Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Biosorption and Leaching of Heavy Metals from Activated Sludge Applied to Soil

A thesis presented in partial fulfilment of the
requirements for the degree of
Doctor of Philosophy in Technology
at Massey University
Palmerston North
New Zealand

Pushpalatha Mahenthiran
November 2002

Dedicated

to my

Beloved Parents

Abstract

Accumulation of heavy metals in sewage sludge and soil and their subsequent movement to ground water and surface water are major environmental issues. Cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni) and chromium (Cr) are the most commonly occurring sludge-borne heavy metals in New Zealand. The potential toxicity of these heavy metals depends more on their availability and mobility than on their total content. This study examined the adsorption-desorption and potential leachability of these heavy metals in sewage sludge and a volcanic soil.

Results of adsorption – desorption experiments using Cd, Cu, Zn and Ni showed that activated sewage sludge sorbed Cd, Cu and Zn more effectively than Ni. Adsorption capacities of Cd, Cu and Zn were 35.7-44.8, 14.1-26.4 and 57.5-59.5 mg/g biomass, respectively. The affinity of activated sewage sludge with Ni was very low thereby no further isotherm study was carried in Ni. Biosorption increased with increases in pH. Adsorption capacity also increased with increases in initial metal ion concentration but the adsorption yield decreased. Chloride ion concentration (0.145 N) had a more significant effect on the reduction of adsorption of Cd than on the reduction of the adsorption of either Cu or Zn. A desorption study was carried out using deionized water, 0.1 N Na_2SO_4, 0.1 N K_2SO_4, 0.1 M Na citrate, and 0.1 M Na_2CO_3 solutions and the results showed that Zn desorbed more in every desorbing agent.

Results of the study of the adsorption behaviour of Zn in volcanic Egmont soil in the presence of phosphate showed an increase in adsorption of Zn and the presence of nitrate did not show any significant difference in adsorption. Both 500 and 1000 mg/kg phosphate levels reduced the water-soluble Zn in volcanic Egmont soil remarkably. The desorption study showed that more Zn was desorbed with 0.1 M KNO_3 than with deionized water and 0.1 M KH_2PO_4.

An in situ leaching study was carried out in volcanic Egmont soil using Zn amended sewage sludge and inorganic Zn as Zn sources and soil columns were pretreated with nitrate and phosphate anions. More Zn leached from inorganic Zn applied soil columns than from Zn amended sewage sludge applied soil columns. There was no substantial difference in the amount of Zn leached between nitrate and phosphate treated columns. Determination of total acid digestible Zn in sewage sludge and inorganic Zn applied soils showed a greater accumulation of Zn in 0-10 cm depth. More Zn moved to the lowest (25-32 cm) depth in the nitrate treated inorganic Zn applied soil column and less Zn moved to the lowest (25-32 cm) soil depth in the phosphate treated sewage sludge applied column.

Fractionation of Zn in Zn amended sewage sludge showed that most of the fractions of Zn were in water-soluble and exchangeable, followed by carbonate and organically complexed forms. However, fractionation of Zn in control volcanic Egmont soil showed that most of the Zn was in oxide and residual forms. After the application of both Zn amended sewage sludge and inorganic Zn, the overall percentages of water-soluble and the exchangeable, carbonate and organically complexed forms of total Zn increased. All the fractions of Zn in both sludge and inorganic Zn applied columns decreased with the increase in soil depthFractionation of Zn in inorganic Zn applied soil showed that the increase in the exchangeable and oxide forms of Zn was higher in the phosphate than in the nitrate treatment. The overall percentage of the water-soluble and the exchangeable and the carbonate forms of total Zn increased except the organic, the oxide and the residual form in inorganic Zn applied soil columns.

The results of this study suggest that activated sewage sludge has a high affinity for Cd, Zn and Cu. Zn desorbed from sewage sludge more easily than Cu indicating that the Zn from the sewage sludge may be more reactive than Cu in soil. Ex situ and in situ studies showed that phosphate remarkably limited the Zn movement in both sewage sludge and inorganic Zn applied soils but nitrate did not have any significant impact on the movement of Zn.

Acknowledgements

I wish to express my sincere thanks and appreciation to a number of people for their contributions towards the completion of this thesis - in particular,

First and most importantly to my chief supervisor, Professor Rao Bhamidimarri, for his wholehearted guidance, unfailing help and advice, patience and understanding during my study period.

To my co-supervisor, Dr. S. Saggar of Landcare Research for his valuable guidance, help, encouragement and understanding during my thesis writing.

To Associate Professor Nanthi S. Bolan and Dr. P. Loganathan of Soil and Earth Science Group, for their valuable guidance and suggestions.

To the Head and staff of the Institute of Technology & Engineering and the Members of the Environmental Engineering Laboratory, in particular Michael Killick, Paul Bickers, John Sykes and Anne Marie for their excellent and willing assistance with all the technical matters during the research.

To the Soil Science Department technicians for their kind assistance in doing a part of the soil analysis and to Mr.T.Thevathasan for his guidance in statistical analysis.

To the New Zealand Vice-Chancellors' Committee for awarding me the Commonwealth Scholarship, and to the Sri Lankan Government and Eastern University of Sri Lanka for allowing me the time to pursue my academic advancement.

To Mrs Manvir Edwards, of Principal's office, and Mrs Joan Brookes, of the Institute of Technology and Engineering, for their timely assistace and to Mrs Karen Stanley, for her comprehensive proof reading of this thesis.

And finally, to my husband, Mahendran, for his patience, support, love and understanding - and special thanks to my daughter, Nirusha, who always brings cheer and happiness.

Table of contents

List of tables

List of figures

List of plates

Chapter One

GENERAL INTRODUCTION

1.1. BACKGROUND OF THIS STUDY

Heavy metals are generally defined as *elements which have a density greater than 6 in their elemental form* (Alloway, 1995). They are potentially toxic to the human and environment. Many industrial discharges are contaminated with these heavy metals such as cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), tin (Sn), and zinc (Zn) (Jones & Jarvis, 1981; Leeper, 1978). Cadmium, Cu, Zn and Ni were selected for this study because of their widespread industrial use and known toxicity to aquatic organism. All these heavy metals are potentially toxic at high concentrations (Purves, 1981). Potential toxicity depends on availability and mobility than their total content.

Cadmium, Cu, Ni and Zn are toxic and ubiquitous in their distribution throughout the world. New Zealand generates about 300,000 tons of industrial waste annually (Naidu et al., 1996). Usage of phosphatic fertilizers, pesticides and fungicides and metal working process, painting, dyeing, diary farming and usage of wood preservatives (CCA solution) are the main contributers of heavy metals such as Cd, Cu, Zn and Ni to the sludge in industrialized areas in New Zealand. Sometimes, these heavy metals containing sewage sludge (solid) effluents are applied to pastures, crops and forestlands. Although Cd, Cu, Cr, Hg, Ni, Pb and Zn are the most important pollutants of the aquatic environment (Smith, 1986) Cd and Zn tend to be more mobile than others are (Lagerwerff et al., 1976; Leeper, 1972; Logan & Chaney, 1983). When they are released into the environment, they tend to migrate and accumulate in the food chain, thus causing a serious threat to the environment, animals and humans.

Sewage sludge has become more important problem in some areas near major urban centres because of recent decisions to cease marine disposal from metropolitan areas (Tiller, 1991). The application of sewage sludge to soil provides a useful source of plant nutrients and also organic matter, which improves the physical condition of soil. In addition, land application of sewage sludge is a cost-effective method of disposal. Because sewage sludge contains potentially toxic heavy metal elements that can accumulate in the soil there has been increased concern about their deleterious effects on soil quality.

