CHAPTER TWO

CHAPTER TWO

LITERATURE REVIEW

2.1 Chemical pollution and the ecosystem

A healthy ecosystem is one that provides a continuous flow of the current benefits and also maintains the capacity to respond to future needs and values. In other words, it must maintain both system structure and function in a sustainable manner. In nature, most systems continuously renew themselves (Vereijken, 1992). The natural ecosystem is subjected to different external stresses that exert their influence, to the natural flow of materials and affect the health and sustainability of the ecosystem.

Chemical pollution from industrial sources is one of the major types of stress that affect the health of ecosystems. Similarly any human activity that adversely affects plant and animal life is also contributing towards pollution (Douglas 1983). There are a large number of commercially produced chemical compounds that are applied directly to the environment or discharged into it after use. Toxic contaminants may be harmful to the environment even in low concentrations. The prevalence of toxic contaminants can directly and indirectly affect on human and ecosystem health by disrupting the biochemical reactions of the fauna and flora (Oliver, 1997). Toxic chemicals often accumulate in the food chain, threatening the health of human and wildlife populations. The slowly degradable and the non-degradable substances accumulating in the food chain can be transformed into more toxic compound resulting in increasing the toxic level of the food chain. Environmental protection can be most effective when complex connections between all parts of an ecosystem and the toxic wastes are taken into account.

2.2. Soil contamination

Soil is the key component of terrestrial ecosystems both natural and agricultural, and the sink for undesirable wastes. It also functions as a filter protecting the ground water from inputs of potentially toxic metals (Singh and Steinnes, 1993 Brady and Weil 1999). The soil is a function of various physical, chemical, and biological processes that are dynamically changing over time. Oliver, (1997) confirmed that soils could affect human health adversely in several ways since all-human food, plant and animal products, derived directly or indirectly from the soil. The chemical properties of soils largely depend on the chemical make-up of the materials from which they were formed and the nature of the processes of formation.

Generally soils have varied ranges of storage capacity for pollutants and contaminants depending on their chemical composition (Alloway, 1995). Dix, (1981) defines soil pollution as " any physical or chemical alteration to soil which causes its use to change and renders it incapable of beneficial use without treatment". As well as their adverse impact on human health soil contaminants have also the potential to reduce soil quality for agricultural production. The use of soils for various purposes may involve change to their chemical characteristics through the application of fertilizers, pesticides, or through pollution from waste disposal or industrial contamination (Alloway, 1995 and Singh and Steinnes, 1993).

Some of the activities that cause soil and ground water pollution include irrigation and drainage, application of fertilizers and other agricultural chemicals and bio-solids and chemical waste. For a long time, industrial wastes have been disposed of in landfills without adequate precautions against leaching of metals sometimes resulting in serious and irreversible contamination of soils, rendering them unfit for future utilization (Holdgate, 1979). Soils are often contaminated for up to hundred kilometers away from the site of emission.

2.3 Heavy metals in soil

Heavy metals are the inorganic soil contaminants of greatest concern (Phillips and Chapple, 1995). They enter agricultural soils mainly through atmospheric deposition and application of soil amendments and agricultural chemicals. The landfilling of domestic and industrial wastes also lead to soil pollution with heavy metals in various ways. Although heavy metals are ubiquitous in the soil parent material, the major anthropogenic source of such metals in the soil environment are mining and metalliferous, agricultural chemicals, sewage sludge, fuel combustion, waste disposal, battery recycling and military training (Alloway, 1995; Singh and Steinnes, 1993).

Heavy metals contamination of soil is common in many industrialized countries; the stress of heavy metals pollution soils represents an important aspect of the sustainability of ecosystem (Alloway and Ayres 1993). Metal contamination in soils has become a widespread problem and metal contaminated soils represent a significant environmental challenge. This is due to widespread industrial usage of various toxic metals, persistence of metals in the environment, established toxicity of various heavy metals and potential pathways for metal dissemination in the environment (Wood, 1974).

Singh and Steinnes (1993) stated that soil contamination with heavy metals tends to be persistent and largely irreversible and the available levels remaining much the same after several years. Oliver, (1997) and Tiller (1998) concluded that the future generation's health demands that the soil resources must be protected against a slow poisoning by heavy metals released by urban and industrial wastes. The increased public awareness of soil and ground water pollution by industrial and agricultural chemicals has created increased attention on the issue of solute movement through soil (Holdgate, 1979). The heavy metals dumped in the soil from mine sites or factories can form soluble salts and therefore may contaminate waterways and ground water, some remain in the soil for ever and that soil will always pose a danger and noxious to future generation who do not know its history.

2.3.1The origin of heavy metals in soils

The origin of heavy metals in the soil can be traced back to the result of two factors, the geochemical origin of heavy metals and the pedogenesis and translocation process of the metals in the soil (Tiller, 1989). As well as human induced contamination there may be areas with naturally occurring elevated levels of heavy metals. Alloway (1995) confirmed that such cases might occur where soils were formed on mineral rich or mineralized sedimentary rocks with naturally high concentrations of heavy metals. Pedogensis is the soil forming and translocation process that results from the interaction of environmental conditions and biological activity on the surface of the weathering rock. The pedogensis process responsible from the redistribution of the metals resulted from the rock weathering into the soil layers (Alloway, 1995)

The heavy metals content in sedimentary rocks is dependent upon the mineralogy of the sedimentary material. According to Rose, (1979) that clays and shales tend to have high concentration of metals. Heavy metals occur naturally in soils in trace amounts, the occurrences of soils that contain such high concentrations of metals are in areas characterized by the presence of metalliferous mines (Alloway, 1995).

2.3.1.1 Cadmium

Cadmium is one of the rare elements in the earth's crust with average concentrations of about 0.2 mg Cd/kg (Lindsay 1979). It is widely distributed and is found in shale and igneous rocks, coal, sandstones, limestone, lake and marine sediments and soils. Natural sources of cadmium include underlying bedrock or transported parent material such as glacial till and alluvium (Wood, 1974). The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 μg/g., but much higher and much lower values have also been cited depending on a large number of factors. Igneous and metamorphic rocks tend to show lower values, from 0.02 to 0.2 μg/g whereas sedimentary rocks have much higher values, from 0.1 to 25 μg/g (Alloway 1995).

