobile in the soil as was established by (Fiegl *et al.,* 2010).The concentration of lead in the soil for different seasons is generally higher than the EPA limit of 0.4 mg/kg, hence the need for phytoremediation of the soil.

Concentration significantly ($p < 0.05$) varies from top soil to depth of 20 cm as shown in appendix i.

Table 4.2 Concentration of lead in soil samples in the Northern location of the industry at different period of the year

	Lead concentration mg/kg			
Soil Depth (cm)	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
Top soil	1.653	2.031	1.359	1.51
5	1.424	1.749	1.231	1.478
10	1.147	1.589	1.016	1.259
15	1.059	1.48	0.958	1.091
20	0.947	1.286	0.679	1.009
Mean	1.246	1.628	1.049	1.269
Standard deviation	0.2877	0.2808	0.2624	0.2242

Control Sample: BDL (Below Detectable Limit)

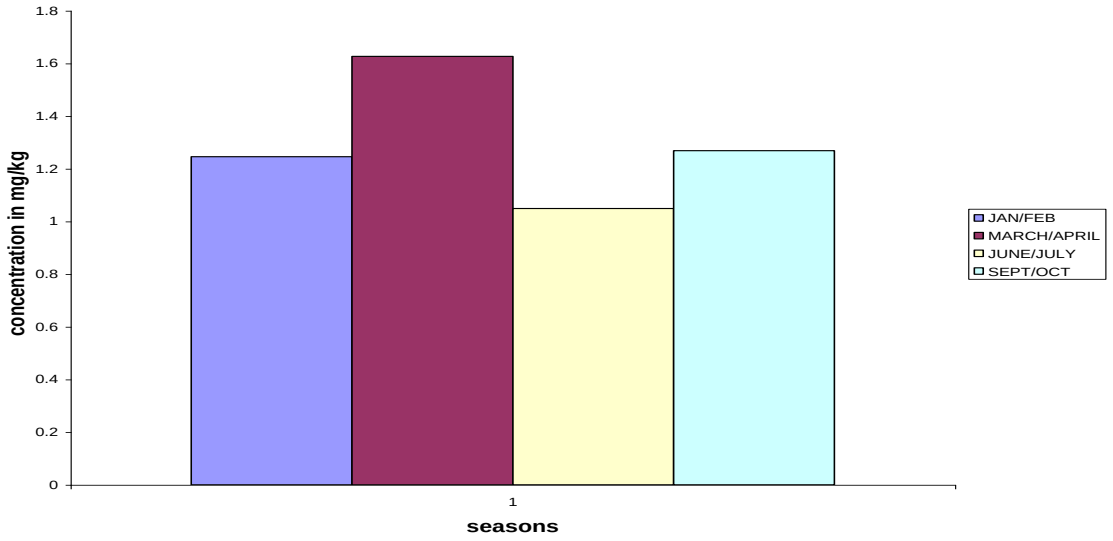

Fig: 4.1 Average concentration of lead in soil sample at the Northern Location of the industry

4.1.3 Concentration of lead in soil samples at the North Eastern location of the industry at different periods of the year.

Table 4.3, Fig 4.2 showed the concentrate of lead in soil sample in both dry and rainy seasons in the North Eastern location of the industry. The average obtained showed that it was slightly higher in dry season than in rainy season. The average of March/ April was 1.079 mg/kg while that of Sept /Oct was 1.067 mg/kg. This could still be attributed to two factors as explained earlier, namely percolation and possible leaching during Rainy season. (De Haan, 1997). The higher values recorded in Sept / Oct as opposed to the value for June /July indicates probably that there were more industrial activities in the months of Sept/Oct. It will be observed here that the lead concentration is above the EPA limit of 0.4 mg/kg.

The lead concentration in the soil is not the same for different soil depths but the same for the seasons as shown in appendix ii

Table 4.3: Concentration of lead in soil samples in the North eastern location of the industry at different periods of the year.

Lead concentration (mg/kg)				
Soil Depth (cm)	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
Top soil	1.637	1.429	1.337	1.338
5	1.571	1.283	1.227	1.305
10	1.010	1.139	1.132	1.126
15	0.937	0.897	0.726	0.808
20	0.622	0.645	0.522	0.758
Mean	1.155	1.079	0.989	1.067
Standard deviation	0.4353	0.3119	0.3484	0.2721

Control Sample: Below Detectable Limit (BDL)

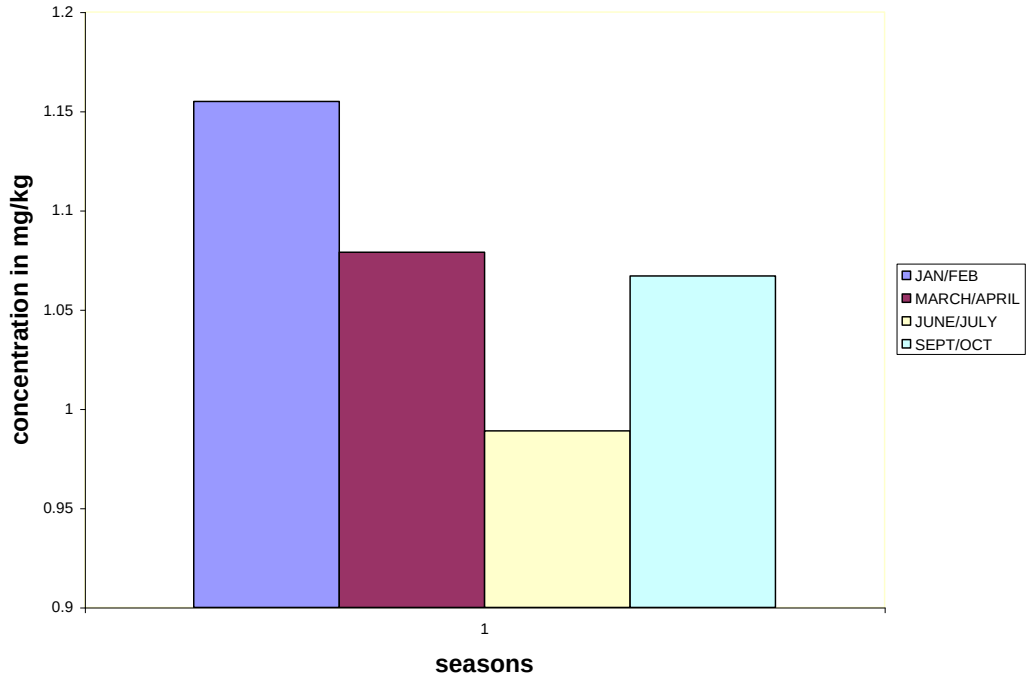

Fig: 4.2 Average concentration of lead in soil sample at the North Eastern Location of the industry

4.1.4 Concentration of lead in soil samples at the Eastern location of the industry at different periods of the year.

Table .4 fig 4.3 showed concentration of lead in the soil sample of different depth in the Eastern location. The results obtained showed that the concentration was higher at the top soil than at 20cm depth. This also supports the facts that lead is highly immobile in the soil unlike other heavy metals.

The lead concentration in the soil is not the same for the different soil depths as well as the seasons as shown in appendix iv. The Pvalues for both soil depths and seasons (0.000 & 0.000) respectively are < than 0.05

Table 4.4: Concentration of lead in soil samples in the Eastern location of the industry at different periods of the year

	Lead concentration (mg/kg)			
Soil Depth (cm)	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
Top soil	2.298	1.657	0.947	1.114
5	1.889	1.478	0.739	1.01
10	1.686	1.311	0.694	0.944
15	1.652	1.113	0.631	0.887
20	1.513	0.791	0.573	0.813
Mean	1.808	1.27	0.717	0.954
Standard Deviation	0.3053	0.3350	0.1432	0.1153

Control Sample: Below Detectable Limit (BDL)

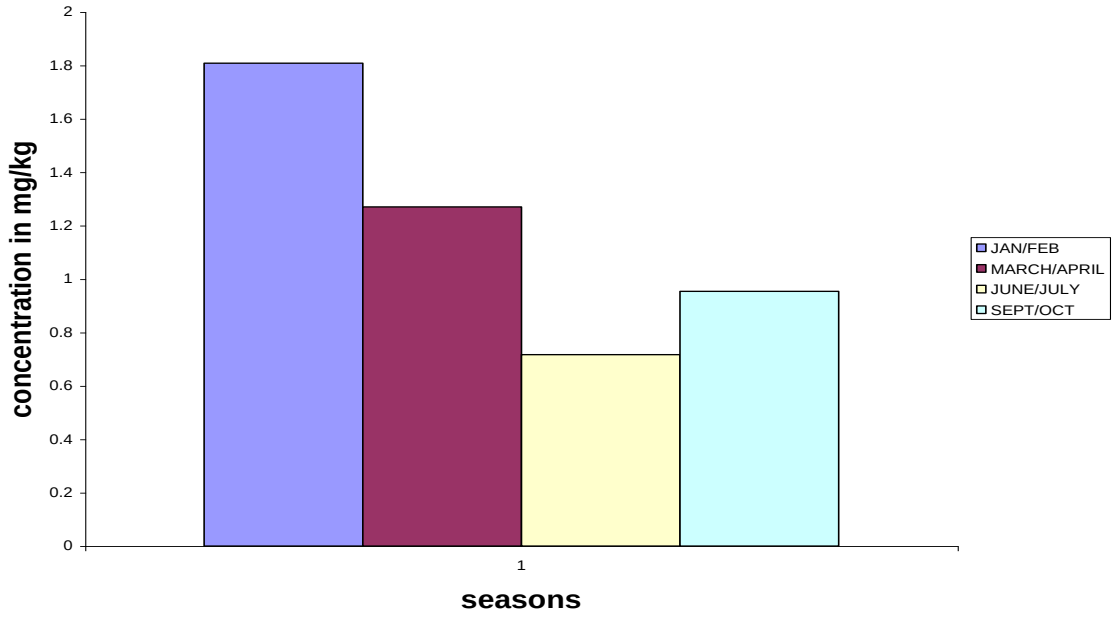

Fig 4.3: Average Concentration of lead in soil sample at the Eastern location of the industry.

4.1.5 Concentration of lead in soil samples at the South Eastern location of the industry at different periods of the year.

Table 4.5 Fig 4.4 showed that the concentration of lead in soil sample during March/April season was higher than Jan/Feb season for the South Eastern location. Furthermore, the concentration of lead in the soil decreases with depth which supports the (Fiegl *et al*., 2010) that lead is immobile in the soil.

The lead concentration significantly ($p < 0.05$) varies from top soil to depth of 20 cm as shown in appendix IV.

Table 4.5: Concentration of lead in soil samples at the South Eastern location of the industry at different periods of the year.