The heavy metal content of sewage sludge has been reported to be normally 0.5-2 % on a dry weight basis (Wong & Henry, 1988) but in some cases as high as 4 % (Lester et al., 1983). The use of these sludges as fertilizer materials is potentially toxic. The Australian government recently banned discharge of sewage, treated or otherwise, into the ocean and has restricted its incineration (Tiller et al., 1997). New Zealand's municipal sewage sludge metal constituents on average were found to be 4 mg/kg Cd, 90 mg/kg Ni, 1300 mg/kg Zn and 460 mg/kg Cu (NZWWA, 2002). Zinc is very common and high in concentration than other sludge born heavy metals and it is highly mobile and represent the greatest risk of bioaccumulation in the food chain and water contamination (Lagerwerff et al., 1976; Leeper, 1972; Logan and Chaney, 1983; McBride, 1995)

Heavy metals present in sewage are concentrated in primary and secondary sludge during wastewater treatment (Brown & Lester, 1982). Previous studies of heavy metal removal in wastewater treatment plants have demonstrated a wide variability in removing the different metals and also for the same metal (Brown & Lester, 1982). Generally 5-20 % removal occurs in the primary sedimentation basin, and an additional 10-80 % removal occurs in the activated sludge process (Nelson et al., 1981). Because of this wide variability of removal, high potential and the deficiency in examining the use of environmental and operational control parameters to repress the inhibitory effect of such heavy metals, further study is needed in the activated sludge process.

The increased volume of wastewater sludge and the ultimate disposal of the residual sludge containing metals have been difficult environmental issues. Disposal of sewage sludge on agricultural land has been practised for several years, and such use has been encouraged because it is seen to be a partial substitute for fertilizers and as a way of improving the physical properties of soil (USEPA, 1983). In addition, because of the increasing restrictions on the dumping of sewage sludge into the sea, and because of the high cost of other disposal options such as incineration and land fill sites, disposal on agricultural land is accepted by many decision makers as the most cost-effective option. However, it is restricted as several researchers are required to deal with suitable soil extractants which predict the bioavailable forms of heavy metals in contaminated areas (Vander Watt et al., 1994). The limit on the amount of metal is considered based on the translocation of metals and their subsequent movement into ground water and surface water (Tiller 1988; Naidu et al., 1996). This is largely determined by soil pH, ionic strength and the nature and the amount of inorganic cations and anions in soils (Boekhold et al., 1993; Naidu et al., 1994).

New Zealand is representing major volcanic soils. Newplymouth has been one of the cities in New Zealand has received high levels of Cu and Zn in its wastewater in excess of proposed guidelines. Volcanic soils are widely distributed in Newplymouth. New Zealand soils in general contain fairly high levels of organic matter when compared to other soils. A number of soils are derived from volcanic material and contain high proportions of allophane and pumice particles. Further, most soils are acidic and have a pH range of 5.5-6.5. These three factors are known to have a marked effect on heavy metal behaviour, especially that of Zn and Cd. Therefore, heavy metal sorption-desorption has to be examined in relation to its effect on movement in the soil profile of volcanic Egmont loam soil.

The purpose of this study is to gain a better understanding of the biosorption, desorption and potential leachability of the sludge born heavy metals in sludge and soil system.

1.2. OBJECTIVES OF THIS STUDY

The information presented in 1.1 was the catalyst for the present study which was undertaken with the following objectives:

1. To characterize biosorption - desorption of Zn, Cd, Cu and Ni by activated sewage sludge biomass and the factors influencing the process.

2. To study the sorption and desorption of Zn in volcanic Egmont soil.

3. To understand the mobility and movement of Zn in activated sludge applied intact volcanic Egmont soil.

4. To understand the speciation of Zn in the native and Zn applied soil (Sludge Zn and inorganic Zn).

1.3. STRUCTURE OF THIS STUDY

In Chapter 2, Part 1 of the review of literature (2.1) provides an introduction, Part 2 provides an overview of heavy metals and the environment; source and origin of heavy metals to the environment, chemistry and binding capacity of heavy metals, forms and amounts of heavy metals in soil and sludge, impact of heavy metals in the environment and control of heavy metals in the environment. Part 3 of the review of literature is about the adsorption technology and the rest of this section is about mobility and transport of heavy metals. Conclusion provides some weak points in the existing metal leaching experiments and the need for undertaking this column leaching study.

In chapter 3, a description of the materials and method utilized in this research is given. Materials include activated sludge (Kapiti coast), volcanic Egmont black loam soil and some selected heavy metals (Cd, Cu and Zn). Methods includes batch adsorption and desorption experiments for sludge and soil, laboratory leaching setup for undisturbed column leaching study.

Chapter 4 (Results and discussion) considers the results of the batch experiments used to assess the biosorption-desorption of some selected heavy metals (Cd, Cu, Zn and Ni) onto activated sludge and the factors affecting the sorption.

Chapter 5 (Results and discussion) considers the results of the batch experiments used to assess the adsorption-desorption of Zn onto the volcanic Egmont loam soil.

Chapter 6 (Results and discussion) considers the results of the Zn leaching and Zn movement *in situ* studies with reference to the anion effect.

Chapter 7 (Results and discussion) considers the results of the fractionation of Zn in control, sewage sludge applied and inorganic Zn applied soil columns of volcanic Egmont soil.

Chapter 8 presents the general discussions and conclusions of this study.

Chapter Two

LITERATURE REVIEW

2.1. INTRODUCTION

Heavy metals are potentially toxic to human life and the environment. The accumulation of heavy metals such as cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), Nickel (Ni) and arsenic (As) in soils and their subsequent movement to ground water and surface water are major environmental issues (Tiller, 1988; Naidu et al., 1996). The accumulation of heavy metals can be due to sewage sludge application, excessive fertilizer and pesticide use, irrigation and atmospheric deposition. Sewage sludge needs to be considered as a source of potentially toxic elements because it is likely to be increasingly used as fertilizer material because of its high neutrient content.

The heavy metal content of sewage becomes trapped in the solid phase of sewage sludge during the sewage treatment either through biosorption or entrapment. Metal concentration in sewage sludge in many industrialized countries ranges up to several thousands -mg/kg sludge on a dry basis (Tiller, 1989). The application of this sewage sludge to the land generally raises readily available heavy metal concentration and leads to leaching of toxic elements into surface and ground water. Among the metals, Cd and Zn are very common in sewage sludge (Lagerwerff et al., 1976). They are highly mobile and represent the greatest risk of bioaccumulation in the food chain and water contamination (Lagerwerff et al., 1976; Leeper, 1972; Logan and Chaney, 1983; McBride, 1995).

Even though initial mobility of heavy metals after the sludge application to the soils largely depends on the form in which they are added (Jones & Jarvis, 1981), the concentrations of metals in soil solution are affected by the water solubility of the specific metal, ion exchange, the adsorption and desorption process, complexation and redox reactions (Helmke & Naidu, 1996). The release of heavy metals into the soil depends on the sorption-desorption phenomena not only at the soil colloidal surface but also at the sludge biomass surface. The other major factors influencing the release of the metals include precipitation and dissolution.

The objective of this review is to collate the existing information and to identify the areas of investigation necessary to understand the environmental impacts of the application of sludge to land.

2.2. HEAVY METALS AND THE ENVIRONMENT

2.2.1. Source and origin of heavy metals in the environment

Major sources of metals in soils include discarded manufactured products as in landfills (As, Cr, Cu, Pb, Mn, and Zn), coal ash (As, Cd, Pb, Mn, Hg, Mo, Ni, Se, V, and Zn) and agricultural and livestock wastes (As, Cu and Zn). Major contributors of metals in the aquatic environment include manufacturing (Sb, Cd, Cr, Cu, Mo and Zn), electric power generation (As and Se), and domestic wastewater (As, Cd, Cr, Cu, Mn, Ni and Zn). The disposal of metals from industrial activities is approximately 10-20 times greater for Cd, Cr, Cu, Pb, Hg, Mo, Se and Zn than the releases from weathering of geologic materials (Adriano, 2001).

The metal load on agricultural soils originates from atmospheric deposition and the input from the addition of fertilizers, biosolids, metal containing pesticides, and wastewater. As far as natural atmospheric sources are concerned, a large propotion of the atmospheric emissions is attributed to ash from forest and bush fires and to direct loss from vegetation. In industrial countries atmospheric deposition can be an important source of metals for soils and plants in agro ecosystems (Haygarth & Jones, 1992). The annual Cd deposition may vary from 0.1 g/ha in remote areas to over 2.4 g/ha in industrialized regions (Kohsiek et al., 1994).