2.3.1.2 Lead

Lead is a natural constituent of the earth's lithosphere, and is present at higher concentrations than any other heavy metal. Lead is present in soil parent material and sedimentary rocks mainly mudstones, black shales that are rich in organic matter and sulfides and limestone (Alloway 1995). Regional variations in parent material chemistry as well as sediment deposition and soil genesis account for some differing levels of lead, with 10 mg kg^{-1} soil as the global lithosphere average, and 1-200 mg kg^{-1}soil as a typical range in natural soils (Bohn *et al*., 1985). Researches reported varied amount of lead in uncontaminated soils. Nriagu (1978) has reported a mean amount of 17 mg lead/kg soil while Ure and Berrow (1982) have reported 29 mg lead/kg soil.

2.3.1.3 Nickel

Nickel and most nickel compounds occur naturally. The naturally occurring nickel is a silvery metal found in the earth's crust in the form of various nickel minerals. The content of nickel in soils varied depending on the nature of the soil parent material and soil forming processes with an average of about 20 mg/kg (Alloway 1995). Ure (1992) reported an average of 34 mg nickel/kg soil.

2.3.1.4Zinc

Zinc is naturally occurring in the lithosphere. Zinc concentrations in soils varying in magnitudes with average concentration 80 mg/kg. Zinc is found in high content in sedimentary rocks, clayey sediments, sandstones and limestone (Kabata and Pendias, 1992 and Robson, 1993).

2.3.2 Sources of heavy metals contaminants in soils

Soils play an important role for the global flux of metals in the environment. Most trash is stored in dumpsites, where metal-containing products often contaminate the soil. Ash from coal combustion is another important source to the soil. Wastes from animal husbandry, agriculture, and industrial processes (Holdgate, 1988). Many industrial products containing heavy metals eventually end up as trash. Emissions from waste incineration are source of lead, cadmium, arsenic, and zinc.

Heavy metals contamination of soils resulted mainly from the atmospheric pollution from industrial sources (Tiller, 1989). Much soil contamination is the result of human activity, including the entry of industrial wastes into soil through atmospheric deposition or application of agrochemicals and sewage waste to the land (Alloway, 1993).

For a long time, industrial wastes have been disposed of in landfills without adequate precautions against leaching of metals and organic chemicals, sometimes resulting in serious and irreversible contamination of soils and ground waters, rendering them unfit for human consumption (Tiller, 1989). Wastes from mines are often particularly troublesome due to gradual toxic discharges of toxic metals into the environment. The mining of gold, toxic metals (such as lead and mercury) or uranium, and of sulfide-containing ores, require close attention. The atmosphere is also an important medium for metals from various sources to find their way to the soil (Alloway, 1995 and Tiller, 1989). It has been established that the content of heavy metals in the disposed waste decides to a large extent the fate of that particular waste in the soil.

2.3.2.1 Cadmium

The anthropogenic input of cadmium to soils occurs by aerial deposition sewage sludge, manure and phosphate fertilizers application. Sewage sludge is the major source of cadmium. The use of cadmium-containing fertilizers and sewage sludge is most often quoted as the primary reason for the increase cadmium content of soils over the last 20 to 30 years in Europe (Jensen and Bro-Rasmussen 1992).

Atmospheric cadmium emissions deposition onto soils has generally decreased significantly over that same time period (Alloway, 1995). Indeed, recent studies in Europe have documented that atmospheric emissions do not presently have a significant impact upon the cadmium content of soils (Bake *et al.*, 1997). Cadmium is a byproduct in the production of zinc and lead, and the hydrometallurgical production of zinc is the most important anthropogenic source to the environment. Other major sources are fossil fuel combustion and waste incineration. Cadmium is used in a wide spectrum of applications, including alloys, pigments, metal coatings, batteries, and in the electronics industry.

The raw materials for iron and steel production contain approximately 0.1 to 5.0 ppm, while those for cement production contain about 2 ppm. Fossil fuels contain 0.5 to 1.5 ppm cadmium, but phosphate fertilizers contain from 10 to 200 ppm cadmium (Alloway, 1995). Three major inputs of cadmium to agricultural lands are atmospheric deposition, application of phosphate fertilizer, and the spreading of sewage sludge. Once the cadmium is in the soil, it can be transported out of the soil by plant uptake surface run-off, and erosion

2.3.2.2 Lead

Soil is contaminated by lead from various sources. Lead particles are deposited in the soil from flaking lead paint, from incinerators, batteries and from motor vehicles that use leaded gasoline (American Academy of Pediatrics, 1987). Urban environments in general have received higher depositions of lead from vehicular emissions than have rural areas. The main anthropogenic sources of lead are mining, and smelting activities, fertilizers and manures, sewage sledges, vehicle exhausts and the disposal of industrial wastes.

The largest source of lead contamination in urban soils is lead-based paint (Alloway, 1995). There are many other activities that can cause lead to accumulate in soils. Some of these activities may have happened in the past, for example, leaded gasoline is no longer used, but residues from its emissions remain in soils near roads. Lead may have also been added to soil from point sources, such as burned trash, metal smelters, jewelry plating operations, or dumped lead batteries. Lead particles are also deposited in the soil from flaking lead paint, from incinerators and from motor vehicles that use leaded gasoline.

2.3.2.3 Nickel

Sources of nickel in soils are sewage sludge, wastewater from municipal sewage treatment plants, and groundwater near landfill sites. Other sources include emissions from mining and refining operations, battery wastes municipal waste incineration and windblown dust. Minor sources of atmospheric nickel are volcanoes, steel production, gasoline and diesel fuel combustion, vegetation, nickel alloy production, and coal combustion (Duke 1980). Primary nickel is recovered from mined ore and nickel matte, and secondary nickel is recovered from scrap metal. Industry uses nickel to make steels and alloys, permanent magnet materials, and nickel- cadmium batteries, and in electroplating and ceramics. Fuel oil combustion leads to releases of nickel to the atmosphere (Alloway 1995).