Lead concentration (mg/kg)				
Soil Depth (cm)	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
Top soil	1.256	1.779	1.035	1.048
5	1.026	1.578	0.967	0.903
10	0.851	1.315	0.634	0.684
15	0.829	1.073	0.523	0.587
20	0.783	0.818	0.426	0.543
Mean	0.949	1.313	0.717	0.753
Standard deviation	0.1948	0.3814	0.2706	0.2156

Control Sample: Below Detectable Limit (BDL)

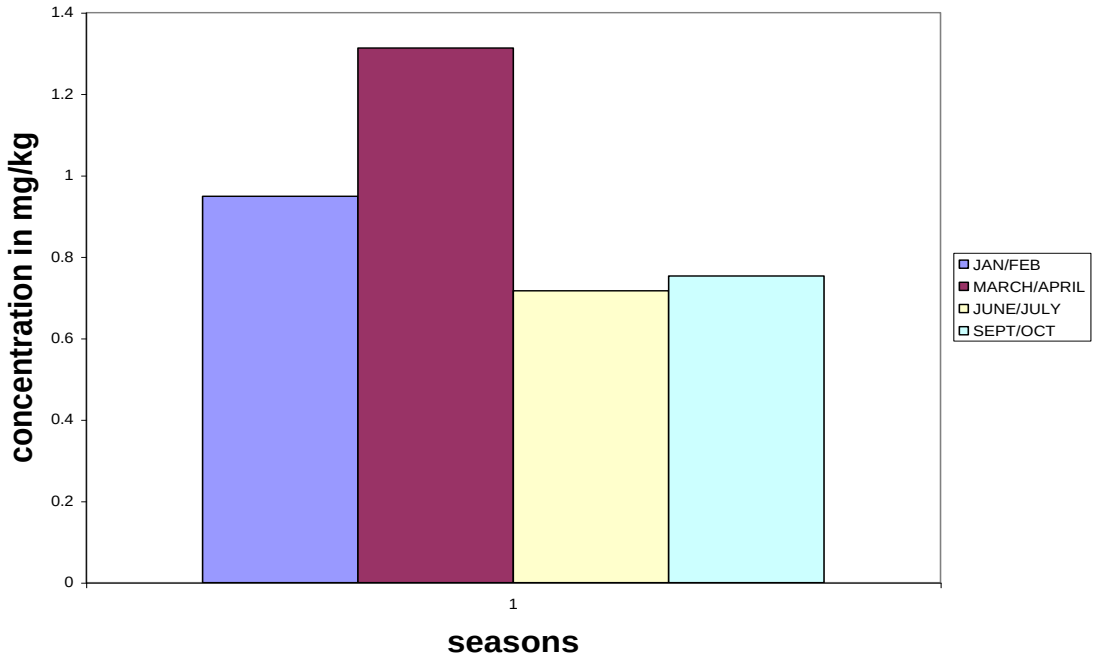

Fig 4.4: Average concentration of lead in soil sample at the south Eastern location of the industry

4.1.6 Concentration of lead in soil samples at the Southern location of the industry at different periods of the year.

Table 4.6 Fig 4.5 showed that the concentration of lead in both dry and rainy seasons. There is discrepancy in the concentration of lead during Sept/Oct season. This could be attributed to the time of peak production of the industry which could result to the increase in lead pollution in the soil sample during the period.The results showed that the concentration of lead in the soil is above the EPA limit of 0.4 mg/kg except 15 cm

and 20 cm depth of Jan/Feb. season with the value of 0.331 mg/kg and 0.276 mg/kg respectively

The lead concentration in the soil is not the same for both soil depth and seasons as also shown in appendix v.

Table 4.6: Concentration of lead in soil samples at the Southern location of the industry at different periods of the year.

Lead concentration (mg/kg)				
Soil Depth (cm)	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
Top soil	0.842	2.198	1.036	1.664
5	0.669	1.975	0.977	1.58
10	0.47	1.786	0.702	1.541
15	0.331	1.565	0.604	1.482
20	0.276	1.256	0.573	1.306
Mean	0.518	1.756	0.778	1.515
Standard deviation	0.2364	0.3642	0.2146	0.1340

Control Sample: Below Detectable Limit (BDL)

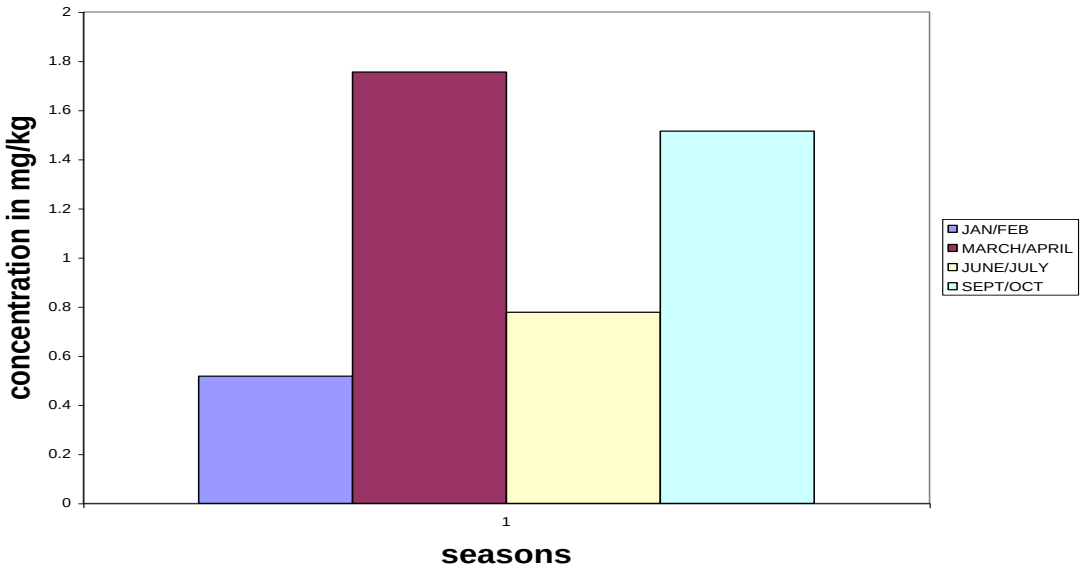

Fig: 4.5: Average concentration of lead in soil sample at the Southern location of the industry

4.1.7 Concentration of lead in soil samples at the Southwestern location of the industry at different periods of the year.

Table 4.7 Fig 4.6 showed that the concentration of lead in the soil sample in both dry and rainy seasons. The results show that the concentration of lead in south Western location in both seasons is relatively low compared to some other locations. This could be the period of lowest production of the industry.

The lead concentration significantly ($p < 0.05$) varies from top soil to depth of 20 cm as shown in appendix vi.

Table 4.7: Concentration of lead in soil samples at the Southwestern location of the industry at different periods of the year.

Lead concentration (mg/kg)				
Soil Depth (cm)	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
Top soil	0.618	0.745	0.689	0.789
5	0.536	0.685	0.594	0.573
10	0.515	0.555	0.469	0.451
15	0.456	0.400	0.352	0.304
20	0.342	0.287	0.203	0.211
Mean	0.493	0.534	0.461	0.466
Standard deviation	0.1026	0.1915	0.1925	0.2276

Control Sample: Below Detectable Limit (BDL)

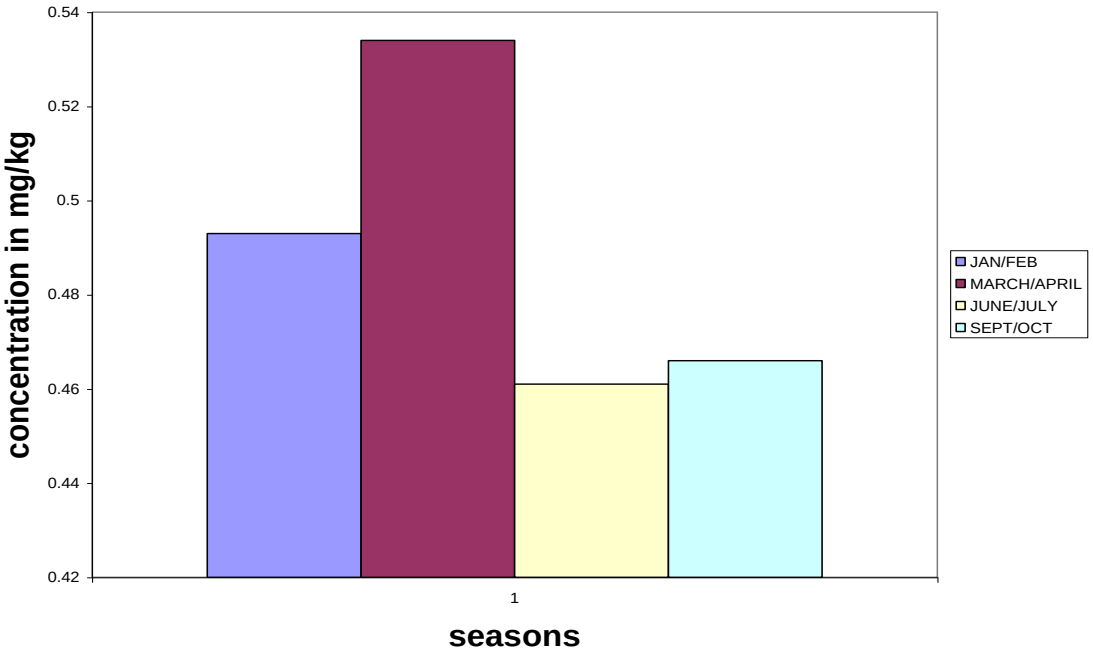

Fig 4.6: Average concentration of lead in soil sample at the South western location of the industry

4.1.8 Concentration of lead in soil samples at the Western location of the industry at different periods of the year.

Table 4.8 Fig 4.7. Also showed that the concentration of lead in soil sample in the Western location. This results show that the concentration in both dry and rainy season is relatively low. The figure or data obtained is slightly higher in dry season than in rainy season. This shows the leaching aspect of the soil.

The lead concentration in the soil is not the same for different soil depths but the same for the seasons as can be seen in appendix vii.

Table 4.8: Concentration of lead in soil samples at the Western location of the industry at different Periods of the year.

Lead concentration (mg/kg)				
Soil Depth (cm)	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
Top soil	0.845	0.942	0.681	0.792
5	0.793	0.803	0.533	0.765
10	0.646	0.636	0.465	0.661
15	0.563	0.517	0.435	0.567
20	0.473	0.449	0.108	0.359
Mean	0.664	0.669	0.444	0.629
Standard Deviation	0.1552	0.2031	0.2107	0.1752

Control Sample: Below Detectable Limit (BDL)

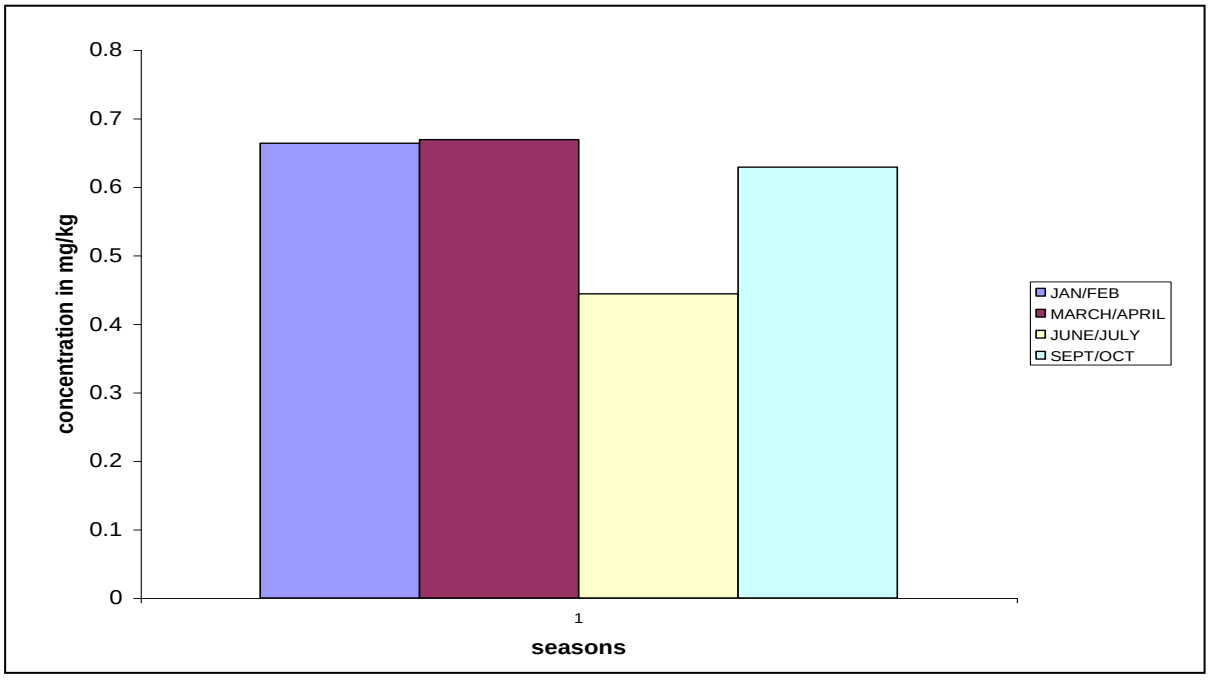

Fig 4.7 Average concentration of lead in soil sample at the Western location of the industry

4.1.9 Concentration of lead in soil samples at the Northwestern location of the industry at different periods of the year.