Phosphatic fertilizers contain varying amounts of Zn, Cd and other trace elements that originated from phosphate rock. Wastewater from fertilizer works in New Zealand has been shown to contain high levels of Cd (20-30 mg/m^3) (Goldstone, 1983). The super phosphate fertilizer produced also contains high levels of Cd (30-69 mg/kg). The most usual Cu fertilizer is $CuSO_4.5H_2O$, although other compounds, mixtures and chelates are also used to supply Cu to soils (Khan, 2001). Copper compounds have been used for many years as fungicides and bactericides. Copper hydroxide has been used in fairly large amounts in sprays (Bordeaux mixture) as a blanket preventive treatment (Florez-Vélez et al., 1996). These sprays can enrich Cu in the soil by as much as 11.2 to 16.8 kg/ ha/yr (Khan, 2001).

Metalworking includes electroplating, galvanizing, anodizing, paint stripping and other metal working processes. The galvanizing and metal plating industry wastes concentrates generally exceed the New Zealand trade waste law limit (5000 mg/m^3) (Smith, 1986). There were 15 enterprises in New Zealand involved in the dyeing, printing and finishing of rugs in 1981/82 (New Zealand Year Book, 1984). Carpet mills in New Zealand use dyes containing Cu, Co, Cr and Ni complexed with organic molecules. In Auckland, laundry, soft drinks and ice cream industrial effluents contain high level of Cu and bakery wastes are high in Ni. Dairy factory wastes contain Cu, Cr, Ni and Zn (Smith, 1986). Piggery effluents contain a high levels of Cu and Zn (Overcash et al., 1978), which are used as growth stimulants and dietary supplements. Sludge from these industrialized areas contains a larger industrial input than that from non-industrialized areas. The wood preservative industry is one of the major markets for Cu (Loebenstein, 1993). McLaren et al. (1994) reported that Cu leached through the lysimeters ranged from 4 to 305 of the total Cu applied from a CCA solution (Cu, Cr and As).

Sewage effluents have been applied to land in Europe and Australia for nearly a hundred years (Adriano, 2001). Cadmium, Zn, Cu, Ni and Pb are important potential hazards if present in wastewater. Sewage sludge typically contains organic matter, trace elements, pathogens, organic chemicals, and essential plant nutrients and dissolved solids. Over 5.5 million dry tons of sewage sludge is produced annually in the United States (U.S. EPA, 1993) and comparable amounts are generated in Western Europe (Davis et al., 1992). Of the total sludge generated in the United States, approximately 33 % is destined for land application, about 33 % for land filling, 16 % for incineration, and the balance for surface and ocean disposal (Adriano, 2001). Zinc is the most bioavailable sludge-borne metal, followed by Cd and Ni (Adriano, 2001). Between 25 % and 40 % of the total annual input of Zn, Cu and Ni (5247, 1821, and 225 tons for Zn, Cu and Ni respectively) to agricultural land was derived from animal manure, and <15 % from sewage sludge (Adriano, 2001). Approximately 52000 tons of dry sludge solids are produced every year in New Zealand. Seventy percent of this was generated at three of the main population centres-Auckland, Wellington and Christchurch (NZ Department of Health, 1992). A typical level of cadmium in New Zealand municipal sewage is 9.2, with 11.6 mg/kg in Auckland and Christchurch respectively. The maximum acceptable Cd, Ni, Cu and Zn concentrations in dry sewage sludge for land application are 15, 200, 1000 and 2000 mg/kg respectively. The maximum allowable soil applications of Cd, Ni, Cu and Zn are 1-5, 60-125, 100-375 and 200- 700 mg/kg for agricultural and non-agricultural land respectively (NZ Department of Health, 1992).

Sewage sludge, until recently, has not been applied in appreciable amounts to agricultural land in Australia or New Zealand. This situation will soon change because of a recent government decision to ban the discharge of sewage, treated or otherwise, into the ocean and to restrict its incineration. This may lead to disposal of the sewage into the land. Therefore, sewage needs to be considered as one of the sources of elements, which are potentially toxic to the environment (Tiller et al., 1997).

2.2.2. Chemistry of heavy metals

The chemistry of heavy metals in the natural water system is complex and dependent upon many factors (Smith, 1986). The ability to classify dissolved metal concentrations into groups of species is important in studying water chemistry and heavy metal toxicity. The determination of total concentration of heavy metal provides very little information about its bioavailability. Depending on the chemical form of the metal, water with a high total metal concentration may be less toxic than one with a lower total metal concentration (Adriano, 1986; Sparks, 1995).

Cadmium belongs to group II B of elements in the periodic system. In aqueous solution it has the stable 2+oxidation state. Cadmium is a d^{10} acceptor and for this reason has interesting solution chemistry (Moore & Ramamoorthy, 1984). Different chemical species can be found in solution and solid phase. The dissolved metal content may be present in the following forms (Alloway, 1995):

(i) Hydrated ions,

(ii) Complexes with inorganic ligands, like chloro, carbonato and hydroxo complexes, that are more or less labile,

(iii) Chelated with organic ligand such as amino, fulvic, humic, nucleic acid and protein and chelators of anthropogenic origin.

The suspended and colloidal particles may also consist of individual or mixed hydroxide, oxide, silicate, sulfide or other compounds that may consist of clay or organic matter to which metals are bound by adsorption, ion exchange or surface complexation (Moore & Ramamoorthy, 1984).

Zinc also belongs to group II B of elements in the periodic system. It can be found as free (hydrated) metal ion, simple metal complexes and metal associated with colloidal particles in organic and inorganic forms. It forms strong complexes with chloride ion and powerful complexes with fulvic acid and sulfide. Zinc adsorbs strongly on ferric hydroxide at pH values above 7 (Alloway, 1995; Pendias & Pendias, 2001).

Copper belongs to group I B of elements in the periodic system. Copper complexes have been isolated in the I, II and III oxidation states. Copper (II) is the normal oxidation state for soluble aqueous complexes. Insoluble aqueous complexes of Cu (I) are also quite stable. Copper (III) complexes are relatively few. Copper (I) is classified as a soft acid and forms stable complexes with typical soft bases (I^-, S^{2-}, $S_2O_3^{2-}$ etc); Cu (II) is considered to lie between the hard and soft acid classification and typically forms bonds with hard bases (CO_3^{2-}, SO_4^{2-}, OH^-, Cl^-)(Alloway, 1995; Kabata-Pendias & Pendias, 2001).

Therefore, the bioavailability and toxicity of the heavy metals depends not only on the total concentration but also on their ability to form complexes with organic and inorganic ligands.

2.2.3. Binding capacity of heavy metals

2.2.3.1. Organic ligands

The uptake of heavy metals by sludge particulate can be significantly affected by dissolved organic matter (DOM) (Huang et al., 1987). The increase in DOM concentration can mask the toxic effects of divalent nickel on the nitrification process (Sherrard, 1983). Kao et al. (1982) also found that the uptake of divalent Cd was reduced by one order of magnitude in the presence of Ethylenediamine tetra acetic acid (EDTA). Tien and Huang (1987) observed that copper uptake decreases with pH in an alkaline region, whereas DOM concentration increases. This could be due to the formation of Cu-DOM complexes that are not significantly absorbable. The same phenomenon was also found by Wang et al. (1996) for Cu and Ni uptake by sludge particulate. Fristoe and Nelson (1983) reported that, at the same DOM concentration, the formation of metal – DOM complexes were significant when pH was greater than 5.

Gardiner (1974) found the amount of Cd bound by humics to be dependent on both pH and organic ligand concentration. He concluded that organic ligand is unprotonated and that some of the ligand molecule complexes contain more than one metal ion. The total functional groups of humic substances are the sum of carboxyl and phenolic OH groups. These functional groups dissociate between pH 5-7 and expected to bear a net negative charge, which forms soluble complexes with metal ions.

At pH 3.5, Cu, Fe, Ni, Pb and Cd all form more stable complexes with fulvic acids than does calcium (Stevenson & Ardakani, 1972). Both relative electro negativity and ionic radius are important parameters in determining the stability of metal organic complexes (Kabata-Pendias & Pendias, 1992; Alloway, 1995). The low affinity of organics for Ca^{2+} can be explained by its large ionic diameter and low relative electro negativity. Aluminum has the smallest ionic radius and highest relative electro negativity of the ions. As a trivalent ion, aluminum may also have a greater affinity for organics. Low concentrations of metals may be more highly complexed at a given humic acid concentration than at higher metal concentrations when less active sites are used (Gardiner, 1974; Jenne & Luoma, 1977). Gardiner (1974) found that the fraction of Cd complexes by humics was only slightly dependent on pH. Binding capacity studies have indicated that the amount of Cd bound by organics is often small. Zinc and Cd do not occupy many of the potential binding sites as compared to Pb and Cu, which occupy all of the acidic functional groups, when possible binding sites are saturated. Zinc and Cd have lower relative electro negativity than does either Cu or Pb.