2.3.2.4 Zinc

Zinc is one of the most widespread elements in soils. Its accumulation may occur from atmospheric deposition originating from smelting activities (in association with lead) or to the use of sewage sludge in agriculture. Of all the micronutrients required by plants, on a worldwide basis zinc is the one that is most commonly deficient (Robson, 1993). However, soil zinc may also reach concentrations that are toxic to plants as a result of application of sewage sludge and industrial wastes. Alloway (1995) summarized the anthropogenic sources of zinc as, the atmospheric fall-out, the agricultural use of sewage sludge and agrochemicals

2.3.3 Chemical behavior of heavy metals in soils

The behavior, transport, and the ultimate fate of heavy metals in the soil environment depend largely on their sorption reactions with the soil particles (Brian, 1980 and Salomons and Stigliani, 1995). Thus, the understanding of metals reaction mechanisms in the soil environment is critical to predict their fate and their potential hazards. According to Brady and Weil (1999) soils have a natural ability to hold on to metals. The concern is that the current input of contaminants might overload this capacity. Many factors affect the sorping capacity, accommodation and release of heavy metals in the soil environment (Salomons, 1993 and Brady and Weil 1999).

In the soil environment, sorption is the dominating speciation process and thus, the largest fraction of heavy metal in a soil is associated with the solid phase of that soil. Pollution problems arise when heavy metals are mobilized into the soil solution and taken up by plants or transported to the surface or ground waters (Brian, 1980).

Absorption is the process by which a metal in the solution or attached to the surface of the solid particle moves into the interior of the solid particle by diffusion into the inner pore space or lattice structure of the solid particle (Lindsay, 1979). Sorption of heavy metals is in particular associated with the colloidal and organic fraction of a soil. And since only a small fraction of these particles can be expected to be mobile in the soil system, metals are thought to be immobilized by sorption (Salomons and Stigliani, 1995).

Desorption is the process by which sorbed species are released to the surrounding environment (Lindsay, 1979). Precipitation is the process by which a soluble metal ion reacts with other soluble ions to form a solid product and dissolution is the reverse process (Lindsay, 1979). Metals precipitate with compounds such as hydroxides, sulfates, sulfites, phosphates, carbonates etc. Some of the precipitates are very stable and unlikely to dissolve once formed (Brian, 1980). Others may decompose when exposed to the right environmental conditions. Depending on the size of the precipitates formed, the specific metal may be immobilized by precipitation (Lindsay, 1979).

The principles of soil chemical reactions and their application to the environment are summarized by Salomons and Stigliani, (1995) as: inorganic and organic soil components, soil solution-solid phase equilibrium, sorption phenomena, ion exchange reactions, kinetics of soil chemical processes, redox chemistry, soil acidity and salinity. The most important chemical reactions mechanisms that control the behavior of heavy metals in soils are summarized by Alloway, (1990) as cation exchange, specific adsorption, co-precipitation, and organic content. These reactions control the exchange of heavy metals between the soil particles and soil water because most heavy metals are stored in the soil, usually attached to organic matter and clay.
Lo *et al.*, (1992) proved the strong relation between organic content of a soil and its metal retention capacity.

The soil texture reflects the particle size distribution of the soil and thus the content of fine particles like oxides and clay. These compounds are important adsorption media for heavy metals in soils. The concentrations of heavy metals in soils vary with soil texture. They are greatest in clay, followed by clay loam, loam, and sand. Heavy metal concentrations in soils are also related to soil order. Gleysols and Luvisols have the highest concentrations, followed by Brunisols and Podzols, that may refer to their mineralogical composition (McBride, 1989). The Cation Exchange Capacity (CEC) of a soil is a measure of the negative charge density of a soil as a function of the soil's ability to adsorb positively charged ions, cations. The CEC is generally considered as an important property of soils in determining the fate and availability of metals in the soil environment (Winistorfer, 1995). A high CEC reflects a soil with a high sorption capacity. The CEC has been used to develop guidelines to limit the application of metals to soils (U.S. EPA, 1986). The guidelines thus formulated, however, are not supported by long-term field experimentation.

Several researchers suggest that the maximum heavy metal concentration in soils be based on the cation exchange capacity of the soil, which is a measure of the soil's ability to retain heavy metal ions. The cation exchange capacity increases with increasing clay content of the soil. Thus, they recommend higher maximum heavy metal concentrations for fine-textured soils, such as clay and clay loam, than for coarse-textured soils, such as sand (McBride, 1989). The oxidation state of a given metal is determined by the redox potential. Different oxidation forms of a metal have different chemical behavior (Merrington, & Alloway 1994). Sorption of heavy metals is strongly pH-dependent.

In general, sorption increases with increasing pH. That is, the lower the pH-value the more metal can be found in solution and thus, more metal is mobilized. Moreover, acidification makes some metals less tightly bound to soil particles. Metals freed in this way become available to plants, to, which they might be toxic, and also leach into waterways (Krishnamurti et al., 1997). Considerable effort has been made by many researchers to understand the influence of all or some of the above soil properties on the kinetics of heavy metals in soil environment (Miner et al., 1997).

The accommodation and release of heavy metals in the soil environment is largely affected by the residence time. Residence time or aging is defined as the length of time soils are exposed to contaminant sources (Daniel and Sparks 1999). Several researchers have noted the kinetics and behaviour of heavy metals in soils is largely affected by the metals residence time (Kuo and Mikkelsen 1980; McLaren et al., 1986; Schultz et al., 1987; Backes et al., 1995; and Smith and Comans 1996).

2.3.3.1 Cadmium

Cadmium in soils tends to be adsorbed by clay minerals, carbonate or hydrous oxides of iron and manganese or it may precipitate as cadmium carbonate, hydroxide and phosphate (Dusley et al., 1991). Several findings reported that in polluted soils the greatest percentage of cadmium was associated with the exchangeable fraction (Tessier et al., 1980; Kuo et al., 1983). The major soil factors governing cadmium behavior in the soil environment are pH, soluble organic matter content, hydrous metal oxide content, clay content and type, presence of organic and inorganic ligands, and competition from other metal ions (Hickey and Kittric 1984).