Table 4.9 Fig 4.8 showed the concentrative of lead in soil sample in different seasons of the year. The result obtained here contradicts the (Fiegl *et al*., 2010). The concentration of lead in the soil was highest in June/ July season (rainy) and least in Jan/Feb season (dry). This could be as a result of time of peak production of the industry which made it higher in rainy season than in dry season. Furthermore, the lead concentrations in the soil are higher than the EPA limit except 20 cm depth of Sept./Oct. season with the value of 0.302 mg/kg.

Concentration significantly ($p < 0.05$) varies from top soil to depth of 20 cm as can be seen in appendix viii.

Table 4.9: Concentration of lead in soil samples in the Northwestern location of the industry at different periods of the year.

Lead concentration (mg/kg)				
Soil Depth (cm)	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
Top soil	0.959	1.039	1.543	1.065
5	0.563	0.892	1.488	0.926
10	0.469	0.869	1.435	0.743
15	0.464	0.740	1.386	0.517
20	0.449	0.594	1.039	0.302
Mean	0.581	0.827	1.378	0.711
Standard deviation	0.2161	0.1679	0.1985	0.3072

Control Sample: Below Detectable Limit (BDL)

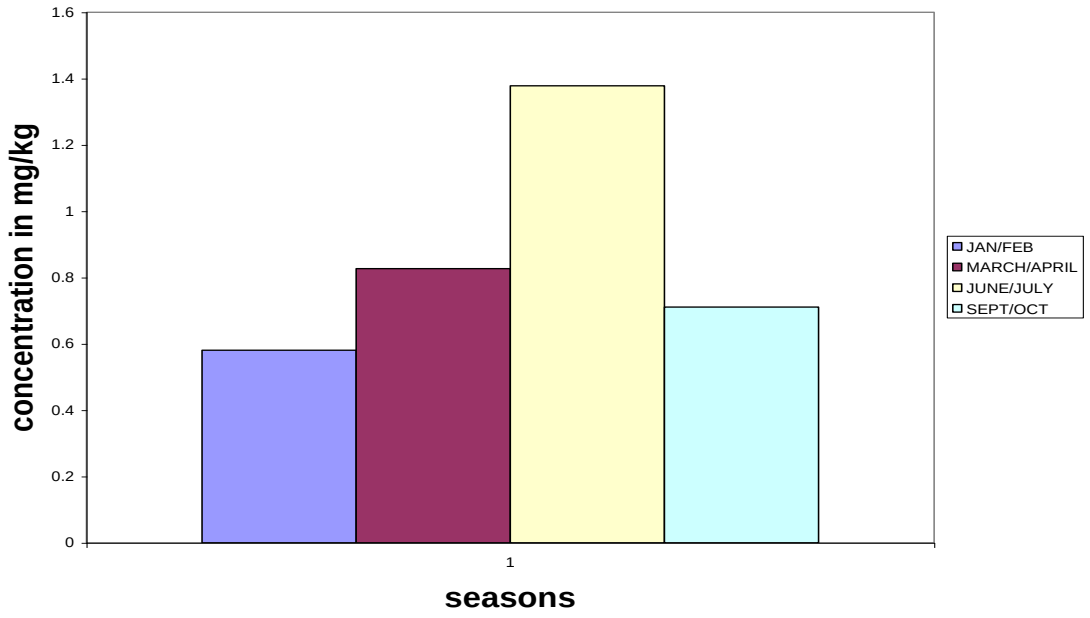

Fig 4.8 Average concentration of lead in soil sample at the North Western location of the industry

4.1.10 Concentration of lead in soil samples at different cardinal points location of the industry at different periods of the year.

Table 4.10 Fig 4.9 showed that concentration of lead in soil sample of the eight cardinal points during both dry and rainy seasons. The values showed that the concentration of lead is more during dry season than rainy season. Reason could be attributed to leaching and percolation that occurs during rainy season (De Haan,1997).The different cardinal location have their concentrations higher than the EPA limit of 0.4 mg/kg except western location of June/July season with a value of 0.301 mg/kg

Table 4.10: Concentration of lead in soil samples at different cardinal points location of the industry at different periods of the year.

Lead Concentration (mg/kg)				
Location	Jan/Feb Season	March/April Season	June/July Season	Sept/Oct Season
North	1.366	1.681	0.936	1.135
North East	1.564	1.187	1.015	1.105
East	1.787	1.256	0.63	0.641
South East	0.719	1.312	0.549	1.093
South	0.519	1.698	0.939	1.108
South West	0.473	0.621	0.449	0.636
West	0.516	0.588	0.301	0.595
North West	0.612	0.794	1.281	0.703
Mean	0.945	1.141	0.763	0.877
Standard deviation	0.5368	0.4380	0.3313	0.2513

Control Sample: Below Detectable Limit (BDL)

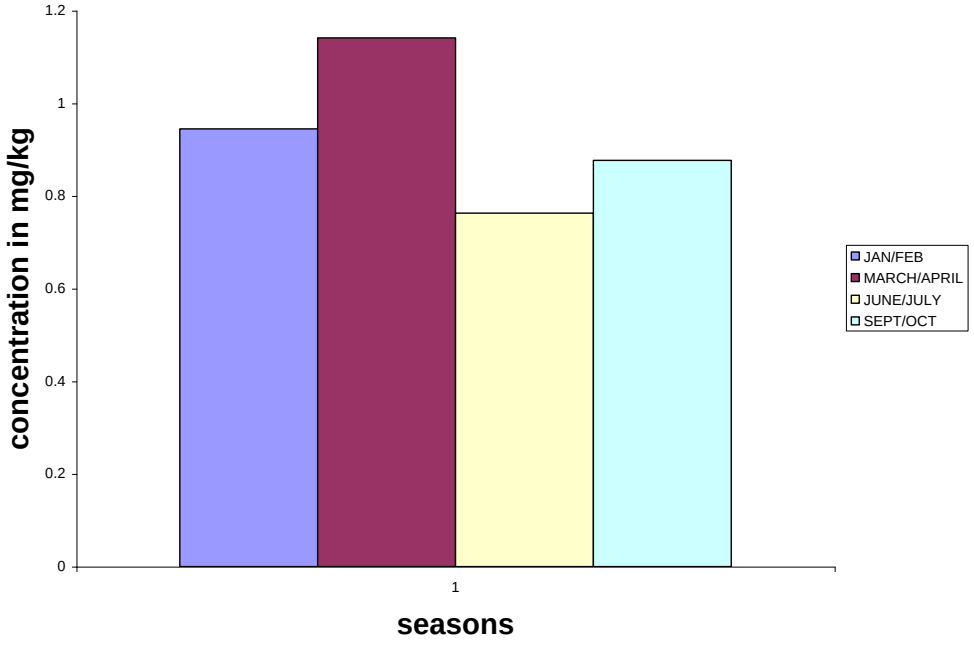

Fig 4.9: Average concentration of lead in soil samples at different cardinal points of the industry.

The results of the investigation into the *phytoremediation* capabilities *of Hibiscus rosasenensis, Ixora coccinea, Euphorbia milivarspendens, Ficus benjamina, Ageratum houstonianum, Gaillardiax grandiflora, Aloe barbadensis* and *Duranta erecta* were shown in Tables (4.11-4.26).

According to (Kumar *et al.,*1995) for phytoremediation to be feasible and cost effectives, the plant used must be able to take up large concentrations of heavy metal into the roots and translocation it to the stem and leaves. However, it is preferable to use plants that will accumulate the metal in the shoot as opposed to the roots, since metal in the shoot can easily be cut off the plant and recovered. Whereas the use of

plants that accumulate metal more in their roots required total uproot of the plant so as to recover the metal, thus increasing the cost of phytoremediation due to the need of additional labour in replanting.

4.1.11 Variation of lead uptake by *Hibiscus rosasinensis* after a Period of 3 months.

The results of the investigation into the amount of lead absorbed by the root stem and leaves of *Hibiscus rosasinensis* at both dry and rainy season were shown in tables 4.11 and 4.12 respectively. The results showed that *Hibiscus rosasinensis* has more of the lead accumulate in the roots than in its shoots (stem and leaves) in both dry and rainy season. Thus the use of this plant is phytoremediation is not highly recommendable as the cost of recovering the metal would be high.

Using statistical analysis, the lead uptake significantly varies ($p < 0.05$) varies from different plant parts as shown in appendix ix.

Table 4.11: Variation of lead uptake by *Hibiscus rosasinensis* after a period of 3 months for Northern location of industry in dry season.

Dry Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
Jan/Feb	0.148	0.08	0.04	1.096	BDL
March/ April	0.18	0.084	0.042	1.340	BDL

BDL: Below Detectable Limit

Table 4.12: Variation of lead uptake by *Hibiscus rosasinensis* after a period of 3 months for Northern location of industry in rainy season.

Rainy Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (Mg/kg)	Residue Soil (mg/kg)	Control
June/ July	0.1	0,0400	0.02	0.775	BDL
Sept/ Oct	0.16	0.05	0.03	1.194	BDL

4.1.12 Variation of lead uptake by *Ixora Coccinea* after a period of 3 months.

The results of the investigation into the amount of lead absorbed by different plant part of *Ixora coccinea* at both dry and rainy season were shown in tables 4.13 and 4.14 respectively. The result showed that the plant absorbed less lead in the root than in the stem and leaves at both season of the year but the quantity or concentration absorbed in the shoot were small. This will take a longer period to clean up a lead polluted site, consequently not recommendable for phytoremediation.

The lead uptake significantly ($p < 0.05$) varies from different plant parts (roots, stem and leaves) as can be seen in appendix x.

Table 4.13: **Variation of lead uptake by *Ixora coccinea* after a period of 3 months for North Eastern location of industry in dry season.**

Dry Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
Jan/Feb	0.03	0.05	0.09	1.392	BDL
March/April	0.025	0.04	0.07	1.050	BDL

Table 4.14: Variation of lead uptake by *Ixora coccinea* after a period of 3 months for North Eastern location of industry in rainy season.

Rainy Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
June/July	0.01	0.04	0.07	0.893	BDL
Sept/Oct	0.011	0.048	0.075	0.980	BDL

3.1.13 Variation of lead uptake by *Euphorbia milivarsplendens* after a period of 3 months.

The results of the investigation into the concentration of lead absorbed by the roots, stem and leaves of *Euphorbia milivarsplendens* at both dry and rainy season were shown in tables 4.15 and 4.16 respectively. The result showed that the plants absorbed a large concentration of lead in the root and translocate it to the stem and leaves. In other words, the concentrations are more on the shoots than on the root. The quantity of lead on the shoot may have been contributed by air lead deposit. Some plants have the ability to accommodate lead dust on the surface of their leaves. Therefore, *Euphorbia milivarspendens* could be used to remediate lead polluted sites. The plant was able to reduce the lead concentration below the EPA limit of 0.4 mg/kg.

The lead uptake significantly ($p < 0.05$) varies from different plant parts as shown in appendix xi.

Table 4.15: **Variation of lead uptake by *Euphorbia milivarsplendens* after a period of 3 months for the Eastern location of the industry in dry season.**

Dry Season	Uptake of Pb In root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
Jan/Feb	0.2	0.3	0.98	0.307	BDL
March/April	0.148	0.2	0.68	0.227	BDL

Table 4.16: Variation of lead uptake by *Euphorbia milivarsplendens* after a period of 3 months at the Eastern location of the industry in rainy season.