It can be concluded that as far as organic complexation is concerned, Cu forms more stable complexes with organic ligand than do Cd and Zn.

2.2.3.2. Complexation with inorganic ligand

Increased concentrations of Cl^- (a border line soft base) significantly affect trace metal speciation while having a limited influence on the speciation of hard acid cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+} and Al^{3+})[Wolt, 1994]. The bio geochemical availability of total Cd in soil solution is significantly influenced by numerous complexation reactions. The complexes of great importance are those with soft bases as Cd^{2+} is a soft acid. The dominant complexes occur with SO_4^{2-} and organic carbon in acid soil. In alkaline soil Cd complexes shift from organic carbon to SO_4^{2-} and CO_3^{2-}. The formation of Cd-Cl complexes increase in both acid and alkaline soils as total Cd increases. Sorption of Cd depends on the dominant complexing ligand in solution. Enhanced sorption in the presence of HCO_3^- may be due to the formation of $CdHCO_3^+$ ion pair and its subsequent sorption or from the precipitation of $CdCO_3$. Decreased sorption in the presence of Cl^- may be due to formation of the $CdCl^+$ ion pair supporting greater total Cd in solution (Wolt, 1994)

Cadmium forms very stable soluble complexes with Cl^- ligands (Alloway, 1995). Evans et al. (1991) found that the reduction in metal adsorption in the presence of Cl^- was Zn<Pb<Cd<Hg and this was directly related to the ability of the metals to form complexes with Cl^-. Zinc also forms complexes with chloride, phosphate, nitrate and sulphate. Zinc sulphate and $ZnHPO_4$ are the most important and may contribute significantly to total Zn in solution (Alloway, 1995).

The relative selectivity for metal cation can be largely explained in terms of the Lewis hard-soft acid base (HSAB) principle. Soft acids prefer soft bases. Soft Lewis acids include Cu^{2+}, Ag^{2+}, As^+, Cd^{2+}, Hg^{2+}. Borderline metals, which do not fit so well into the classification, include Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Sb^{3+} and Pb^{4+}. Complexing ligands can complicate the application of HSAB principles as in the case of Cl^-, which reacts with Cd^{2+} and reduces the amounts of Cd adsorbed (Alloway, 1995).

Inorganic ligand plays an important role in the retention and mobility of heavy metal. Therefore, inorganic ligands play an important role in the control of heavy metal in the environment.

2.2.4. Heavy metals in sludge

The metal concentrations in sludge (aerobic or anaerobic) are relatively high in all treatment because most metals accumulate in the solids fractions during wastewater treatment. Seventy to 90% of the heavy metals are removed and retained in solid fraction, which forms sewage sludge (Nelson et al., 1981). Soil amended with sewage sludge causes an increase in soil concentration of heavy metals. Treating soil with sewage sludge shifts the solid phases of soil metals away from the residual form (immobile) to a form that is potentially more mobile, labile and available to soil organisms.

2.2.4.1. Forms and amount of heavy metals in sludge

Amounts of heavy metal in sludge from different sources are variable. So each sludge sample needs to be assessed individually prior to its application to land. Normally, smaller cities with little industrial waste components contain lower concentrations of heavy metals except for Cu and Zn, which probably result from the erosion of pipes. Extraction of digested sewage sludge with water or a weak salt solution has shown 1.5-14.3% of Ni, 7-11% of Cd, .3-6% of Cu, <1-1.7% Zn in solution as free metal ion (Lake et al., 1984). Reimers (1983) suggested that the heavy metal affinity for sorption on the sludge particles depend on the sludge type. Under the aerobic condition, the carboxylic group is the organic functional group. The hard Pearson acids such as Cr^{3+}, Fe^{3+}, Mn^{3+} Co^{3+} have a high affinity for aerobic waste sludge. $Cadmium^{2+}$, Cu^{2+}, Pb^{2+}, Zn^{2+} and others have a greater affinity for anaerobic waste sludge that contains amine and the sulfahydryl organic functional group. Nevertheless, beyond the dissimilarities between aerobic and anaerobic digested sludge, there are more important differences between digested and undigested sludge. The freshly precipitated sulfides as well as the carbonates play an important role in aerobic sludge (NATO, 1983).

The principal metal forms in sludge are soluble, precipitated, co-precipitated with metal oxides, adsorbates and associated with biological residues (Lester et al., 1983). The distribution of metals between the specific forms varies widely according to the chemical properties of the individual metal and the characteristics of the sludge, which are a function of the physical and chemical properties imposed by the particular sludge treatment process. These include such parameters as pH, temperature, oxidation-reduction potential, the presence of complexing agents and the concentration of precipitant ligands (Gould & Genetelli, 1978).

The occurrence of water-soluble forms of heavy metals in digested sludge has been investigated by simple aqueous extraction. Extraction of air dried, digested sludge with tap water or 0.06 M $CaCl_2$ solution resulted in approximately 2% of "Cu" being leached while 11 % of Cd and 36 % of Zn were water soluble (Lagerweff et al., 1976). Extraction techniques based on acidification or chelating organics, which have been used to determine "available" forms of metals in soils, have also been applied to sludge. Cadmium and Zn occurred in sludge predominantly in carbonate form (Emmerich et al., 1982a). Ethylenediamine tetra-acetic acid (EDTA) extracted greater than 90 % of Cu and Zn carbonate but only 68 % of $CdCO_3$.

2.2.4.2. Heavy metal fractionation from soil and sludge

Where pollution has occured by heavy metals, it is important to identify the available and unavailable forms to ensure that the soil is managed in such a way as to prevent the unavailable forms from becoming available. The most common and simplest way to identify the forms in which heavy metals are found in soils is to use sequential extraction in which heavy metals loosely held by the soil components are extracted first, followed by those more tightly bonded (Beckett, 1989). The various forms of the heavy metals thus sequentially extracted can be classified as dissolved, exchangeable, organically bound or bound to oxides. Only those fractions which are soluble or which may be solubilised are bio available. It is therefore important to distinguish between the total quantities and the amounts which can be transferred into more soluble forms. The total amount of Zn in soils is distributed over distinct fractions; water soluble, exchangeable, metal bound to organic ligand; bound with primary silicate and bound with secondary minerals. The distribution of Zn among these forms is governed by the equilibrium constants of the corresponding reactions in which Zn is involved.

The neutral salts like potassium nitrate (KNO_3), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$) are assumed to take-up "exchangeable" forms of heavy metals, sodium hypo chloride or pyrophosphate or hydrogen peroxide (Shuman, 1985) associated with organically bound form and the carbonates associated with Na_2-EDTA form. Reducing agents such as ammonium oxalate have been widely used to release metals bound in Fe and Mn oxides, while strong concentrated or boiling nitric acid with-or without-hydroflouric acid or perchloric acid has been used to assess residual or occluded metals in soils.

Beckett (1989) extensively studied several extractants. He suggested organic solvent treatment might increase the efficiency of water-soluble extractants. Anyhow, several researchers have concluded that Cd, Pb and Zn are dissolved in the non-polar organic solvents. Therefore, no attempt was made to use organic solvent in the extraction of metal from sludge.

Excellent reviews of extraction techniques used for determination of soil metal fractions are given by Lake et al. (1984) and Beckett (1989). Single chemical extraction is generally used to determine "available" amounts of soil metals and usually aims to extract the water soluble, easily exchangeable and some of the organically bound metals. Other metal fractions may become available over time through chemical weathering or organic matter decomposition, but metals occluded by stable secondary minerals may not become available in the short or medium term.

Sludge metals are mainly present in carbonate and sulfide form with substantial amounts of organically bound metals. Sposito et al. (1982) found that Zn, Cd and Pb were mainly present in carbonate form. Irrespective of sludge application rate, exchangeable amounts of metals were very low, averaging between 1.1 and 3.7% (Sposito et al., 1982). In sludge amended soils Zn was mainly present as carbonate and Fe oxides, while Cd was mainly present in residual and carbonate forms.