Kuo et al., (1983) reported that at pH values greater than 6 cadmium is adsorbed by the soil solid or precipitated and cadmium in the soil solution is greatly reduced. Cadmium in agricultural soils is likewise relatively immobile under normal conditions, but could become more mobile under certain conditions such as increased soil acidity, which enables the cadmium to form soluble complexes with inorganic and organic ligands and increases the cadmium mobility in soils.

2. 3.3.2 Lead

Lead has a tendency to form compounds of low solubility with the major anions found in the soil. The accumulation of lead in soil is primarily a function of the rate of deposition from the atmosphere and the other contamination sources. Soluble lead added to the soil react with clays, phosphates, sulfates carbonates, hydroxides and organic matter such that the solubility of the metal is greatly reduced. There are various environmental soil factors such as temperature, salinity, pH, and the presence of organic matter that influence the fate of lead in soil. The fate of lead is affected mainly by the specific or exchange adsorption at mineral interfaces, the precipitation of sparingly soluble solid phases, and the formation of relatively stable organo-metal complexes or chelates with the organic matter in soil (McBride, 1989 and McBride et al., 1997a). In soils with pH of greater than or equal to 5 and with at least 5% organic matter, atmospheric lead is retained in the upper 2-5 cm of undisturbed soil (McBride, 1989).

Lead may mobilize from soil when lead-bearing soil particles run off to surface waters during heavy rains. Lead may also mobilize from soil to atmosphere by downwind transport of smaller lead- containing soil particles entrained in the prevailing wind (McBride et al., 1997a). The downward movement of lead from soil by leaching is very slow under most natural conditions The conditions that induce leaching are the presence of lead in soil at concentrations that either approach or exceed the sorption capacity of the soil, the presence in the soil of materials that are capable of forming soluble chelates with lead, and a decrease in the pH of the leaching solution (Basta et al., 1993) and Amacher et al., (1988) demonstrated a decreasing sorption of lead in the presence of complexing ligands.

2.3.3.3 Nickel

In polluted soils nickel retention in soils is exclusively through the adsorption mechanism because nickel dose not form insoluble precipitate. Under neutral soil pH is bound strongly by clays, soil organic matter and hydrous oxides of iron and manganese (Duke, 1990). The mobility of nickel in soils is enhanced by the formation of complexes of nickel with both organic and inorganic ligands. Nickel behaviour in soils is dependent on many parameters including the sources and mineralogy of particulates depositing into the soil, the age of the soil, historical land uses, the presence of naturally-occurring humic acid complexing ligands (Dudka *et al*., 1996). Duke (1990) reported significant amounts of nickel, for example, could be strongly bound to the surfaces of hydrous oxides and silica.

2.3.3.4 Zinc

Clay minerals, carbonates or hydrous oxides of iron and manganese readily adsorb zinc in soils. Due to the relatively high solubility of zinc compounds, precipitation is not a major mechanism of zinc retention in soils. Tessier *et al*., (1980) and Kuo *et al*., (1983) found that the greatest percent of zinc in unpolluted soils was associated with iron and manganese oxides. Soil pH, soil organic matter, and the interaction with amorphous hydroxides govern the chemical behavior of zinc. Precipitation may become a more important mechanism of zinc retention in polluted soils (Kuo *et al*., (1983). Robson, (1993) stated that the availability of zinc decreases at higher pH; at low pH Zn minerals are increasingly adsorbed by negatively charged colloidal soil particles. High levels of phosphorous in the soil may also decrease zinc availability and uptake by plants.

2.3.4 The speciation and bioavailability of heavy metals in the soil

Understanding metals content and behavior in the soil environment requires those environmentally significant fractions in terms of bioavailability, toxicity, and mobility to be identified and measured (Tack and Verloo, 1995 and Sager and Stoeppler 1992). The speciation of heavy metals, i.e. the way that a metal is distributed among its different chemical forms and physical phases, determines how it is distributed in the environment. In the soil environment a heavy metal ion can undergo a number of processes and reactions (Tack and Verloo (1995). These affect how the total metal content of a soil is distributed into fractions that can be found in the water phase, i.e. the mobile phase, or the solid phase, i.e. the immobile phase, respectively.

Tack and Verloo (1995) defined the chemical speciation of metals as the identification and quantification of the different and defined forms, species or phases in which an element occurs. Sager and Stoeppler (1992), defined fractionation as the analytical preparations for separating the chemical forms of a metal. The chemical speciation also focuses upon the quantitative distribution of an element between the chemical forms and the oxidation states involved (Soon and Bates, 1982 and Legret 1993). The term chemical fractionation emphasizes the concept of subdividing the total content of a metal and it is frequently used intermittently with chemical speciation.

Viets (1962) summarized that the occurrence of heavy metals in soils can theoretically include different chemical forms. Metal cations in the soil are divided in the following recognizable chemical pools, pool A (the water-soluble), B (the easily exchangeable pool), pool C (Complexed, adsorbed and exchangeable only by other cations with higher affinities), pool D (co-precipitated with metal oxides) and pool E (held in the primary minerals).

According to Soon, and Bates (1982) the water soluble, exchangeable and the complexed pools are believed to be in reversible equilibrium with one another, the equilibrium being affected by the soil properties and the metal concentration. Due to its greatest size pool C is believed by many researchers to be the most significant source for plant uptake of metal cations. The co-precipitated pool D is not an important immediate source of plant available metals because the equilibrium between this pool and the pools A, B and C is normally established only very slowly and over a long period of time. The advantage of the chemical pools concept is that it is relatively easy to relate the availability of heavy metals to their successive pools. The successive pools representing a decreasing degree of availability that ranging from ions in soil solution to ions in soil crystal lattice (Soon, and Bates, 1982). Legret (1993) conclude that the determination of the total content of contaminants in the soil is clearly important, however, the quantification of the bioavailable fraction of the contaminant is equally if not more important. Chemical speciation defines the oxidation state, concentration and composition of each of the chemical species present in the environmental sample (Soon, and Bates, 1982).