Rainy Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (Mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
June/July	0.048	0.099	0.342	0.142	BDL
Sept/Oct	0.07	0.101	0.603	0.166	BDL

4.1.14 Variation of lead uptake by *Ficus benjamina* after a period of 3 months.

From the result shown in tables 4.17 and 4.18, the root of *Ficus benjamina* absorbed less concentration of lead as compared to the shoots (stem and leaves), consequently, the metal absorbed by the shoot could easily be recovered. Also the amount of lead on the leaves may also be as a result of air-borne lead. Generally, the uptake by the parts of the plant may be expressed in the order leaves>stem> root. This shown that this plant could be used for phytoremediation of lead polluted environment.

Also the lead uptake significantly ($p > 0.05$) varies from different plant parts as shown in appendix xii.

Table 4.17: Variation of lead uptake by *Ficus benjamina* after a period of 3 months in South eastern location of the industry in dry season

Dry Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
Jan/Feb	0.08	0.18	0.2	0.257	BDL
March/April	0.1	0.2	0.6	0.410	BDL

Table 4.18: Variation of lead uptake by *Ficus benjamina* after a period of 3 months for the Southern location of the industry in rainy season.

Rainy Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (Mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
June/July	0.06	0.083	0.211	0.195	BDL
Sept/Oct	0.061	0.24	0.62	0.372	BDL

4.1.15 Variation of lead uptake by *Ageratum houstonianum* after a period of 3 months.

The result of the investigation into the quantity of lead absorbed by the different parts of *Ageratum houstonianum* at both dry and rainy seasons were shown in tables 4.19 and 4.20 respectively. The results showed that the plant absorbed more lead in the roots than in the stem or leaves at both seasons. This could be as a result of the precipitation or immobilization of the lead contaminants in the soil surface, or within the root tissues (phytosequestration)(Pueyo and Sastre,2015). The plant has to be uprooted before the metal could be recovered which will take a longer period of time and additional labour.

Therefore, *Ageratum houstonianum* is highly not recommendable for phytoremediation of lead polluted environment.

The lead uptake significantly ($p < 0.05$) varies from different plant parts (root, stem and leaves) as shown in appendix xiii.

Table 4.19: Variation of lead uptake by *Ageratum houstonianum* is after a period of 3 months for the Southern location in dry season.

Dry Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
Jan/Feb	0.102	0.04	0.03	0.346	BDL
March/April	0.5	0.083	0.045	1.061	BDL

Table 4.20: Variation of lead uptake by *Ageratum houstonianum* is after a period of 3 months for the Southern location in rainy season.

Rainy Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
June/July	0.314	0.022	0.006	0.595	BDL
Sept/Oct	0.342	0.111	0.056	0.968	BDL

4.1.16 Variation of lead uptake by *Gaillardiax grandiflora* after a period of 3 months.

Table 4.21 and 4.22 showed the result of the investigation into amount of lead absorbed by different plant parts and at different seasons of the year. The results showed that *gaillardiax grandiflora* could not absorbed lead as the plant died 3 weeks after yellowing of its leaves. This could be attributed to the poisoning of the plant by lead. Therefore, the plant could not be used for phytoremediation of lead polluted site.

Table 4.21: Variation of lead uptake by *Gaillardiax grandiflora* after a period of 3 months for the South Western location of the industry in dry season.

Dry Season	Uptake of Pb in root (mg/kg)	Uptake of Pb In stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
Jan/Feb	ND	ND	ND	0.4728	BDL
March/April	ND	ND	ND	0.619	BDL

ND: Not Detected

Table 4.22: Variation of lead uptake by *Gaillardiax grandiflora* after a period of 3 months for the South Western location of the industry in rainy season.

Rainy Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
June/July	ND	ND	ND	0.448	BDL
Sept/Oct	ND	ND	ND	0.635	BDL

4.1.17 Variation of lead uptake by *Aloe barbadensis* after a period of 3 months.

The results of the investigation into the lead concentration absorbed by the root, stem and leaves of *Aloe barbadensis* at both dry and rainy seasons were shown in tables 4.23 and 4.24 respectively. The result obtained was similar to that of *Gaillardiax grandiflora*. This plant could not absorb any lead as it dies after a short period of time. This could be as a result of lead poisoning and therefore cannot in any way be used to treat lead polluted sites.

Table 4.23: Variation of lead uptake by *Aloe barbadensis* after a period of 3 months for the Western location of the industry dry season.

Dry Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
Jan/Feb	ND	ND	ND	0.515	BDL
March/April	ND	ND	ND	0.588	BDL

Table 4.24: Variation of lead uptake by *Aloe barbadensis* after a period of 3 months for the Western location of the industry in rainy season.

Rainy Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
June/July	ND	ND	ND	0.301	BDL
Sept/Oct	ND	ND	ND	0.593	BDL

4.1.18 Variation of lead uptake by *Duranta erecta* after a period of 3 months

The results of the investigation into the amount of lead absorbed by different parts of Duranta erecta in both seasons of the year were shown in tables 4.25 and 4.26 respectively. The result showed that the plant plants absorbed large concentration of lead into the roots and then translocate it to the stem and leaves. In order words, the plant accumulates more lead in the shoot (stem and leaves) as opposed to the root. This could be as a result of the process of phytovolatilization taking place (Kumar *et al*, 1995). Therefore, the plant could be used for phytoremediation of lead polluted environment since it supports the statement made by (Kumar *et al*, 1995) that the

feasibility of the phytoremediation lies in its ability to absorb large concentration is of the heavy metal in the roots, then translocate it to the shoot, and to grow rapidly and reach a high biomass, which can be harvested. The plant was able to reduce the lead concentration below the EPA limit of 0.4 mg/kg.

The lead uptake significantly ($p > 0.05$) varies from different plant parts as shown in appendix xiv

Table 4.25: Variation of lead uptake by *Duranta erecta* after a period of 3 months for the North Western location of the industry in dry season.

Dry Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
Jan/Feb	0.062	0.104	0.28	0.165	BDL
March/April	0.015	0.680	0.5	0.210	BDL

Table 4.26: Variation of lead uptake by *Duranta erecta* after a period of 3 months in the North Western location of the industry in rainy season.

Rainy Season	Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	Uptake of Pb in leaves (mg/kg)	Residue Soil (mg/kg)	Control
June/July	0.044	0.327	0.522	0.405	BDL
Sept/Oct	0.026	0.28	0.31	0.180	BDL

CHAPTER FIVE

CONCLUSIONS, RECOMMENDATIONS AND CONTRIBUTION TO KNOWLEDGE

5.1 Conclusions

The result showed that the pH of the soil sample was slightly acidic with a range of 5.5-5.7 while the mean concentration of Lead was higher in dry season than in rainy season probably due to leaching and percolation of the soil during the rainy season.

Lead levels are of the order March/April(1.141 mg/kg)>Jan/Feb (0.945 mg/kg)>Sept/Oct(0.877 mg/kg)>June/July(0.763 mg/kg).

Further, it was concluded that some non-edible flowing plants could be used to clean up lead polluted environment.

Gaillardiax grandiflora and *Aloe barbadensis* died after three weeks because they are unsuitable for plant absorption and therefore could not be used for phytoremediation.

Moreso, Ixora coccinea absorbed more lead in the shoot than in the root, but the quantity absorbed in the shoot was very small. Thus cannot be economically viable to remediate lead polluted sites.

However, Euphorbia *Milivarspendens, Ficus benjamina* and *Duranta erecta* could be used to remove lead contaminants from the soil because they were able to absorb relatively large concentrations of the lead into the roots and translocate it to the shoots.

These plants Euphorbia *Milivarspendens, Ficus benjamina* and *Duranta erecta* were able to reduce the Lead concentration below the EPA limit of 0.4 mg/kg.

5.2 Recommendations

It is recommend that the species of non-edible flowering plants such as *Euphorbia milivarspendens, Ficus benjamina* and *Duranta erecta* be used to check for the hyper accumulator.

Also, non-edible flowering plants/trees which are not seasonal in nature and has short life time could be used in order to reduce the remediation time.

Finally, plant species which produce high biomass could be used.

5.3 Contribution to Knowledge

Phytoremediation of Arsenic and Lead using *Brassica rapa* by Brittiany and John (2003) indicated that the plant absorbed arsenic but not lead.In this work, the plant *Ficus benjamina*,*Duranta erecta* and *Euphorbia milivarspendens* were able to absorb lead to the concentrations of 0.2 mg/kg,0.28 mg/kg and 0.98 mg/kg respectively.

Furthermore,phytoremediation of lead by Huang and Cunningham (1997) using *Zeamays* (corn) which is edible plant and could be detrimental to human health if consumed,nevertheless non edible flowering plants such as *Ficus benjamina*,*Duranta erecta* and *Euphorbia milivarspendens* were used to remediate polluted soil.

These plants, *Ficus benjamina*,*Duranta erecta* and *Euphorbia milivarspendens* have been shown to absorb more than 60% of lead contaminants in the soil..

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APPENDIX

Appendix I: Concentration of Lead in soil sample in the Northern Location

Univariate Analysis of Variance (ANOVA)

Descriptive Statistics

Dependent Variable: Soil concentration

Soil depth (cm)	Seasons	Mean	Std. Deviation	N
	Jan/Feb Season	1.63700	.	1
	March/April Season	1.42900	.	1
0	June/July Season	1.33700	.	1
	Sept/Oct Season	1.33800	.	1
	Total	1.43525	0.141248	4
	Jan/Feb Season	1.57100	.	1
	March/April Season	1.28300	.	1
5	June/July Season	1.22700	.	1
	Sept/Oct Season	1.30500	.	1
	Total	1.34650	0.153226	4
	Jan/Feb Season	1.01000	.	1
	March/April Season	1.13900	.	1
10	June/July Season	1.13200	.	1
	Sept/Oct Season	1.12600	.	1
	Total	1.10175	0.061397	4
	Jan/Feb Season	0.93700	.	1
	March/April Season	0.89700	.	1
15	June/July Season	0.72600	.	1
	Sept/Oct Season	0.80800	.	1
	Total	0.84200	0.094273	4
	Jan/Feb Season	0.62200	.	1
	March/April Season	0.64500	.	1
20	June/July Season	0.52200	.	1
	Sept/Oct Season	0.75800	.	1
	Total	0.63675	0.096876	4
	Jan/Feb Season	1.15540	0.435321	5
	March/April Season	1.07860	0.311928	5
Total	June/July Season	0.98880	0.348373	5
	Sept/Oct Season	1.06700	0.272088	5
	Total	1.07245	0.324323	20

Tests of Between-Subjects Effects

Dependent Variable: Soil concentration

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Model	24.875[a]	8	3.109	294.526	0.000
Soil Depth	1.802	4	0.451	42.675	0.000
Season	0.070	3	0.023	2.202	0.141
Error	0.127	12	0.011		
Total	25.002	20			

a. R Squared = .995 (Adjusted R Squared = .992)

Soil depth (cm)

Multiple Comparisons

Dependent Variable: Soil concentration

LSD

(I) Soil depth (cm)	(J) Soil depth (cm)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	5	0.08875	0.072654	0.245	-0.06955	0.24705
	10	0.33350*	0.072654	0.001	0.17520	0.49180
	15	0.59325*	0.072654	0.000	0.43495	0.75155
	20	0.79850*	0.072654	0.000	0.64020	0.95680
5	0	-0.08875	0.072654	0.245	-0.24705	0.06955
	10	0.24475*	0.072654	0.006	0.08645	0.40305
	15	0.50450*	0.072654	0.000	0.34620	0.66280
	20	0.70975*	0.072654	0.000	0.55145	0.86805
10	0	-0.33350*	0.072654	0.001	-0.49180	-0.17520
	5	-0.24475*	0.072654	0.006	-0.40305	-0.08645
	15	0.25975*	0.072654	0.004	0.10145	0.41805
	20	0.46500*	0.072654	0.000	0.30670	0.62330
15	0	-0.59325*	0.072654	0.000	-0.75155	-0.43495
	5	-0.50450*	0.072654	0.000	-0.66280	-0.34620
	10	-0.25975*	0.072654	0.004	-0.41805	-0.10145
	20	0.20525*	0.072654	0.015	0.04695	0.36355
20	0	-0.79850*	0.072654	0.000	-0.95680	-0.64020

5	-0.70975*	0.072654	.000	-0.86805	-0.55145
10	-0.46500*	0.072654	.000	-0.62330	-0.30670
15	-0.20525*	0.072654	.015	-0.36355	-0.04695

Based on observed means.
The error term is Mean Square(Error) =0 .011.
*. The mean difference is significant at the 0.05 level.