2.2.5. Impact of heavy metals in the environment

There are only limited data available on the impact of atmospherically sourced heavy metals onto agricultural land. Increases in Cd concentrations in soil due to phosphatic fertilization have been estimated in different Australian reports, with measured increases in Cd concentrations in surface soils of up to 0.14 and 0.18 mg/kg soil for cereal and pasture soils near Canberra (Williams & David, 1973). An issue of greater importance than the total concentrations is the concentration of phyto and bioavailable heavy metals controlled by soil and environmental factors. The CSIRO Land and Water Soil Contamination group has used an exhaustive EDTA extraction (Clayton & Tiller, 1979) as a first approximation of the total potentially available toxic metal. Even metals are immobile in managed agricultural soil (McBride, 1995); factors that enhance mobility could result in more plant uptake or leaching of metals to the ground water.

Cadmium and Ni poisoning in humans causes severe dysfunction of the kidneys, reproductive system, liver, brain, and central nervous system. Also, it has been known to be carcinogenic and is reported to be bio accumulated into flora and fauna, thus creating an ecological problem. Their chemical form profoundly affects the toxicity of heavy metals. Copper found in natural waters is very toxic to algae.

The metals in sewage sludge are bound tightly by organic matter and their bioavailability will be much less than equivalent concentrations present as soluble metal salts. Smith (1995) showed evidence of heavy metal movement in a sandy soil treated with sewage sludge after a period of 25 years. Direct leaching of metals has also been reported by Lamy et al. (1993). However, in both studies, concentration of metals in drainage leachate remained below drinking water limits. If wastes contain significant quantities of metals in the form of simple inorganic salts, leaching to ground water is more likely to be a problem. In spite of this, some studies have shown that application of metal containing sewage sludge to land can have a deleterious effect on soil microorganisms, particularly after sludge application has ceased and the organic matter content of the soil has declined (Brookes & McGrath, 1984; Giller et al., 1989; McGrath et al., 1988).

Certain concentrations of heavy metals are toxic to most microorganisms and often cause serious upsets in biological waste treatment systems. Many different species of bacteria isolated from activated sludge have been shown to be able to produce polymers or capsules. It has been reported that different metal adsorption sites exist on neutral polysaccharides and anionic polysaccharides. The hydroxyl group (R-OH) of the hexose and the carboxyl group of nucleic acids, proteins and carbohydrates with uranic acid residues may be the metal binding sites of sludge solids (Neufeld & Hermann, 1975). Activity of a metal ion in a given biological treatment system generally depends upon its species and concentration. It has been reported that only soluble metal ions cause toxicity (Sherrard, 1983).

The mechanism by which heavy metals affect the microorganisms is not clear. Heavy metals may block the enzyme systems or interfere with certain essential cellular metabolites of most bacteria and some protozoa. The heavy metals are also known to coagulate and precipitate proteins, many of which are denatured by this action. Copper and chromium react with certain R-SH compounds by neutralizing the thiol (-SH) group within the cell (NATO, 1983).

Burgess et al., (1999) concluded that a concentration of 1 mg/L Cu, Ni or Zn had detectable effects on purification by the activated sludge process: these were an increase in turbidity and a reduction in nitrification. Gelmann (1955) also reported that 1 mg/L of copper affects the activated sludge process. He found that the copper toxicity decreased at a pH between 5-6.5. However, Sherrard (1983) reported that increasing the concentration of Cu from 1-10 mg/L had no effect on the proportion of ammonia oxidized, but a further increase to 20 mg/L started to decrease the degree of nitrification.

The mean cell residence time is considered to be another important parameter determining the magnitude of the metal effects (Bagby & Sherrard, 1981; Bailey, 1986; Neufeld & Hermann, 1975; Sherrard, 1983). However, the overall performance of the unit was found to be highly dependent on the type and the concentration of the heavy metal. Up to 10 mg/L, Ni did not adversely affect the activated sludge kinetics (Dilek and Yetis, 1992).

If the present emission policies and limit regulations are maintained long term in the future, environmental Zn and Cu concentrations will continue to rise, possibly leading to further ecological damage (McBride 1995; Tiller et al., 1997).

Table 2.1. European Community Limits for the Use of Sewage Sludge on Agricultural Land[a]

Metal	Concentration in Soil (mg/kg)	Concentration in Dry Sewage Sludge (mg/kg)	Annual Application Rate (kg /ha/ y) [b]
Cadmium	1--3	20-40	0.15
Copper	50-140	1000-1750	12
Nickel	30-75	300-400	3
Lead	50-300	750-1200	15
Zinc	150-300	2500-4000	30
Mercury	1--1.5	16-25	0.10

[a] Assumes soil pH in range 6-7.

[b] Based on 10-year average.

Table 2.2. U.S. Environmental Protection Agency Limits for the Use of Sewage Sludge on Land[a]

Pollutant	Limit Con. for Sludge[b] (mg /kg dry wt)	Cumulative Loading limit Area basis (kg /ha)	Cumulative Loading Limit Soil Basis[c] (mg/ kg)	Limit Con.. for "Safe Sludge"[d] (mg/ kg soil).	Annual Loading Limit (kg /ha/y)
Arsenic	75	41	31	41	2.0
Cadmium	85	39	29	39	1.9
Chromium	3000	3000	2260	1200	150
Copper	4300	1500	1130	1500	75
Lead	840	300	226	300	15
Mercury	57	17	13	17	0.85
Molybdenum	75	18	14	18	0.90
Nickel	420	420	316	420	21
Selenium	100	100	75	36	5.0
Zinc	7500	2800	2100	2800	140

[a] USEPA.1993

[b] Absolute for beneficial use.

[c] Soil limit based on 10cm plow depth x bulk density=1.3 t m^{-3}; values would be correspondingly lower for deeper plow layers.

[d] Unrestricted.

Table 2.3. New Zealand guidelines for maximum permissible applications of heavy metals to land*

Element	Max. annual Application (kg/ha)	Max. Concentration in soil (mg/kg)
Arsenic	-	10
Cadmium	0.2	3
Chromium	15	600
Copper	12	140
Lead	15	300
Mercury	0.1	1
Nickel	3.0	35
Zinc	30	300

* NZ Department of Health, 1992.

2.2.6. Control of heavy metals in the environment

The global perspective of the increasing accumulation of heavy metals has stimulated the efforts to control emissions and disposal and to rehabilitate contaminated lands. It is well recognized that prevention of contamination of agricultural land should have the highest priority of all strategies to protect soil, crop and water quality and-ultimately-human and animal health. For this Australia and New Zealand are in the process of establishing stricter controls on industrial atmospheric emissions and on water used for agricultural purposes. However, where soil contamination has occurred, strategies are needed to control the transfer of contaminants from soil through the food chain to animals or humans.

There is a direct link between fertilizer use and heavy metal contamination. Sparrow et al. (1993) showed that for potato production, addition of P increases tuber Cd concentration at constant rates of Cd addition. In Australia there has been little work on the interaction between fertilizer application and heavy metal uptake. Sparrow et al. (1994) found that potato crops fertilized with potassium sulfate instead of potassium chloride had lower tuber Cd concentrations.

During recent decades it has been known that soil pH has a key role in controlling the mobility and availability of trace metals to crops. McLaughlin et al. (1994) demonstrated that soil salinity increased the phytoavailability of Cd for crops.

Crops such as wheat and potatoes also have been bred to limit the uptake of undesirable soil contaminants. Since these varieties were not chosen on the basis of their ability to adsorb soil Cd, there is a real risk that inadvertent accumulation of Cd may occur (Tiller et al., 1997).

National guidelines are being prepared by the National Health and Medical Research Council (NHMRC) and the Australian and New Zealand Environment and Conservation Council (ANZECC) to initiate some investigation in to limiting soil contamination. The NHMRC/ANZECC and other guidelines are established primarily for contaminated sites affected by industrial on-site and atmospheric sources of heavy metals. New Zealand has no regulations regarding permitted concentrations of heavy metals in fertilizers, although its fertilizer manufacturers are currently adopting voluntary controls similar to those in Australia.

The European Community has established regulations (CEC, 1986) for the disposal of sludge on land. These restrict the quality of the sludge being applied to the amount of pollutant metal that can be added over a prescribed period. The U.S. Environmental Protection Agency (USEPA, 1993) has revised rules and regulations, commonly referred to as Part 503, for the disposal of sewage sludge on land. The USEPA rules were developed in terms of ceiling concentrations (limit values)- above which sludge cannot be used on land-and a cumulative pollutant loading, which effectively defines a limit when soil background values are included. Pollutant limit concentrations are also defined for a “clean sludge” which may be used without restriction.