It is generally recognized that the specific physiochemical form of a heavy metal determines the particular behavior of that metal in the environments (Sager and Stoeppler, 1992). There have been many attempts within the scientific community to relate the concentration of heavy metals extracted from soils by chemical reagents to bioavailability under both field and laboratory conditions. Ma and Uren (1996) stated that the partial chemical extractants assess the relative mobility or geochemical partitioning of a heavy metal in the soil, but are unlikely to represent bioavailability. Several sequential extraction methods have been and still being developed and applied to study the chemical speciation and fractionation of heavy metals in the soil (Daniel and Sparks 1999). The readily soluble fraction of a contaminant is generally considered to be bioavailable. Mench and Horong, (1993) stated that the knowledge of chemical speciation of heavy metals in soils is essential to understand their chemical, biological interactions and transport mechanisms.

Many evidence indicate that the bioavailability and uptake of many heavy metals to plant are much more related to their chemical form rather than to their total concentration (Winistorfer, 1995). The content of the contaminant metals in the soil solution provides a good measure of the plant available amount. Sequential extraction has frequently been used to correlate operationally defined metal species to the observed effects (Winistorfer, 1995). These procedures use increasingly strong extractants to release trace metals associated with exchangeable carbonates, metal oxides or reducible organics and sulfides and residual mineral phases.

2.3.4.1 Cadmium

Once the cadmium is in the soil, it can be transported out of the soil by plant uptake, surface run-off and erosion. Cadmium is very mobile in soil; even minimal amounts in soil that has a low pH or humus level will result in cadmium uptake into plants (Brewers *et al.*, 1987 and McLaughlin and Singh 1999). A common approach for assessing the potential availability and the environmental role of cadmium in soils has been to conduct a series of sequential extractions using stronger extractants with each step (Ross 1994). Several chemical speciation and fractionation methods have been developed and applied to study the environmental behavior of cadmium in soils (Boon and Soltanpou, 1991; Tack and Verloo 1995 and McLaughlin and Singh 1999).

The distribution of the various chemical forms of cadmium in soils have been summarized by many researchers as free ions, exchangeable, oxidizable, acid soluble, reducible and residual fraction (Legret, 1993; Jeng and Singh 1993; Narwal et al., 1999; Robert et al., 1995 and Liang and Schoenau, 1996). Liang et al., (1996) and Narwal et al., (1999) reported that relatively high percentage of cadmium added to soils is present as labile and exchangeable forms while Robert et al., (1995) reported a low percentage of exchangeable and water-soluble forms of and a relatively high percentage of residual form in cadmium treated soils.

2.3.4.2 Lead

Lead in the environment is strongly absorbed by soil particles, and is therefore largely unavailable to plants and animals (Rooney et al., 1999). Many of the inorganic salts of lead are not readily soluble in water and are sequestered in the soil. Many authors have shown that the metal toxicity and plant availability of lead in soils are controlled by the free metal rather than the dissolved concentration (Sebsatien et al., 1997). Many studies relate the results of sequential extractions procedures to the bioavailability measurements (Rooney et al., (1999)

Robert et al., 1995 and Sposito and Coves (1995) reported that significant amount of lead entered in the soil system will remain in the residual fraction and low percentage of free ion. Sebsatien et al., 1997 findings indicated a strong relation between the free ions in various contaminated soils with the soil pH. Liang et al., (1996) stated that most of the lead added to soils present in the weak acid labile fraction at low soil pH and he also reported that at high soil pH only most of the added lead is associated with hydrated iron oxide.

2.3.4.3 Nickel

The nickel soluble compounds in soils include nickel acetate, nickel sulfate hexa-hydrate, nickel nitrate hexahydrate, and nickel chloride. The various nickel oxide species have markedly different physicochemical characteristics and biological effects. Much research work was performed to distinguish the various chemically reactive nickel species in the soil environment (Liang et al., 1996; Narwal et al., 1999; Singh et al., 1995; Dudka et al., 1990 and Uren, 1992).

Narwal et al., (1999) reported that only small amount of the added nickel was in the exchangeable form at low soil pH. The findings of Liang *et al*., (1996); Uren, (1992); Adamo et al., (1996) and Singh et al., (1995) concluded that only a small percentage of nickel were found in mobile fraction, and higher percentage were in complexed and precipitated forms. Dudka et al., 1990 and Adamo et al., 1996) reported greater association of nickel with Fe and Mn oxides.

2.3.4.4 Zinc

Many researchers extensively studied the chemical speciation of zinc added to soils (Narwal et al., 1999; Chlopecka et al., 1996; Robert et al., 1995; Singh et al., 1995; Jeng and Singh, 1993 Calvet et al., 1990; Kuo et al., 1983).

Although zinc is considered as a very mobile metal it can also react with clay minerals and oxides. Calvet et al., (1990) reported that zinc is retained on oxyhyroxides by surface complexation and can only be solubilized through mineral dissolution. Several investigators have found that when zinc was added to soil it associated with Fe and Mn oxides (Jeng and Singh 1993 Kuo et al., 1983;). Narwal et al., (1999); Robert et al., (1995) and Calvet et al.,

(1990) stated that high percentage of zinc added to soils was readily found in exchangeable form. Narwal et al., (1999) and Robert et al., (1995) reported high percentages of zinc in the exchangeable fraction. Furthermore, Boon and Soltanpou, (1991) and Singh et al., (1995) found that a higher concentration of zinc entered the soil was available for plant uptake.

2.3.5 Environmental consequences of heavy metals pollution of soils

The environmental consequences of heavy metals pollution are varied and related to their mobility and solubility. Once they entered the soil water, heavy metals may move within the soil profile, become available to plants then bioaccumulate in the food chain, posing a toxicity problem for fauna and humus alike, and can be leached into groundwater. Soil monitoring and their analytical screening provide preventive measures for pollution control (Tiller, 1989). The assessment and management of heavy metals in the environment appears to be the basic instrument for the achievement of socially and economically accepted levels of human health.