Appendix II: Concentration of Lead in soil sample in the North eastern Location:
Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Soil concentration

Soil depth (cm)	Seasons	Mean	Std. Deviation	N
	Jan/Feb Season	1.63700	.	1
	March/April Season	1.42900	.	1
0	June/July Season	1.33700	.	1
	Sept/Oct Season	1.33800	.	1
	Total	1.43525	0.141248	4
	Jan/Feb Season	1.57100	.	1
	March/April Season	1.28300	.	1
5	June/July Season	1.22700	.	1
	Sept/Oct Season	1.30500	.	1
	Total	1.34650	0.153226	4
	Jan/Feb Season	1.01000	.	1
	March/April Season	1.13900	.	1
10	June/July Season	1.13200	.	1
	Sept/Oct Season	1.12600	.	1
	Total	1.10175	0.061397	4
	Jan/Feb Season	0.93700	.	1
	March/April Season	0.89700	.	1
15	June/July Season	0.72600	.	1
	Sept/Oct Season	0.80800	.	1
	Total	0.84200	0.094273	4
	Jan/Feb Season	0.62200	.	1
	March/April Season	0.64500	.	1
20	June/July Season	0.52200	.	1
	Sept/Oct Season	0.75800	.	1
	Total	0.63675	0.096876	4
	Jan/Feb Season	1.15540	0.435321	5
	March/April Season	1.07860	0.311928	5
Total	June/July Season	0.98880	0.348373	5
	Sept/Oct Season	1.06700	0.272088	5
	Total	1.07245	0.324323	20

Tests of Between-Subjects Effects

Dependent Variable: Soil concentration

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Model	24.875[a]	8	3.109	294.526	0.000
Soil Depth	1.802	4	0.451	42.675	0.000
Season	0.070	3	0.023	2.202	00.141
Error	0.127	12	0.011		
Total	25.002	20			

a. R Squared =0 .995 (Adjusted R Squared =0 .992)

Soil depth (cm)

Multiple Comparisons

Dependent Variable: Soil concentration

LSD

(I) Soil depth (cm)	(J) Soil depth (cm)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	5	0.08875	.072654	0.245	-0.06955	0.24705
	10	0.33350*	.072654	0.001	0.17520	0.49180
	15	0.59325*	.072654	0.000	0.43495	0.75155
	20	0.79850*	.072654	0.000	0.64020	0.95680
5	0	-0.08875	.072654	0.245	-0.24705	0.06955
	10	0.24475*	.072654	0.006	0.08645	0.40305
	15	0.50450*	.072654	0.000	0.34620	0.66280
	20	0.70975*	.072654	0.000	0.55145	0.86805
10	0	-0.33350*	.072654	0.001	-0.49180	-0.17520
	5	-0.24475*	.072654	0.006	-0.40305	-0.08645
	15	0.25975*	.072654	0.004	0.10145	0.41805
	20	0.46500*	.072654	0.000	0.30670	0.62330
15	0	-0.59325*	.072654	0.000	-0.75155	-0.43495
	5	-0.50450*	.072654	0.000	-0.66280	-0.34620
	10	-0.25975*	.072654	0.004	-0.41805	-0.10145
	20	0.20525*	.072654	0.015	0.04695	0.36355
20	0	-0.79850*	.072654	0.000	-0.95680	-0.64020
	5	-0.70975*	.072654	0.000	-0.86805	-0.55145
	10	-0.46500*	.072654	0.000	-0.62330	-0.30670
	15	-0.20525*	.072654	0.015	-0.36355	-0.04695

Based on observed means.

The error term is Mean Square(Error) =0 .011.

*. The mean difference is significant at the0 .05 level.

Appendix III: Concentration of Lead in soil sample in the Eastern Location:

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Soil concentration

Soil depth (cm)	Seasons	Mean	Std. Deviation	N
	Jan/Feb Season	2.29800	.	1
	March/April Season	1.65700	.	1
0	June/July Season	0.94700	.	1
	Sept/Oct Season	1.11400	.	1
	Total	1.50400	0.609971	4
	Jan/Feb Season	1.88900	.	1
	March/April Season	1.47800	.	1
5	June/July Season	0.73900	.	1
	Sept/Oct Season	1.01000	.	1
	Total	1.27900	0.508482	4
	Jan/Feb Season	1.68600	.	1
	March/April Season	1.31100	.	1
10	June/July Season	0.69400	.	1
	Sept/Oct Season	0.94400	.	1
	Total	1.15875	0.433314	4
	Jan/Feb Season	1.65200	.	1
	March/April Season	1.11300	.	1
15	June/July Season	0.63100	.	1
	Sept/Oct Season	0.88700	.	1
	Total	1.07075	0.434657	4
	Jan/Feb Season	1.51300	.	1
	March/April Season	0.79100	.	1
20	June/July Season	0.57300	.	1
	Sept/Oct Season	0.81300	.	1
	Total	0.92250	0.408299	4
	Jan/Feb Season	1.80760	0.305330	5
	March/April Season	1.27000	0.334964	5
Total	June/July Season	0.71680	0.143217	5
	Sept/Oct Season	0.95360	0.115331	5
	Total	1.18700	0.475447	20

Tests of Between-Subjects Effects

Dependent Variable: Soil concentration

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Model	32.290[a]	8	4.036	263.153	0.000
Soil Depth	0.773	4	0.193	12.598	0.000
Season	3.338	3	1.113	72.542	0.000
Error	0.184	12	0.015		
Total	32.474	20			

a. R Squared = 0.994 (Adjusted R Squared = 0.991)

Soil depth (cm)

Multiple Comparisons

Dependent Variable: Soil concentration

LSD

(I) Soil depth (cm)	(J) Soil depth (cm)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	5	0.22500*	0.087573	0.025	0.03419	0.41581
	10	0.34525*	0.087573	0.002	0.15444	0.53606
	15	0.43325*	0.087573	0.000	0.24244	0.62406
	20	0.58150*	0.087573	0.000	0.39069	0.77231
5	0	-0.22500*	0.087573	0.025	-0.41581	-0.03419
	10	0.12025	0.087573	0.195	-0.07056	0.31106
	15	0.20825*	0.087573	0.035	0.01744	0.39906
	20	0.35650*	0.087573	0.002	0.16569	0.54731
10	0	-0.34525*	0.087573	0.002	-0.53606	-0.15444
	5	-0.12025	0.087573	0.195	-0.31106	0.07056
	15	0.08800	0.087573	0.335	-0.10281	0.27881
	20	0.23625*	0.087573	0.019	0.04544	0.42706
15	0	-0.43325*	0.087573	0.000	-0.62406	-0.24244
	5	-0.20825*	0.087573	0.035	-0.39906	-0.01744
	10	-0.08800	0.087573	0.335	-0.27881	0.10281
	20	0.14825	0.087573	0.116	-0.04256	0.33906
20	0	-0.58150*	0.087573	0.000	-0.77231	-0.39069
	5	-0.35650*	0.087573	0.002	-0.54731	-0.16569
	10	-0.23625*	0.087573	0.019	-0.42706	-0.04544
	15	-0.14825	0.087573	0.116	-0.33906	0.04256

Based on observed means.

The error term is Mean Square(Error) = 0.015.

*. The mean difference is significant at the 0.05 level.

Appendix IV: Concentration of Lead in soil sample in the South Eastern Location:

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Soil Concentration (mg/kg)

Season	Soil Depth (cm)	Mean	Std. Deviation	N
jan/feb	0	1.256000	.	1
	5	1.026000	.	1
	10	0.851000	.	1
	15	0.829000	.	1
	20	0.783000	.	1
	Total	0.949000	0.1947678	5
march/april	0	1.779000	.	1
	5	1.578000	.	1
	10	1.315000	.	1
	15	1.073000	.	1
	20	0.818000	.	1
	Total	1.312600	0.3840603	5
june/july	0	1.035000	.	1
	5	0.967000	.	1
	10	0.634000	.	1
	15	0.523000	.	1
	20	0.426000	.	1
	Total	0.717000	0.2705688	5
sept/oct	0	1.048000	.	1
	5	0.903000	.	1
	10	0.684000	.	1
	15	0.587000	.	1
	20	0.543000	.	1
	Total	0.753000	0.2156050	5
Total	0	1.279500	0.3480541	4
	5	1.118500	0.3104239	4
	10	0.871000	0.3102010	4
	15	0.753000	0.2507535	4
	20	0.642500	0.1891322	4
	Total	0.932900	0.3507556	20

Tests of Between-Subjects Effects

Dependent Variable: Soil Concentration (mg/kg)

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Model	19.624[a]	8	2.453	245.105	0.000
Season	1.117	3	0.372	37.206	0.000
Soil Depth	1.100	4	0.275	27.490	0.000
Error	0.120	12	0.010		
Total	19.744	20			

a. R Squared = 0.994 (Adjusted R Squared = 0.990)

Season

Multiple Comparisons

Dependent Variable: Soil Concentration (mg/kg)

Tukey HSD

(I) Season	(J) Season	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
	march/april	-0.363600*	0.0632699	0.000	-0.551442	-0.175758
jan/feb	june/july	0.232000*	0.0632699	0.015	0.044158	0.419842
	sept/oct	0.196000*	0.0632699	0.040	0.008158	0.383842
	jan/feb	0.363600*	0.0632699	0.000	0.175758	0.551442
march/april	june/july	0.595600*	0.0632699	0.000	0.407758	0.783442
	sept/oct	0.559600*	0.0632699	0.000	0.371758	0.747442
	jan/feb	-0.232000*	0.0632699	0.015	-0.419842	-0.044158
june/july	march/april	-0.595600*	0.0632699	0.000	-0.783442	-0.407758
	sept/oct	-0.036000	0.0632699	0.939	-0.223842	0.151842
	jan/feb	-0.196000*	0.0632699	0.040	-0.383842	-0.008158
sept/oct	march/april	-0.559600*	0.0632699	0.000	-0.747442	-0.371758
	june/july	0.036000	0.0632699	0.939	-0.151842	0.223842

Based on observed means.

The error term is Mean Square(Error) = 0.010.

*. The mean difference is significant at the 0.05 level.