Many countries are regulating sewage sludge application to land to avoid present and future metal toxicity. Ross (1994) has suggested that other parameters such as pH, Fe and Mn oxides and soil organic matter content might be more appropriate predictors of soil metal retention. New South Wales and South Australia have recently (NSWEPA, 1994; SAEPA, 1996) published provisional guidelines for the application of sewage sludge on land, which provide limitations relating to sludge quality and land use. Although the general approach is similar to that of the USEPA, the quality of sludge for unrestricted use and the total permitted loading of contaminants are much more restrictive, especially for Cd. Tiller et al. (1997) and McLaughlin et al. (1996) showed that unacceptably high concentrations of Cd in agricultural crops could be produced on saline soils in Australia, even on soils with less than 0.5 mg Cd/kg.

Although some research is currently underway in New South Wales and some research on sewage sludge has been published (De Vries & Tiller, 1978; Ross et al., 1992), environmental authorities are under pressure to develop guidelines without access to locally relevant data.

The 1992 New Zealand guidelines for maximum permissible applications of heavy metals to land and maximum concentrations in soil are shown in Table 2.3. McBride (1995) concluded that the current regulations might not be able to protect soil health and productivity.

2.3. ADSORPTION

Adsorption is *a process by which material accumulates at the interface between two phases*. Adsorption onto solid adsorbents has great environmental significance, since it can effectively remove pollutants from both aqueous and gaseous streams. This process is suitable for the control of certain inorganic compounds such as heavy metals and gases. *Biosorption* is *the passive or physio-chemical binding of chemical species to biopolymers of biomass types* (Maranon & Sastre, 1991; Volesky & Holan, 1995; Gardea-Torres dey et al., 1996). It is more economical as waste material can be employed as adsorbents.

Adsorption is a surface phenomenon. As the result of surface forces between adsorbent and adsorbate, the molecules or atoms of adsorbate are bound to the surface of the adsorbing material. Adsorption is typically without a permanent chemical reaction at the interface, while absorption refers to a permanent chemical reaction or changes of the phase.

The adsorbent is generally porous, with an external surface, which is only a small part of the total surface.

2.3.1. Adsorption principles

There are two principal mechanisms involved in biosorption. (1) Ion exchange (Physical sorption), wherein ions such as Na, K, Mg and Ca become displaced by heavy metal ions; (2) Complexation between metal ions (Chemical sorption) and various functional groups, such as carboxyl, amino, thiol, hydroxyl, phosphate, and hydroxyl-carboxyl, that can interact in a coordinated way with metal ions (Volesky and Holan, 1995). It has been suggested that two stages are involved in the kinetics of metal uptake. The first stage, thought to be surface adsorption on the cell wall, is a reversible reaction and occurs a short time after the microorganism comes into contact with the metal. This first stage is characterized by a relatively low enthalpy of biosorption. The second stage, usually referred to as *active uptake*, is a slower intracellular bioaccumulation, is often irreversible and is related to the metabolic activity. The slower phase of metal uptake can be due to a number of mechanisms, including covalent bonding, surface precipitation, redox reactions, crystallization on the cell surface or membrane transport of the metal ions into cell cytoplasm and binding to proteins and other intracellular sites (Zouboulis et al, 1999). This second phase will form only mono-layer and characterized by difficulty of desorbing the adsorbed layer (Lawson et al., 1984)

2.3.2. Factors influencing equilibrium adsorption

Molecules of solutes are removed from the solution by the adsorbent during the adsorption process. Simultaneously, the adsorbed molecules are desorbed into the solution. The process will continue until the concentration of solute remaining in solution is in equilibrium with the concentration of the adsorbed molecules. As it is a reversible reaction, adsorption still occurs in the equilibrium stage. The rate of adsorption is equal to the rate of desorption at that point (Volesky and Holen, 1995; Zouboulis, 1999).

2.3.3. Characteristics of the adsorbent

The adsorption process depends primarily on the characteristics of the adsorbent. Some of the properties of the adsorbent which have been studied are a) surface area b) particle size c) uniformity coefficient d) bulk density e) particle density f) iodine number g) molasses number (Chareonsudjai, 1994).

The larger the surface area the greater the adsorption capacity. Iodine number and molasses number are the standard tests for measuring the volume of the adsorbent pore size. The Iodine number is used to determine the pore size from 10-28 A° in diameter, whereas the molasses number measures the pore size greater than 28 A°(Chareonsudjai, 1994). These numbers show the adsorbability for low and high molecular weight molecules respectively.

2.3.4. Bio-sorption sites

The anionic character of bacterial surfaces acts like a sponge that can soak up metal ions (McLean & Beveridge, 1990). There are two main active functional groups on cell wall exopolymer. The carboxyl groups and hydroxyl groups are available to react with cationic metal ion. The electronegative charge from the lone- pair electron of oxygen in both groups is the active site for metal binding (Brown & Lester, 1982).

Gram-positive bacteria have a thick layer of peptidoglycan on the cell wall. This structure will have at least one carboxyl group on the terminal of every amino acid of the peptide chain. Every carboxyl group gives a negative charge along the repeating units of the chain. Phosphate groups also contribute to the anionic characters on the chain. These negative charges will react with the positive charges of the cationic metals by the chemisorption process (Chareonsudjai, 1994).

Extracellular polymers (slime and capsule) are the important active sites for metal binding. Anionic groups of exopolymer may be different from those on the cell wall. Composition of the capsule is different among bacteria. Most capsules consist of linear polymers of polysaccharide or amino acid repeating units (Sutherland, 1997). They may sometimes contain other anionic groups, such as carboxyl groups and occasionally phosphate and sulfate groups (Smiley & Wilkinson, 1983). Carboxyl groups in a capsule can react with metal ion like those in the cell wall.

One difference between the cell wall and capsule is the ridge structure of the cell wall. Cross-linked bonding between adjacent molecules fixes the structure of the wall, while the structure of the capsules is loose. The amount of metal bound by bacterial extra cellular polymers may be quite high.

Geesey and Jang (1990) reported that exopolymer is the most important biosorption site. The sub unit composition and structure of extra cellular polymers determine their physical properties. Most microbial exopolysaccharides are extremely hygroscopic. More than 99 % of the volume of a hydrated polymer is contributed by water.

The capsules of most bacteria contain uronic acids from 5-25 % (Sutherland, 1980). Certain species produce ketal-linked pyruvate (Boyle & Reade, 1983; Dewitt & Rowe, 1961). These subunits of capsule show an anionic character because of their carboxyl groups.

Furthermore, polysaccharides also contain an abundance of hydroxyl groups in their sugar rings. The electronegative oxygen atom of the hydroxyl group is likely to participate in metal ions. This hydroxyl site was shown to be the most important biosorption site by Brown and Lester (1979).

2.3.5. Characteristics of the adsorbate

Solubility of the adsorbate is the main factor believed to influence the adsorption. The more soluble compound generally adsorbs less than the insoluble compound because the more soluble compound has stronger affinity with the solvent than does the less soluble one. However, efforts to determine a quantitative relationship between adsorbability and solubility have met with only limited success (Benefield et al., 1982)

Molecular size of the adsorbate is another factor affecting the adsorbabilty. Since the adsorbate molecule must enter the micro pore of the adsorbent, molecular size would be important for adsorption. Hassler (1974) reported that adsorption usually increases as the size of the molecule becomes greater in a homologous series of aliphatic acids, aldehydes, or alcohol. Benefield et al. (1982) debated that if the molecule is too big to fit in the micro pore, the adsorption will decrease because the bulky molecule will block the pore size.

2.3.6. Characteristics of system

Since hydrogen and hydroxide ions often interact with adsorbents used in the aqueous phase, the adsorption of other ions may be influenced by solution pH. Benefield et al. (1982) reported that the rate of adsorption depends on the amount of agitation in the system. If relatively little agitation occurs then the surface film of liquid around the particle will be thick and film diffusion will be the rate-limiting step. In contrast, if adequate mixing is provided the rate of film diffusion will increase.