Large concentrations of heavy metals in soils present a number of concerns. These concerns include the toxic effects on plants resulting from the uptake of heavy metals by plants grown in contaminated soils. Eating contaminated plant tissues as well as eating and breathing of soil and dust, particularly by children; the possible harmful effect of direct skin contact with metals, pollution of water resources, and the chemical attack on building materials (Tiller, 1989). The relationships of heavy metals to the problem of soil fertility and plant nutrition and their potential toxicity have been extensively studied (Tiller, 1989). The accumulation and persistence of many heavy metals creates an important ecological problem.

The threat that heavy metals pose to human and animal health is aggravated by their long-term persistence in the environment. For instance, lead (Pb), one of the more persistent metals, was estimated to have a soil retention time of 150 to 5000 years (Tiller, 1989). Also, the average biological half-life of cadmium, another "accumulation poison" similar to lead, has been estimated to be about 18 years (McLaughlin and Singh 1999). Heavy metal pollutants can affect man directly such as the acute effects from exposure to a toxic pollutant reaching man through air, water or food, the long-term effects due to the prolonged exposure to a pollutant at levels lower than those giving rise to over toxic effects. It is already widely known that the health effects of heavy metals and exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage, and even death in some instances of exposure to very high concentrations (Oliver, 1997).

The indirect effects on man may result from reduction of food supply or deterioration of the environment. Such effects include damage to plants and animals, damage to the human habitat, water pollutants that destroy the recreational value of the inland waters, air pollutants that destroy forests and corrode buildings and alteration of the ecological cycles such that a previous harmless species becomes a pest (Brady and Weil 1999).

2.3.5.1 Cadmium

Cadmium contamination of soils has been viewed as the most dangerous form of trace element contamination of soil. In the past, there have been examples of marked cadmium contamination in areas where food has been grown (McLaughlin and Singh, 1999). In general, soils that have been historically contaminated with cadmium from industrial operations are no longer used for agricultural purposes. In those cases where old industrial installations which are cadmium-contaminated are subsequently employed for growing crops, suitable remediation techniques do exist to immobilize the cadmium resent in the soil and thus to control the risk to human health.

There is, however, no doubt that old sites which are so contaminated do require proper risk management and control by cleaning up or immobilizing the existing excess cadmium in the soil.

Cadmium is an especially toxic heavy metal that is very mobile in soil. Even minimal amounts in soil that has a low pH or humus level will result in cadmium uptake into plants. Cadmium is toxic to most forms of life. It can be taken up directly from water, and to some extent from air and via food, and it has a tendency to accumulate in both plants and animals (McLaughlin and Singh, 1999). Its major hazard to human health where chronic accumulation in the kidneys can cause their disfunction. Cadmium is also a potentially toxic metal with no known requirement by living organisms. The FAO recommends a maximum tolerable intake of cadmium (Cd) of 70 μg/day. Cadmium accumulates in kidneys and livers of grazing animals. The primary risk posed by Cd contamination is through the ingestion of vegetables grown on Cd-contaminated soil. The presence of high cadmium levels in the food chain may be used in the future as a trade barrier to the agricultural products.

In higher animals, cadmium accumulates in the kidneys and liver, where most of it binds to a special protein that makes the metal harmless to the animal. Among the 27 contaminant metals, cadmium, lead and nickel are potential hazard to human health. If the uptake is greater than this natural defense, cadmium can damage the kidneys and upset metabolism of vitamin D and calcium. Kidney damage and a decalcification of the skeleton are the serious chronic effects of high cadmium exposure. Kidney damage in seabirds has been seen at cadmium levels in the tissue of 60 to 480 micrograms per gram.

2.3.5.2 Lead

A strong positive correlation is found between exposure to lead-contaminated soils and Pb blood levels (Tiller, 1989). Lead poisoning is a very serious issue for young children and pregnant women. Lead is toxic to growing brains and nervous systems of fetuses and young children. Lead accumulates in the liver, kidney, spleen, and skeleton. Once it has been integrated into the skeleton, it takes several years to leave the body (Tiller, 1989). Lead can also accumulate in eggs and embryos. Damage to the nervous system and gastrointestinal symptoms are the main signs of lead poisoning. Lead also interferes with the formation of red blood cells, leading to anemia. Lead is especially toxic to the growing brain and can affect the behavioral development of young, even at low concentrations

Studies on the effects of lead in children have demonstrated a relationship between exposure to lead and a variety of adverse health effects. These effects include impaired mental and physical development, decreased heme biosynthesis and elevated hearing threshold. The neurotoxicity of lead is of particular concern, because evidence from prospective longitudinal studies has shown that neurobehavioral effects, such as impaired academic performance and deficits in motor skills, may persist even after Pb levels have returned to normal (Tiller, 1989).

2.3.5.3 Nickel

The most common adverse effects of nickel exposure are skin allergies, specifically dermatitis. Rhinitis, nasal sinusitis, and nasal mucosal injury are among the effects reported in workers chronically exposed to nickel compounds (Poulik 1997).

Recently an increased attention has been focused on nickel due to its dangerous effect on crops and animals (Bazzaz *et al.*, 1974).. The most common adverse effects of nickel exposure are skin allergies, specifically dermatitis. Rhinitis, nasal sinusitis, and nasal mucosal injury are among the effects reported in workers chronically exposed to nickel compounds. Asthma has been reported in nickel workers exposed to nickel sulfate and nickel oxides (Poulik 1997).

2.3.5.4 Zinc

Zinc is an essential trace metal. There have been instances of zinc excesses that result in toxicity and zinc nutrient deficiencies have been reported in several environmental systems. The phytotoxicity of Zn has been extensively studied by several authors (Cummings and Tomsett, 1992; Boon and Soltanpour 1992; Chang *et al.*, 1992 and Holmgren *et al.*, 1993).