Soil Depth (cm)

Multiple Comparisons

Dependent Variable: Soil Concentration (mg/kg)

Tukey HSD

(I) Soil Depth (cm)	(J) Soil Depth (cm)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval
					Lower Bound
0	5	0.161000	0.0707379	0.218	-0.064472
	10	0.408500*	0.0707379	0.001	0.183028
	15	0.526500*	0.0707379	0.000	0.301028
	20	0.637000*	0.0707379	0.000	0.411528
5	0	-0.161000	0.0707379	0.218	-0.386472
	10	0.247500*	0.0707379	0.029	0.022028
	15	0.365500*	0.0707379	0.002	0.140028
	20	0.476000*	0.0707379	0.000	0.250528
10	0	-0.408500*	0.0707379	0.001	-0.633972
	5	-0.247500*	0.0707379	0.029	-0.472972
	15	0.118000	0.0707379	0.486	-0.107472
	20	0.228500*	0.0707379	0.046	0.003028
15	0	-0.526500*	0.0707379	0.000	-0.751972
	5	-0.365500*	0.0707379	0.002	-0.590972
	10	-0.118000	0.0707379	0.486	-0.343472
	20	0.110500	0.0707379	0.546	-0.114972
20	0	-0.637000*	0.0707379	0.000	-0.862472
	5	-0.476000*	0.0707379	0.000	-0.701472
	10	-0.228500*	0.0707379	0.046	-0.453972
	15	-0.110500	0.0707379	0.546	-0.335972

Appendix V: Concentration of Lead in soil sample in the Southern Location:

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Soil concentration

Soil depth (cm)	Seasons	Mean	Std. Deviation	N
	Jan/Feb Season	0.84200	.	1
	March/April Season	2.19800	.	1
0	June/July Season	1.03600	.	1
	Sept/Oct Season	1.66400	.	1
	Total	1.43500	0.617916	4
	Jan/Feb Season	0.66900	.	1
	March/April Season	1.97500	.	1
5	June/July Season	0.97700	.	1
	Sept/Oct Season	1.58000	.	1
	Total	1.30025	0.587797	4
	Jan/Feb Season	0.47000	.	1
	March/April Season	1.78600	.	1
10	June/July Season	0.70200	.	1
	Sept/Oct Season	1.54100	.	1
	Total	1.12475	0.637163	4
	Jan/Feb Season	0.33100	.	1
	March/April Season	1.56500	.	1
15	June/July Season	0.60400	.	1
	Sept/Oct Season	1.48200	.	1
	Total	0.99550	0.620711	4
	Jan/Feb Season	0.27600	.	1
	March/April Season	1.25600	.	1
20	June/July Season	0.57300	.	1
	Sept/Oct Season	1.30600	.	1
	Total	0.85275	0.509558	4
	Jan/Feb Season	0.51760	0.236439	5
	March/April Season	1.75600	0.364248	5
Total	June/July Season	0.77840	0.214617	5
	Sept/Oct Season	1.51460	0.134044	5
	Total	1.14165	0.571239	20

Tests of Between-Subjects Effects

Dependent Variable: Soil concentration

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Model	32.122[a]	8	4.015	331.921	0.000
Soil Depth	0.865	4	0.216	17.882	0.000
Season	5.190	3	1.730	142.997	0.000
Error	0.145	12	.012		
Total	32.267	20			

a. R Squared = 0.996 (Adjusted R Squared = 0.993)

Soil depth (cm)

Multiple Comparisons

Dependent Variable: Soil concentration

LSD

(I) Soil depth (cm)	(J) Soil depth (cm)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	5	0.13475	0.077772	0.109	-0.03470	0.30420
	10	0.31025*	0.077772	0.002	0.14080	0.47970
	15	0.43950*	0.077772	0.000	0.27005	0.60895
	20	0.58225*	0.077772	0.000	0.41280	0.75170
5	0	-0.13475	0.077772	0.109	-0.30420	0.03470
	10	0.17550*	0.077772	0.043	0.00605	0.34495
	15	0.30475*	0.077772	0.002	0.13530	0.47420
	20	0.44750*	0.077772	0.000	0.27805	0.61695
10	0	-0.31025*	0.077772	0.002	-0.47970	-0.14080
	5	-0.17550*	0.077772	0.043	-0.34495	-0.00605
	15	0.12925	0.077772	0.122	-0.04020	0.29870
	20	0.27200*	0.077772	0.004	0.10255	0.44145
15	0	-0.43950*	0.077772	0.000	-0.60895	-0.27005
	5	-0.30475*	0.077772	0.002	-0.47420	-0.13530
	10	-0.12925	0.077772	0.122	-0.29870	0.04020
	20	0.14275	0.077772	0.091	-0.02670	0.31220
20	0	-0.58225*	0.077772	0.000	-0.75170	-0.41280
	5	-0.44750*	0.077772	0.000	-0.61695	-0.27805

10	-0.27200*	0.077772	0.004	-0.44145	-0.10255
15	-0.14275	0.077772	0.091	-0.31220	0.02670

Based on observed means.
The error term is Mean Square(Error) = 0.012.

*. The mean difference is significant at the0 .05 level.

Multiple Comparisons

Dependent Variable: Soil concentration
LSD

(I) Seasons	(J) Seasons	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Jan/Feb Season	March/April Season	-1.23840*	0.069562	0.000	-1.38996	-1.08684
	June/July Season	-0.26080*	0.069562	0.003	-0.41236	-0.10924
	Sept/Oct Season	-0.99700*	0.069562	0.000	-1.14856	-0.84544
March/April Season	Jan/Feb Season	1.23840*	0.069562	0.000	1.08684	1.38996
	June/July Season	0.97760*	0.069562	0.000	0.82604	1.12916
	Sept/Oct Season	0.24140*	0.069562	0.005	0.08984	0.39296
June/July Season	Jan/Feb Season	0.26080*	0.069562	0.003	0.10924	0.41236
	March/April Season	-0.97760*	0.069562	0.000	-1.12916	-0.82604
	Sept/Oct Season	-0.73620*	0.069562	0.000	-0.88776	-0.58464
Sept/Oct Season	Jan/Feb Season	0.99700*	0.069562	0.000	0.84544	1.14856
	March/April Season	-0.24140*	0.069562	0.005	-0.39296	-0.08984
	June/July Season	0.73620*	0.069562	0.000	0.58464	0.88776

Based on observed means.
The error term is Mean Square(Error) = 0.012.

*. The mean difference is significant at the 0.05 level.

Appendix VI: Concentration of Lead in soil sample in the South Western Location:

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Soil concentration

Soil depth (cm)	Seasons	Mean	Std. Deviation	N
	Jan/Feb Season	0.61800	.	1
	March/April Season	0.74500	.	1
0	June/July Season	0.68900	.	1
	Sept/Oct Season	0.78900	.	1
	Total	0.71025	0.073871	4
	Jan/Feb Season	0.53600	.	1
	March/April Season	0.68500	.	1
5	June/July Season	0.59400	.	1
	Sept/Oct Season	0.57300	.	1
	Total	0.59700	0.063377	4
	Jan/Feb Season	0.51500	.	1
	March/April Season	0.55500	.	1
10	June/July Season	0.46900	.	1
	Sept/Oct Season	0.45100	.	1
	Total	0.49750	0.046858	4
	Jan/Feb Season	0.45600	.	1
	March/April Season	0.40000	.	1
15	June/July Season	0.35200	.	1
	Sept/Oct Season	0.30400	.	1
	Total	0.37800	0.065115	4
	Jan/Feb Season	0.34200	.	1
	March/April Season	0.28700	.	1
20	June/July Season	0.20300	.	1
	Sept/Oct Season	0.21100	.	1
	Total	0.26075	0.066083	4
	Jan/Feb Season	0.49340	0.102625	5
	March/April Season	0.53440	0.191525	5
Total	June/July Season	0.46140	0.192472	5
	Sept/Oct Season	0.46560	0.227635	5
	Total	0.48870	0.171871	20

Tests of Between-Subjects Effects

Dependent Variable: Soil concentration

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Model	5.294[a]	8	0.662	180.964	0.000
Soil Depth	0.500	4	0.125	34.212	0.000
Season	0.017	3	0.006	1.545	0.254
Error	0.044	12	0.004		
Total	5.338	20			

a. R Squared = 0.992 (Adjusted R Squared = 0.986)

Soil depth (cm)

Multiple Comparisons

Dependent Variable: Soil concentration

LSD

(I) Soil depth (cm)	(J) Soil depth (cm)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	5	0.11325*	0.042760	0.021	0.02008	0.20642
	10	0.21275*	0.042760	0.000	0.11958	0.30592
	15	0.33225*	0.042760	0.000	0.23908	0.42542
	20	0.44950*	0.042760	0.000	0.35633	0.54267
5	0	-0.11325*	0.042760	0.021	-0.20642	-0.02008
	10	0.09950*	0.042760	0.038	0.00633	0.19267
	15	0.21900*	0.042760	0.000	0.12583	0.31217
	20	0.33625*	0.042760	0.000	0.24308	0.42942
10	0	-0.21275*	0.042760	0.000	-0.30592	-0.11958
	5	-0.09950*	0.042760	0.038	-0.19267	-0.00633
	15	0.11950*	0.042760	0.016	0.02633	0.21267
	20	0.23675*	0.042760	0.000	0.14358	0.32992
15	0	-0.33225*	0.042760	0.000	-0.42542	-0.23908
	5	-0.21900*	0.042760	0.000	-0.31217	-0.12583
	10	-0.11950*	0.042760	0.016	-0.21267	-0.02633
	20	0.11725*	0.042760	0.018	0.02408	0.21042
20	0	-0.44950*	0.042760	0.000	-0.54267	-0.35633
	5	-0.33625*	0.042760	0.000	-0.42942	-0.24308
	10	-0.23675*	0.042760	0.000	-0.32992	-0.14358
	15	-0.11725*	0.042760	0.018	-0.21042	-0.02408

Based on observed means.

The error term is Mean Square(Error) = 0.004.

*. The mean difference is significant at the 0.05 level.

Multiple Comparisons

Dependent Variable: Soil concentration

LSD

(I) Seasons	(J) Seasons	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Jan/Feb Season	March/April Season	-0.04100	0.038245	0.305	-0.12433	0.04233
	June/July Season	0.03200	0.038245	0.419	-0.05133	0.11533
	Sept/Oct Season	0.02780	0.038245	0.481	-0.05553	0.11113
March/April Season	Jan/Feb Season	0.04100	0.038245	0.305	-0.04233	0.12433
	June/July Season	0.07300	0.038245	0.080	-0.01033	0.15633
	Sept/Oct Season	0.06880	0.038245	0.097	-0.01453	0.15213
June/July Season	Jan/Feb Season	-0.03200	0.038245	0.419	-0.11533	0.05133
	March/April Season	-0.07300	0.038245	0.080	-0.15633	0.01033
	Sept/Oct Season	-0.00420	0.038245	0.914	-0.08753	0.07913
Sept/Oct Season	Jan/Feb Season	-0.02780	0.038245	0.481	-0.11113	0.05553
	March/April Season	-0.06880	0.038245	0.097	-0.15213	0.01453
	June/July Season	0.00420	0.038245	0.914	-0.07913	0.08753

Based on observed means.

The error term is Mean Square(Error) = 0.004.

Appendix VII: Concentration of Lead in soil sample in the Western Location:

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Soil Concentration (mg/kg)

Season	Soil Depth (cm)	Mean	Std. Deviation	N
jan/feb	0	0.845000	.	1
	5	0.793000	.	1
	10	0.646000	.	1
	15	0.563000	.	1
	20	0.473000	.	1
	Total	0.664000	0.1552482	5
march/apri	0	0.942000	.	1
l	5	0.803000	.	1
	10	0.636000	.	1
	15	0.517000	.	1
	20	0.449000	.	1
	Total	0.669400	0.2031485	5
june/july	0	0.681000	.	1
	5	0.533000	.	1
	10	0.465000	.	1
	15	0.435000	.	1
	20	0.108000	.	1
	Total	0.444400	0.2106580	5
sept/oct	0	0.792000	.	1
	5	0.765000	.	1
	10	0.661000	.	1
	15	0.567000	.	1
	20	0.359000	.	1
	Total	0.628800	0.1752376	5
Total	0	0.815000	0.1088026	4
	5	0.723500	0.1280143	4
	10	0.602000	0.0919094	4
	15	0.520500	0.0613487	4
	20	0.347250	0.1668779	4
	Total	0.601650	0.1962191	20

Tests of Between-Subjects Effects

Dependent Variable: Soil Concentration (mg/kg)

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Model	7.936[a]	8	0.992	338.729	0.000
Season	0.170	3	0.057	19.316	0.000
Soil Depth	0.527	4	0.132	44.960	0.000
Error	0.035	12	0.003		
Total	7.971	20			

a. R Squared = .996 (Adjusted R Squared = .993)

Season

Multiple Comparisons

Dependent Variable: Soil Concentration (mg/kg)

Tukey HSD

(I) Season	(J) Season	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
	march/april	-0.005400	0.0342264	0.999	-0.107015	0.096215
jan/feb	june/july	0.219600*	0.0342264	0.000	0.117985	0.321215
	sept/oct	0.035200	0.0342264	0.737	-0.066415	0.136815
	jan/feb	0.005400	0.0342264	0.999	-0.096215	0.107015
march/april	june/july	0.225000*	0.0342264	0.000	0.123385	0.326615
	sept/oct	0.040600	0.0342264	0.646	-0.061015	0.142215
	jan/feb	-0.219600*	0.0342264	0.000	-0.321215	-0.117985
june/july	march/april	-0.225000*	0.0342264	0.000	-0.326615	-0.123385
	sept/oct	-0.184400*	0.0342264	0.001	-0.286015	-0.082785
	jan/feb	-0.035200	0.0342264	0.737	-0.136815	0.066415
sept/oct	march/april	-0.040600	0.0342264	0.646	-0.142215	0.061015
	june/july	0.184400*	0.0342264	0.001	0.082785	0.286015

Based on observed means.