The pH and temperature are the most important parameters influencing the adsorbability. Hydrogen ions are strongly adsorbed on the surface of adsorbents. In addition, pH influences the ionization of many compounds. According to Benefield et al. (1982) organic acids are more adsorbable in an acidic condition, whereas the adsorption of organic bases prefers higher pH. However, the optimum pH for any adsorption must be determined by laboratory testing. Since adsorption is an exothermic reaction, adsorption at lower temperatures is better than at the higher ones. However, the rate of adsorption depends on the temperature. At higher temperatures, the kinetic energy of molecules is high and the collision energy between the adsorbate molecule and the adsorbent is high enough to cross the activation energy.

Examination and preliminary testing of solid – liquid sorption systems are usually based on two types of investigation:

a) Equilibrium batch sorption tests

b) Dynamic continuous flow sorption studies.

The two widely accepted and easily linearized equilibrium adsorption isotherm models for single solute systems used in the literature are the following:

Langmuir: $q = \frac{b\, C_t Q_{max}}{1+bC_t}$

Freundlich: $q = K\, C_t^{\ 1/n}$

Where q is the uptake of solute (metal), Q_{max} is the maximum uptake; C_t is the equilibrium (final) concentration of solute in the solution. b and n are constants related to the energy of adsorption (or affinity) and K is a constant. Some researchers used both models to fit the adsorption data in activated sewage sludge (Aksu & Yener, 1998). Some researchers used Freundlich model than Langmuir model (Chareonsudjai, 1994; Sidle & Kardos, 1977).

The basic evaluation of a sorption system relies on the classical sorption isotherm derived from equilibrium batch contact experiments carried out under controlled environmental conditions. A quantitative comparison of two different sorption systems can be done only at the same equilibrium (final, residual) concentration.

2.4. HEAVY METAL DYNAMICS IN SOILS

The fate of heavy metals added to a soil is controlled by a complex set of chemical reactions and by a number of biophysical processes acting within the soil as shown in figure 2.1. In some respects the chemical behaviour of different metals may be similar, but there is no overall uniformity. Although the initial mobility of these metals after additions to soils largely depends on the form in which they are added (Jones & Jarvis, 1981), their concentrations in soil solutions are affected by solubility phenomena, ion exchange and adsorption-desorption processes, complexation and redox reactions (Helmke & Naidu, 1996).

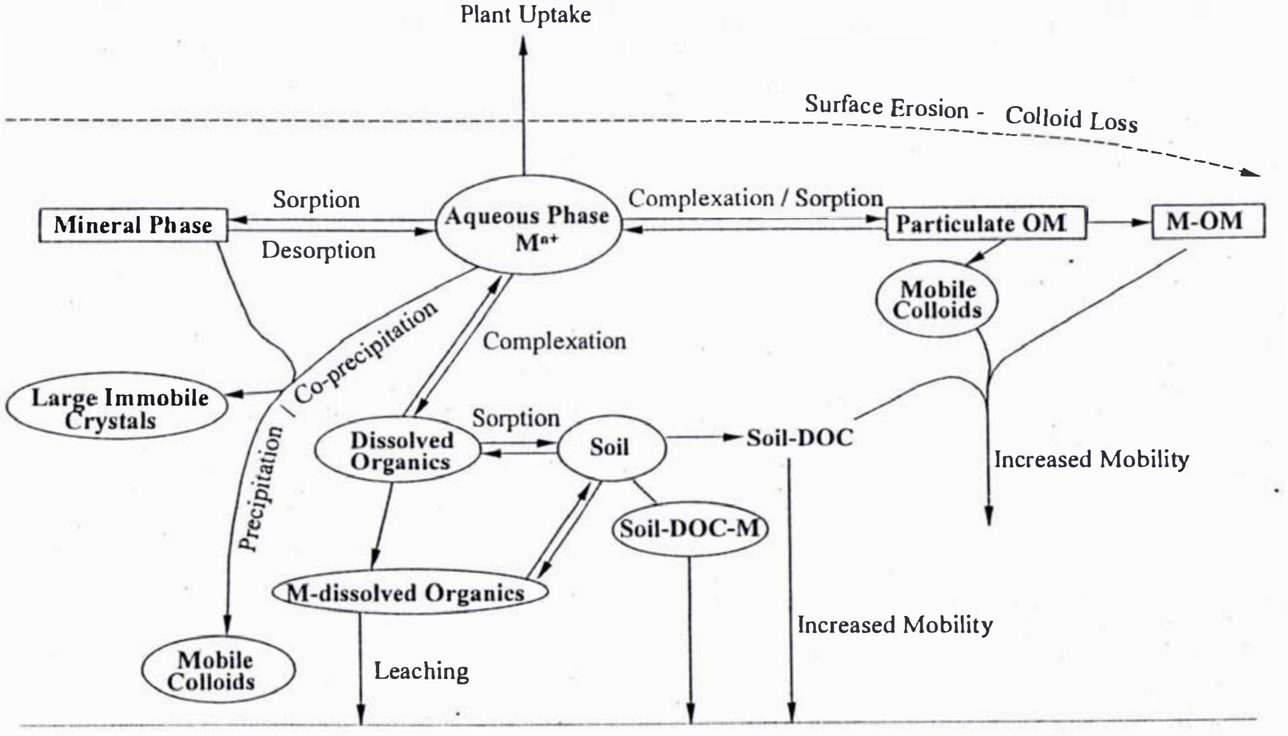


Figure 2.1. **Heavy metal dynamics in soil environment [*Source*, Adriano (2001)]**

2.4.1. Speciation of metals in soil solution

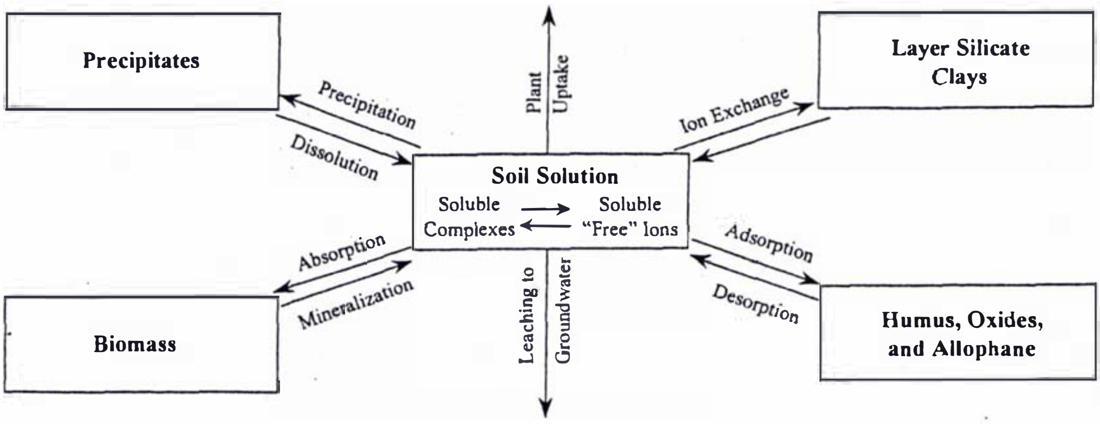


Figure 2.2. **Schematic of key interactive process in the soil system affecting the partitioning of trace metals between aqueous and solid phases [*Source*, Adriano (2001)]**

A schematic representation of the process controlling the partitioning of the metals in the soil is given in Figure 2.2. Metal ions undergo a series of reactions involving both the aqueous and solid phases. These are described in this section. Only a small fraction of the total amount of each element present in the soil system is exchangeable and an even smaller fraction is water-soluble. All free heavy metal ions occur as cations in solution and form hydroxyl compounds (MOH) in the soil. If the metal concentration is sufficiently high precipitates also can form. The free ions may complex with organic and inorganic anions. Chelation with organic ligands usually forms very stable organo-metal anions (Beckett, 1989).

Most of the dissolved Cd and Zn in water extract is present as the free cation (Alloway 1995). Most of the dissolved Cu is in the form of Cu fulvate complexes except at higher pH where the hydroxide ion is competing for the complexation of Cu (Adriano, 2001). Cu^{2+} ion dominates at pH <5, but as the pH increases the contributions of $CuCO_3$, and $Cu(OH)^+$ increase depending on the carbonate content of the water.