2.3.6 Prediction of the environmental impact of heavy metals pollution of soils

The risk assessment and the environment impact of heavy metals pollution can be approached in different ways. Tiller, (1989) approached the environmental impact of heavy metals in soils by assessing the degree of soil pollution, assessing the geographical extent and by predicting the effect on plant, animal and human heath.

2.3.6.1 Degree of soil pollution

The assessment of the degree of soil pollution requires the measurement of the total concentration and their comparison with the background situation and with an appropriate reference soil using the same means of analysis (Tillert 1989).

Many scientists argue that the knowledge of the total amount of an element present in the environment is insufficient because such concentration does not reflect the actual chemical species that matter much in the environment. According to (Soon and Bates, 1982) the total elemental composition of soils is a poor indicator of the environmental polluting role of a specific contaminant.

2.3.6.2 Prediction of uptake by means of soil analysis

Soil testing may be defined as any physical or chemical measurement of soil properties and. Soil testing has been utilized to one degree or another, and for various reasons. Recently soil analysis has been used to predict the contamination status of a soil and the expected effect of such contamination on the biomass (Hani et al., 1996).

For metals analysis soil samples are generally mixed with an extracting solution of some kind. The mixture is then shaken and then filtered resulting in a clear liquid extract, which is then subjected to various chemical tests (Heinz, 1996). The extracting solution may be distilled water, although with most laboratories one or more dilute acids are used to extract nutrients from soil samples. The theory is that the extracting solutions disolve from the soil those metals that are reasonably available to plants or human uptake (Hawley, 1985).

There are many soil extraction methods. However the different extracting solutions vary in the amount of metals they pull out of a soil (Daniel and Sparks 1999 and Lo et al., 1992). Distilled water as an extracting solution indicates the immediate available portion, and does not give much of an idea of what the reserve levels are. Therefore, using dilute, weak acids as extractants will generally reveal levels of metals in forms that will likely be available to the plant.

Sequential extraction procedures provide information about the differentiation of the relative binding strength of metals on the solid phase and about their potential reactivity under different physiochemical environmental conditions (Legret 1993). From the sequential extraction procedures it is possible to estimate the mobility and availability of metals in the environment.

2.3.6.3 Prediction of uptake by means of plant analysis

Plants can concentrate essential and non-essential heavy metals in their roots and shoots to levels far exceeding those present in the soil and they are normally used as biomonitors for a broad range of heavy metals concentrations in the soil (Mench and Horonug 1993). Ali (1993) stated that some plants actively accumulate metals in their aboveground tissues and can be roughly divided into two groups: indicators and hyperaccumulators. Scientists suggest that the metal levels in the tissues of an indicator species generally reflect metal levels in the soil. While the hyperaccumulators can concentrate metals in their aboveground tissues to levels far exceeding those really present in the soil or in the non-accumulating species growing nearby (Ali, 1993).

Many research workers extensively studied the specificity, transport and accumulation; third, the physiological, biochemical and molecular mechanisms of accumulation of metal uptake by indicator plants (Alfani *et al.*, 1996 and Albasel, 1985).

2.3.6.4 Background levels of heavy metals in soil

Metal concentrations in soil vary greatly, depending on vicinity to pollution sources and on local geology. According to Alloway, (1995) that the levels of heavy metals in the biota of terrestrial ecosystems represent weathering of local bedrock combined with input from distant and local pollution sources. In order to interpret the results of soil test in terms of heavy metal content, the natural background level of such metals in soil must be known.

Away from pollution sources, metal levels in soils depend on the type of bedrock, movement of water, weathering, and biological processes. The background (uncontaminated) levels of heavy metals in soils are generally low and are related to the geochemistry of the soil parent material. They are several areas of high levels of natural background concentrations worldwide and there are standard values that have been published for comparison with any tested soil data (Badri, 1995).

2.3.7 Modeling the fate and speciation of heavy metals in polluted soils.

The impact of waste disposal on soils can lead to worsening of environment resulting in changes in properties of soils, toxicity effect on plants and animals. Consequently, there is a need for detailed studies of the deposition and availability of pollutants and to develop pollutant transfer models including interactions between soil and pollutants, their impact on biota and their residual accumulation in soils (Selim, 1999 and Mattigod, 1995). Modeling is the main tool of investigations under such conditions. The modeling allows predicting the fate of heavy metals in soils.

Some models have been primarily focused on the geochemical aspects of the problem (Selim, 1999). Knowledge of speciation modeling provide insight into the underlying chemical relations and give significant contribution for the studies of bioavailability of contaminant, Therefore the speciation modeling approach provide significant knowledge about the cheaper and better decisions about wastes disposal options, risk assessment, and clean-up procedures of contaminated soils (Mattigod, 1995).

Speciation models are needed in virtually all aspects of management of metal contamination of the soil environment, including risk assessment, site remediation, and waste disposal (Johns, 1999). Models that attempt to predict the fate of heavy metals in soils have focused primarily on the geochemical aspects of the problem.

The difficulty associated with using models to simulate the fate of a heavy metal in the root-soil environment is properly accounted for all interactions between metals and soil processes as well as between water movement, contaminant transport, uptake of water and metals by plant roots. Selim (1999) summarized three great obstacles in the prediction of metal speciation in field systems as the heterogeneity of environmental materials, such as humic substances or the surfaces of rocks and minerals, slow kinetics of chemical reactions, such as phase transitions (precipitation-dissolution reactions), and the chemical changes that accompany the variation in water content in the unsaturated zone

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Over the recent years many computer programs have been developed to assess the chemical speciation in aqueous systems at equilibrium using the total concentrations of metals in the soil (Tack and Verloo 1995). All the solution speciation models like GEOCHEM (Parker *et al.*, 1995), SOILCHEM (Sposito and Coves 1995) and MINTEQA2/PRODEFA2 (Allison and Brown, 1995) may give rise to some discrepancies due to the limitation of both analytical and computational sides. The main disadvantage of several models developed using such programs lays in the basic assumption of equilibrium among dissolved species.