The error term is Mean Square(Error) = 0.003.

*. The mean difference is significant at the 0.05 level.

Soil Depth (cm)

Multiple Comparisons

Dependent Variable: Soil Concentration (mg/kg)

Tukey HSD

(I) Soil Depth (cm)	(J) Soil Depth (cm)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval
					Lower Bound
0	5	0.091500	0.0382663	0.183	-0.030471
	10	0.213000*	0.0382663	0.001	0.091029
	15	0.294500*	0.0382663	0.000	0.172529
	20	0.467750*	0.0382663	0.000	0.345779
5	0	-0.091500	0.0382663	0.183	-0.213471
	10	0.121500	0.0382663	0.051	-0.000471
	15	0.203000*	0.0382663	0.001	0.081029
	20	0.376250*	0.0382663	0.000	0.254279
10	0	-0.213000*	0.0382663	0.001	-0.334971
	5	-0.121500	0.0382663	0.051	-0.243471
	15	0.081500	0.0382663	0.269	-0.040471
	20	0.254750*	0.0382663	0.000	0.132779
15	0	-0.294500*	0.0382663	0.000	-0.416471
	5	-0.203000*	0.0382663	0.001	-0.324971
	10	-0.081500	0.0382663	0.269	-0.203471
	20	0.173250*	0.0382663	0.005	0.051279
20	0	-0.467750*	0.0382663	0.000	-0.589721
	5	-0.376250*	0.0382663	0.000	-0.498221
	10	-0.254750*	0.0382663	0.000	-0.376721
	15	-0.173250*	0.0382663	0.005	-0.295221

Appendix VIII: Concentration of Lead in soil sample in the North Western Location:

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Soil concentration

Soil depth (cm)	Seasons	Mean	Std. Deviation	N
0	Jan/Feb Season	0.95900	.	1
	March/April Season	1.03900	.	1
	June/July Season	1.54300	.	1
	Sept/Oct Season	1.06500	.	1
	Total	1.15150	0.264869	4
5	Jan/Feb Season	0.56300	.	1
	March/April Season	0.89200	.	1
	June/July Season	1.48800	.	1
	Sept/Oct Season	0.92600	.	1
	Total	0.96725	0.383824	4
10	Jan/Feb Season	0.46900	.	1
	March/April Season	0.86900	.	1
	June/July Season	1.43500	.	1
	Sept/Oct Season	0.74300	.	1
	Total	0.87900	0.406543	4
15	Jan/Feb Season	0.46400	.	1
	March/April Season	0.74000	.	1
	June/July Season	1.38600	.	1
	Sept/Oct Season	0.51700	.	1
	Total	0.77675	0.423406	4
20	Jan/Feb Season	0.44900	.	1
	March/April Season	0.59400	.	1
	June/July Season	1.03900	.	1
	Sept/Oct Season	0.30200	.	1
	Total	0.59600	0.318485	4
Total	Jan/Feb Season	0.58080	0.216139	5
	March/April Season	0.82680	0.167922	5
	June/July Season	1.37820	0.198468	5
	Sept/Oct Season	0.71060	0.307197	5

Total	0.87410	0.375587	20	

Tests of Between-Subjects Effects

Dependent Variable: Soil concentration

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Model	17.816[a]	8	2.227	184.534	0.000
Soil Depth	0.690	4	0.172	14.291	0.000
Season	1.846	3	0.615	50.974	0.000
Error	0.145	12	0.012		
Total	17.961	20			

a. R Squared = 0.992 (Adjusted R Squared = 0.987)

Multiple Comparisons

Dependent Variable: Soil concentration

LSD

(I) Soil depth (cm)	(J) Soil depth (cm)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	5	0.18425*	0.077681	0.035	0.01500	0.35350
	10	0.27250*	0.077681	0.004	0.10325	0.44175
	15	0.37475*	0.077681	0.000	0.20550	0.54400
	20	0.55550*	0.077681	0.000	0.38625	0.72475
5	0	-0.18425*	0.077681	0.035	-0.35350	-0.01500
	10	0.08825	0.077681	0.278	-0.08100	0.25750
	15	0.19050*	0.077681	0.030	0.02125	0.35975
	20	0.37125*	0.077681	0.000	0.20200	0.54050
10	0	-0.27250*	0.077681	0.004	-0.44175	-0.10325
	5	-0.08825	0.077681	0.278	-0.25750	0.08100
	15	0.10225	0.077681	0.213	-0.06700	0.27150
	20	0.28300*	0.077681	0.003	0.11375	0.45225
15	0	-0.37475*	0.077681	0.000	-0.54400	-0.20550
	5	-0.19050*	0.077681	0.030	-0.35975	-0.02125
	10	-0.10225	0.077681	0.213	-0.27150	0.06700
	20	0.18075*	0.077681	0.038	0.01150	0.35000
20	0	-0.55550*	0.077681	0.000	-0.72475	-0.38625
	5	-0.37125*	0.077681	0.000	-0.54050	-0.20200
	10	-0.28300*	0.077681	0.003	-0.45225	-0.11375
	15	-0.18075*	0.077681	0.038	-0.35000	-0.01150

Based on observed means.

The error term is Mean Square(Error) = 0.012.

*. The mean difference is significant at the 0.05 level.

Seasons

Multiple Comparisons

Dependent Variable: Soil concentration

LSD

(I) Seasons	(J) Seasons	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Jan/Feb Season	March/April Season	-0.24600*	0.069480	0.004	-0.39738	-0.09462
	June/July Season	-0.79740*	0.069480	0.000	-0.94878	-0.64602
	Sept/Oct Season	-0.12980	0.069480	0.086	-0.28118	0.02158
March/April Season	Jan/Feb Season	0.24600*	0.069480	0.004	0.09462	0.39738
	June/July Season	-0.55140*	0.069480	0.000	-0.70278	-0.40002
	Sept/Oct Season	0.11620	0.069480	0.120	-0.03518	0.26758
June/July Season	Jan/Feb Season	0.79740*	0.069480	0.000	0.64602	0.94878
	March/April Season	0.55140*	0.069480	0.000	0.40002	0.70278
	Sept/Oct Season	0.66760*	0.069480	0.000	0.51622	0.81898
Sept/Oct Season	Jan/Feb Season	0.12980	0.069480	0.086	-0.02158	0.28118
	March/April Season	-0.11620	0.069480	0.120	-0.26758	0.03518
	June/July Season	-0.66760*	0.069480	0.000	-0.81898	-0.51622

Based on observed means.

The error term is Mean Square(Error) = 0.012.

*. The mean difference is significant at the 0.05 level.

Appendix IX: Variation of Lead Uptake by Hibiscus rosasinensis at the Northern location in both dry and rainy seasons.

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Hibiscus Rosasinensis

Season	Lead Uptake	Mean	Std. Deviation	N
Dry	Uptake of Pb in root (mg/kg)	0.16400	0.022627	2
	Uptake of Pb in stem (mg/kg)	0.08200	0.002828	2
	Uptake of Pb in leaves (mg/kg)	0.04100	0.001414	2
	Total	0.09567	0.056941	6
Rainy	Uptake of Pb in root (mg/kg)	0.13000	0.042426	2
	Uptake of Pb in stem (mg/kg)	0.04500	0.007071	2
	Uptake of Pb in leaves (mg/kg)	0.02500	0.007071	2
	Total	0.06667	0.053541	6
Total	Uptake of Pb in root (mg/kg)	0.14700	0.034000	4
	Uptake of Pb in stem (mg/kg)	0.06350	0.021810	4
	Uptake of Pb in leaves (mg/kg)	0.03300	0.010132	4
	Total	0.08117	0.054828	12

Tests the null hypothesis that the error variance of the dependent variable is equal across groups.[a]

a. Design: season + LU

Tests of Between-Subjects Effects

Dependent Variable: Hibiscus Rosasinensis

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Model	0.109[a]	4	0.027	81.675	0.000
Season	0.003	1	0.003	7.531	0.025
Lead Uptake	0.028	2	0.014	41.589	0.000
Error	0.003	8	0.000		
Total	0.112	12			

Levene's Test of Equality of Error Variances[a]

Dependent Variable: Hibiscus Rosasinensis

F	df1	df2	Sig.
10.479	5	6	0.006

a. R Squared = 0.976 (Adjusted R Squared = 0.964)

Multiple Comparisons

Dependent Variable: Hibiscus Rosasinensis

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	Mean Difference (I-J)	Std. Error	Sig.
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	0.08350*	0.012942	0.001
	Uptake of Pb in leaves (mg/kg)	0.11400*	0.012942	0.000
Uptake of Pb in steam (mg/kg)	Uptake of Pb in root (mg/kg)	-0.08350*	0.012942	0.001
	Uptake of Pb in leaves (mg/kg)	0.03050	0.012942	0.104
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	-0.11400*	0.012942	0.000
	Uptake of Pb in stem (mg/kg)	-0.03050	0.012942	0.104

Multiple Comparisons

Dependent Variable: Hibiscus Rosasinensis

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	95% Confidence Interval	
		Lower Bound	Upper Bound
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	0.04652*	0.12048
	Uptake of Pb in leaves (mg/kg)	0.07702*	0.15098
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	-0.12048*	-0.04652
	Uptake of Pb in leaves (mg/kg)	-0.00648	0.06748
Uptaked of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	-0.15098*	-0.07702
	Uptake of Pb in stem (mg/kg)	-0.06748	0.00648

Appendix X: Variation of Lead Uptake by Ixora coccinea at the North eastern location in both dry and rainy seasons.

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Ixora Coccinea

Season	Lead Uptake	Mean	Std. Deviation	N
Dry	Uptake of Pb in root (mg/kg)	0.02750	0.003536	2
	Uptake of Pb in stem (mg/kg)	0.04500	0.007071	2
	Uptake of Pb in leaves (mg/kg)	0.08000	0.014142	2
	Total	0.05083	0.024983	6
Rainy	Uptake of Pb in root (mg/kg)	0.01050	0.000707	2
	Uptake of Pb in stem (mg/kg)	0.04400	0.005657	2
	Uptake of Pb in leaves (mg/kg)	0.07250	0.003536	2
	Total	0.04233	0.027919	6
Total	Uptake of Pb in root (mg/kg)	0.01900	0.010033	4
	Uptake of Pb in stem (mg/kg)	0.04450	0.005260	4
	Uptake of Pb in leaves (mg/kg)	0.07625	0.009465	4
	Total	0.04658	0.025646	12

Tests of Between-Subjects Effects

Dependent Variable: Ixora Coccinea

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Model	0.033[a]	4	0.008	150.288	0.000
Season	0.000	1	0.000	3.968	0.082
Lead Uptake	0.007	2	0.003	60.240	0.000
Error	0.000	8	5.462E-005		
Total	0.033	12			

a. R Squared = .987 (Adjusted R Squared = .980)

Multiple Comparisons

Dependent Variable: Ixora Coccinea

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	Mean Difference (I-J)	Std. Error	Sig.
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	-0.02550*	0.005226	0.003
	Uptake of Pb in leaves (mg/kg)	-0.05725*	0.005226	0.000
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	0.02550*	0.005226	0.003
	Uptake of Pb in leaves (mg/kg)	-0.03175*	0.005226	0.001
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	0.05725*	0.005226	0.000
	Uptake of Pb in stem (mg/kg)	0.03175*	0.005226	0.001

Multiple Comparisons

Dependent Variable: Ixora Coccinea

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	95% Confidence Interval	
		Lower Bound	Upper Bound
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	-0.04043*	-0.01057
	Uptake of Pb in leaves (mg/kg)	-0.07218*	-0.04232
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	0.01057*	0.04043
	Uptake of Pb in leaves (mg/kg)	-0.04668*	-0.01682
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	0.04232*	0.07218
	Uptake of Pb in stem (mg/kg)	0.01682*	0.04668

Based on observed means.