2.4 Heavy metals in Malaysian soils

The enhanced urbanization and industrialization progress in Malaysia led to an increased usage of metals and consequently an increased metal output in the environment (Ahmed (1995). It is fortunate enough that there is a physical separation of the industrial areas from the residential areas and the centers of urban growth. Malaysia has almost all the heavy metals related industries (Dean et al., 1972).

No comprehensive data exists on either total pollution loads or pollution intensities in Malaysia a constraint to full understanding of the extent and cost of the industrial pollution problem. Partially in response to this constraint, the World Bank's Industrial Pollution Projection System (IPPS) has been developed to provide an approximate means to estimate trends in industrial pollution. According to Badri *et al.*, (1995) the main source of heavy metals in the Malaysian environment is transportation due to increased number of vehicles per kilometre of road and the high levels of heavy metals at the roadsides of Jalan Pudu, Jalan Parlimen, Masjid Negara and Istana Negara areas. Many research workers in Malaysia (Ahmed (1995); Ahmed et al., 1995); Badri et al (1985) have studied heavy metals in Malaysian soils. Generally, it is recognized that heavy metals concentration is higher in the Malaysian urban area, mainly at the roadsides of the highways and landfill areas (Badri (1994); Mohd Noor (1990) and Abdul Halim (1998). Recently Fifadara (1999) recorded extremely elevated concentrations of cadmium, lead and nickel around Sabak Bernam landfill in Selangor.

Although there is considerable research work done on the concentration of heavy metals in Malaysian soils little is known about the chemical distribution of heavy metal cations dumped into the soil as wastes or chemical by product.

2.5 Lettuce and heavy metals

The toxicity level of heavy metals is varied among plants. Leafy vegetables have been extensively used as bio-indicators in soil pollution monitoring studies due to their ability to adsorb and tolerate heavy metals (Singh, 1994). Heavy metals content of fresh leafy vegetables is essentially dependent on the heavy metals content of the soil. It has been established that leafy vegetables had higher contents of heavy metals than other vegetables grown in the same soil (Chaney *et al.*, 1993).

Several workers have reported that lettuce is among plant species that have high ability to accumulate heavy metals (Calton, 1980; Singh. 1994 and Singh et al., 1995). Bevacqua and Mellano (1994); Srivastava et al., (1993); Hernandez et al., (1992); Poulik, (1999), Roca and Pomares (1991) and Liang and Schoenau (1995) showed the significance of using lettuce as biomointor by proving positive correlation between the heavy metals content of the lettuce plant with the extractable metals in the nourished soil.

It has been established by Venter, (1993); Logan et al., (1997); Sterrett et al., (1996) and Hernandez et al., (1992) that lettuce accumulates significant high concentration of heavy metals, which exceeded the reported toxicity limit of the metals.

2.5.1 Cadmium

Cadmium is the heavy metal of greatest concern in agricultural soils. It is not required for the growth and development of either plants or animals and can be toxic to both. In animals, it accumulates in the liver and kidneys and can cause kidney damage. Cadmium is loosely held by soil constituents and is readily available to plants. Thus, increased concentrations in soil result in increased concentrations in crops. Cadmium accumulation in plant materials varies with crop type and plant part. In general, broadleaf plants accumulate more cadmium than grasses, and plant leaves and stems accumulate more than seeds. Broad-leaves vegetables, such as lettuce and swiss chard, accumulate more cadmium than most other plants. Cadmium reaches variable concentrations in different plant-organs of different species. Species such as oats, soybeans, corn and tomato accumulate more Cd in roots than in the aerial parts of the plant. Conversely, lettuce, carrot and potato accumulate more in the leaves (Kabata-Pendias, 1991; Sauebeck, 1991).

2.5.2 Lead

Lead is less mobile and is absorbed by plant roots only in exceptional cases. Even minimal contents in soil can negatively affect plant growth and damage soil organisms. The highest accumulation of lead is reported to occur in leafy vegetables (Kabata-Pendias, 1990).

2.5.3 Nickel

The concentration of nickel in plants generally reflects the metal in the soil; elevated levels of Ni are reported in nickel hyperaccumulating plants growing in highly contaminated soils (Hutchinson 1981).

2.5.4 Zinc

The uptake and accumulation of zinc by plants are varied among different plant species. Lettuce was found to one of six vegetables that readily uptake and accumulate zinc from soil solution (Henry _et al_., 1992).

2.6 Battery wastes and heavy metals

One of the most wide spread and an oldest form of pollution is that arising from contamination of the environment by hazardous solid material disposed of as waste. Determining which waste is hazardous is a dynamic process; influenced by new concerns, research findings and development of test methodology (Stoeppler, 1992).

Battery industry is among the significant sources that contribute in the inorganic contamination of the environment (Alloway, 1995). The battery waste disposal is a great environmental challenge since almost all kind of batteries contains high concentrations of at least two of the hazardous heavy metals cadmium, copper, lead, manganese, mercury, nickel, or zinc (Eklund, 1995). Eklund, (1995) reported high levels of cadmium and lead in soils and plants around battery plants in Sweden

Nickel-cadmium battery cell contain 20-30% nickel and 13-25% cadmium on weight bases. Due to that nickel-cadmium battery waste is the most significant sources of Ni and Cd in the environment since the potential major market for nickel-cadmium batteries is the electric vehicle market, which continuously grow (Alloway, 1995). While cadmium is naturally present in low concentrations in soil (< 10 ppb), its concentration can be more than reach the 100-ppm range in areas immediately adjacent to Ni-Cd battery plants (Alloway, 1995)

Mercury batteries cell contains 20-30% mercury by weight. Their disposal can cause adverse health effects because high levels of mercury may damage the brain. On the other hand lead acid battery cell contain 60-77% lead since the anode is lead and the cathode is lead oxide. Skinner and Salin (1995) estimated large concentrations of lead in soils surrounding a former lead-acid battery manufacturing plant in Canada.

In carbon-zinc battery the anode contains zinc, the cathode contains manganese, and the electrolyte is an aqueous solution of ammonium chloride and zinc chloride. Excessive zinc concentrations in soils relate to possible crop uptake (Alloway, 1995).