The error term is Mean Square(Error) = 5.462E-005.

*. The mean difference is significant at the 0.05 level.

Appendix XI: Variation of Lead Uptake by Euphorbia milivarsplendens at the Eastern location in both dry and rainy seasons.

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Euphorbia milivarsplendens

Season	Lead Uptake	Mean	Std. Deviation	N
Dry	Uptake of Pb in root (mg/kg)	0.17400	0.036770	2
	Uptake of Pb in stem (mg/kg)	0.25000	0.070711	2
	Uptake of Pb in leaves (mg/kg)	0.83000	0.212132	2
	Total	0.41800	0.336559	6
Rainy	Uptake of Pb in root (mg/kg)	0.05900	0.015556	2
	Uptake of Pb in stem (mg/kg)	0.10000	0.001414	2
	Uptake of Pb in leaves (mg/kg)	0.47250	0.184555	2
	Total	0.21050	0.219962	6
Total	Uptake of Pb in root (mg/kg)	0.11650	0.070283	4
	Uptake of Pb in stem (mg/kg)	0.17500	0.095746	4
	Uptake of Pb in leaves (mg/kg)	0.65125	0.262594	4
	Total	0.31425	0.291929	12

Tests of Between-Subjects Effects

Dependent Variable: Euphorbia milivarsplendens

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Model	2.002[a]	4	0.501	33.369	0.000
Season	0.129	1	0.129	8.610	0.019
Lead Uptake	0.688	2	0.344	22.938	0.000
Error	0.120	8	0.015		
Total	2.122	12			

a. R Squared = 0.943 (Adjusted R Squared = 0.915)

Multiple Comparisons

Dependent Variable: Euphorbia milivarsplendens

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	Mean Difference (I-J)	Std. Error	Sig.
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	-0.05850	0.086609	0.784
	Uptake of Pb in leaves (mg/kg)	-0.53475*	0.086609	0.001
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	0.05850	0.086609	0.784
	Uptake of Pb in leaves (mg/kg)	-0.47625*	0.086609	0.001
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	0.53475*	0.086609	0.001
	Uptake of Pb in stem (mg/kg)	0.47625*	0.086609	0.001

Multiple Comparisons

Dependent Variable: Euphorbia milivarsplendens

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	95% Confidence Interval	
		Lower Bound	Upper Bound
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	-0.30598	0.18898
	Uptake of Pb in leaves (mg/kg)	-0.78223*	-0.28727
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	-0.18898	0.30598
	Uptake of Pb in leaves (mg/kg)	-0.72373*	-0.22877
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	0.28727*	0.78223
	Uptake of Pb in stem (mg/kg)	0.22877*	0.72373

Based on observed means.

The error term is Mean Square(Error) = 0.015.

*. The mean difference is significant at the 0.05 level.

Appendix XII: Variation of Lead Uptake by Ficus benjamina at the Southern eastern location in both dry and rainy seasons..

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Ficus benjamina

Season	Lead Uptake	Mean	Std. Deviation	N
Dry	Uptake of Pb in root (mg/kg)	0.09000	0.014142	2
	Uptake of Pb in stem (mg/kg)	0.19000	0.014142	2
	Uptake of Pb in leaves (mg/kg)	0.40000	0.282843	2
	Total	0.22667	0.190018	6
Rainy	Uptake of Pb in root (mg/kg)	0.06050	0.000707	2
	Uptake of Pb in stem (mg/kg)	0.16150	0.111016	2
	Uptake of Pb in leaves (mg/kg)	0.41550	0.289207	2
	Total	0.21250	0.214380	6
Total	Uptake of Pb in root (mg/kg)	0.07525	0.018892	4
	Uptake of Pb in stem (mg/kg)	0.17575	0.066675	4
	Uptake of Pb in leaves (mg/kg)	0.40775	0.233724	4
	Total	0.21958	0.193280	12

Tests of Between-Subjects Effects

Dependent Variable: Ficus benjamina

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Model	0.812[a]	4	0.203	9.138	0.004
Season	0.001	1	0.001	0.027	0.873
Lead Uptake	0.233	2	0.116	5.237	0.035
Error	0.178	8	0.022		
Total	0.990	12			

a. R Squared = 0.820 (Adjusted R Squared = 0.731)

Multiple Comparisons

Dependent Variable: Ficus benjamina

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	Mean Difference (I-J)	Std. Error	Sig.
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	-0.10050	0.105382	0.624
	Uptake of Pb in leaves (mg/kg)	-0.33250*	0.105382	0.032
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	0.10050	0.105382	0.624
	Uptake of Pb in leaves (mg/kg)	-0.23200	0.105382	0.131
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	0.33250*	0.105382	0.032
	Uptake of Pb in stem (mg/kg)	0.23200	0.105382	0.131

Multiple Comparisons

Dependent Variable: Ficus benjamina

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	95% Confidence Interval	
		Lower Bound	Upper Bound
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	-0.40162	0.20062
	Uptake of Pb in leaves (mg/kg)	-0.63362*	-0.03138
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	-0.20062	0.40162
	Uptake of Pb in leaves (mg/kg)	-0.53312	0.06912
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	0.03138*	0.63362
	Uptake of Pb in stem (mg/kg)	-0.06912	0.53312

Based on observed means.

The error term is Mean Square(Error) = 0.022.

*. The mean difference is significant at the 0.05 level.

Appendix XIII: Variation of Lead Uptake by Ageratum houstonianum at the Southern location in both dry and rainy seasons. .

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Ageratum houstonianum

Lead Uptake	Mean	Std. Deviation	N
Uptake of Pb in root (mg/kg)	0.30100	0.281428	2
Uptake of Pb in stem (mg/kg)	0.06150	0.030406	2
Uptake of Pb in leaves (mg/kg)	0.03750	0.010607	2
Total	0.13333	0.181742	6
Uptake of Pb in root (mg/kg)	0.32800	0.019799	2
Uptake of Pb in stem (mg/kg)	0.06650	0.062933	2
Uptake of Pb in leaves (mg/kg)	0.03100	0.035355	2
Total	0.14183	0.148887	6
Uptake of Pb in root (mg/kg)	0.31450	0.163629	4
Uptake of Pb in stem (mg/kg)	0.06400	0.040456	4
Uptake of Pb in leaves (mg/kg)	0.03425	0.021639	4
Total	0.13758	0.158460	12

Tests of Between-Subjects Effects

Dependent Variable: Ageratum houstonianum

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Model	0.417[a]	4	0.104	9.649	0.004
Season	0.000	1	0.000	0.020	0.891
Lead Uptake	0.190	2	0.095	8.774	0.010
Error	0.086	8	0.011		
Total	0.503	12			

a. R Squared = 0.828 (Adjusted R Squared = 0.742)

Multiple Comparisons

Dependent Variable: Ageratum houstonianum

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	Mean Difference (I-J)	Std. Error	Sig.
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	0.25050*	0.073494	0.022
	Uptake of Pb in leaves (mg/kg)	0.28025*	0.073494	0.013
Uptake of Pb in stem (mg/kg)	Uptak of Pb in root (mg/kg)	-0.25050*	0.073494	0.022
	Uptake of Pb in leaves (mg/kg)	0.02975	0.073494	0.915
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	-0.28025*	0.073494	0.013
	Uptake of Pb in stem (mg/kg)	-0.02975	0.073494	0.915

Multiple Comparisons

Dependent Variable: Ageratum houstonianum

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	95% Confidence Interval	
		Lower Bound	Upper Bound
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	0.04050*	0.46050
	Uptake of Pb in leaves (mg/kg)	0.07025*	0.49025
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	-0.46050*	-0.04050
	Uptake of Pb in leaves (mg/kg)	-0.18025	0.23975
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	-0.49025*	-0.07025
	Uptake of Pb in stem (mg/kg)	-0.23975	0.18025

Based on observed means.

The error term is Mean Square(Error) = 0.011.

*. The mean difference is significant at the 0.05 level.

Appendix XIV: Variation of Lead Uptake by Duranta erecta at the North western location in both dry and rainy seasons.

Univariate Analysis of Variance

Descriptive Statistics

Dependent Variable: Duranta erecta

Season	Lead Uptake	Mean	Std. Deviation	N
Dry	Uptake of Pb in root (mg/kg)	0.03850	0.033234	2
	Uptake of Pb in stem (mg/kg)	0.39200	0.407294	2
	Uptake of Pb in leaves (mg/kg)	0.39000	0.155563	2
	Total	0.27350	0.267160	6
Rainy	Uptake of Pb in root (mg/kg)	0.03500	0.012728	2
	Uptake of Pb in stem (mg/kg)	0.30350	0.033234	2
	Uptake of Pb in leaves (mg/kg)	0.41600	0.149907	2
	Total	0.25150	0.188155	6
Total	Uptake of Pb in root (mg/kg)	0.03675	0.020646	4
	Uptake of Pb in stem (mg/kg)	0.34775	0.241402	4
	Uptake of Pb in leaves (mg/kg)	0.40300	0.125629	4
	Total	0.26250	0.220606	12

Tests of Between-Subjects Effects

Dependent Variable: Duranta erecta

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Model	1.140[a]	4	0.285	10.272	0.003
Season	0.001	1	0.001	0.052	0.825
Lead Uptake	0.312	2	0.156	5.620	0.030
Error	0.222	8	0.028		
Total	1.362	12			

Multiple Comparisons

a. R Squared = 0.837 (Adjusted R Squared = 0.756)

Multiple Comparisons

Dependent Variable: Duranta erecta

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	Mean Difference (I-J)	Std. Error	Sig.
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	-0.31100	0.117792	0.069
	Uptake of Pb in leaves (mg/kg)	-0.36625*	0.117792	0.035
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	0.31100	0.117792	0.069
	Uptake of Pb in leaves (mg/kg)	-0.05525	0.117792	0.887
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	0.36625*	0.117792	0.035
	Uptake of Pb in stem (mg/kg)	0.05525	0.117792	0.887

Dependent Variable: Duranta erecta

Tukey HSD

(I) Lead Uptake	(J) Lead Uptake	95% Confidence Interval	
		Lower Bound	Upper Bound
Uptake of Pb in root (mg/kg)	Uptake of Pb in stem (mg/kg)	-0.64758	0.02558
	Uptake of Pb in leaves (mg/kg)	-0.70283*	-0.02967
Uptake of Pb in stem (mg/kg)	Uptake of Pb in root (mg/kg)	-0.02558	0.64758
	Uptake of Pb in leaves (mg/kg)	-0.39183	0.28133
Uptake of Pb in leaves (mg/kg)	Uptake of Pb in root (mg/kg)	0.02967*	0.70283
	Uptake of Pb in stem (mg/kg)	-0.28133	0.39183

Based on observed means.

The error term is Mean Square(Error) = 0.028.

*. The mean difference is significant at the 0.05 level.