However, recent work indicates that a large amount of Cu in fresh water may be associated with humic or other organic material (Martinez and McBride, 1999). Zinc complexes with organic and inorganic ligands are sufficiently soluble (Shuman, 1993). The principal species of Cd in the solution is Cd^{2+} but the metal can also form $CdCl^{+}$, $CdOH^{+}$, $CdHCO_3^{+}$, $CdCl_4^{2-}$, $Cd(OH)_3^{-}$ and $Cd(OH)_4^{2-}$ together with organic complexes (Alloway, 1995; Wolt ,1994)

Two types of soluble complexes are formed between metals and complexant ligand in soil solution (Nederlof and Riemsdijk, 1995). Those are *outer sphere* and *inner sphere* complex formation, also the simple accumulation of an ion swarm near the solid surface. Outer sphere complexes are relatively weak electrostatic associations formed between a hydrated cation and ligands. It is described as nonspecific interaction. Inner sphere complexes or specific interactions are strong associations between metals and ligands. They are characterized a by covalent bond between metal and ligand (Helmke & Naidu, 1996; Nederlof and Riemsdijk, 1995).

Cation exchange refers to *the exchange between the counter ions balancing the surface charge on the colloids and the ions in the solution.* In order to maintain electro neutrality, the surface negative charge is balanced by an equal quantity of cations. Heavy metal cations in solution exhibit typical cation exchange behaviour that is a reversible, diffusion controlled stoichiometric process (Alloway, 1995). The negative charges are permanent and pH dependent. These charges are due to the dissociation of protons from carboxyl and phenolic groups on polymers and hydroxyl groups. The portion of heavy metal cations held by non-specific adsorption is low due to the low solution concentration, relative to base cations such as Ca^{2+}, Mg^{2+} and K^{+} (Swift & McLaren, 1991; Ross, 1994).

Specific adsorption involves the exchange of heavy metal cations with surface ligands to form partly covalent bonds. Heavy metal ions are specifically adsorbed to a far greater extent than that expected from soil CEC (Alloway, 1995). Specific adsorption is strongly pH dependent and is related to the hydrolysis by the heavy metal ion. The metals most able to form hydroxyl complexes are specifically adsorbed to the greatest extent. Ions are retained strongly by covalent and co-ordinate forces (Swift &

McLaren, 1991) and are more readily displaced by other metals than base cations (Beckett, 1989).

Metal ions can also diffuse into the minerals. The diffusion rate of the metal ions increases with increasing pH (Bolan et al., 1999a). The maximum relative diffusion rate for Cd, Ni and Zn decreases in the order Ni>Zn>Cd and can be related to the ion diameter. The dynamic equilibrium between the metal ions in solution and that adsorbed in the solid phase depends on the pH, the chemical nature of the metal species, stability of metal complexes, the binding power of the functional group and the ionic strength of solution and competing ions.

Based on the above discussion it is apparent that complexed, exchangeable and organically bound metals from the labile pool would be bioavailable depending on the factors pH, Eh and ligand concentration.

2.4.2. Sorption into Inorganic Colloids

2.4.2.1. Sorption into silicates

Soil particles especially those found within clay size fraction (<2mm) have an electric charge. Ions in the soil solution are attracted to the charged surfaces. Structural or permanent charges are associated with the phyllosilicate clay minerals where the charge results from charge imbalances due to isomorphous substitution of Al for Si and Mg for Al (McBride, 1994). The charged sites on soil compounds are important for the retention of elements. Cations and anions in the soil solution can neutralize the intrinsic charges on the soil particles by forming either inner sphere or outer sphere complexes (Sposito, 1984). Most soils have net negative charge. Cations in the solution are attracted by electrostatic forces to the negatively charged edges and surfaces of soil particles. These types of cation exchange reactions are generally rapid and readily reversible (McBride ,1994)

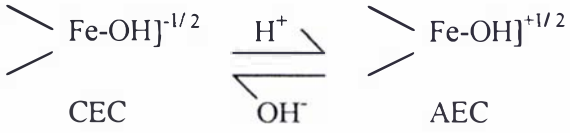
$$\equiv \text{Si-O}^- + \text{M}\,(\text{H}_2\text{O})^{n+}_y \quad = \quad \equiv \text{Si-O}^-\text{----M}(\text{H}_2\text{O})^{n+}_y$$

-Si OH groups at clay edges also can show some specific adsorption and irreversibility at higher pH. This can be due to the formation of hydroxyl polymers of the heavy metals at the silicate surfaces (Tiller et al., 1984).

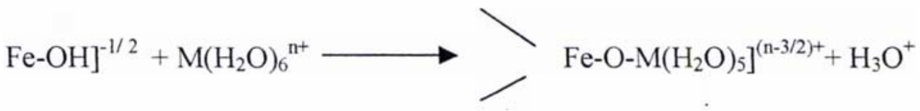
2.4.2.2. Sorption on oxides and aluminosilicates (Allophane)

Unlike the silicate layer, oxides and hydroxides of Al, Fe and non-crystalline alumino silicates possess no permanent surface charge but generate cation and anion exchange capacity as a result of adsorption of protons and hydroxyl ions (McBride, 1994). These retain heavy metal ions by direct co-ordination to the surface, which can be termed *chemisorption*. This specific adsorption involves the exchange of heavy metal cations with surface ligands to form partly covalent bonds (Sposito, 1984). Specific adsorption is strongly pH dependent and is related to the hydrolysis of the heavy metal cations (Brummer, 1986; Alloway, 1995). The metals most able to form hydroxy complexes are specifically adsorbed to the greatest extent.

$$M^{2+} + H_2O = MOH^{+} + H^{+}$$



The H$^+$ could be released into solution and adsorption could originate from the oxide surface or the primary hydration sheath of the adsorbing ion. (Jones & Jarvis, 1981). Non-crystalline aluminosilicates have high specific surface areas, so that their CEC or AEC can be much higher than that of the oxides.



Chemisorption reaction releases H$^+$ ions for each metal cation adsorbed. This is the specific feature that distinguishes it from cation exchange reactions. A high degree of specificity is shown by particular minerals for particular trace metals.

Electro negativity is an important factor in determining which of the trace metals chemisorb with the highest preference. The more electronegative metals should form the strongest covalent bonds with O atoms on any particular mineral surface. For the metals chosen for this project, the predicted order of bonding was Cu>Cd>Zn.

2.4.3. Sorption with soil organic matter

Soil organic matter is an important factor affecting the behaviour of heavy metals in soils. Organic matter is capable of binding heavy metal ions strongly due to the complex formation involving the various functional groups which include COOH, phenolic, alcoholic and –OH and carbonyl (C = O) (Swift & McLaren, 1991). Metals can react with soil organic matter by ion exchange, complexation and precipitation reactions. Complexation reactions are thought to dominate (Helmke & Naidu, 1996). The extent of retention of metals by soil organic matter at pH 5.8 decreases in the order Cu>Cd>Zn>Ni (Schnitzer, 1978). The sequence of the affinity of heavy metal ions for soil organic matter related to selected properties of the metals is: Cu>Ni>Zn>Cd at pH5. Cadmium, a relatively "soft acid" by the Pearson classification of Lewis acids, should prefer soft bases such as sulfur containing ligands, which could generate very high preferences for Cd^{2+}. Copper^{2+}and Zn^{2+} are "borderline" acids with intermediate behaviour (Moore & Ramamoorthy, 1984; Alloway, 1995).

Freundlich isotherm results indicated that Cd, Ni and Zn tend to displace one H^+ ion and Cu two H^+ ions for each complex formed (Gould & Genetelli, 1978). Some researchers say that complexes of Cu are particularly stable and this allows the metal to migrate into the subsoil without being stripped from the complexes by soil adsorption sites (Del-Castilho et al., 1993). Some researchers say Cu forms strong complexes with surface and soluble organics and is less mobile in soil (McBride, 1996). Although metal organic complexation generally leads to decreased mobility, metal- organic complexes can become soluble at pH greater than 7 (McBride, 1994). Numerous studies (Elliott et al., 1986; Tyler & McBride, 1982) have shown that the relative mobility of these elements in soil is Cd>Zn>Cu. Also, as the organic matter in soil decomposes, it could release soluble metal organic complexes. Cadmium and Zn are not bound as strongly to organic matter and therefore the bioavailability would not be as greatly affected by sludge decomposition (McBride, 1995).

$$\mathrm{R{-}COOH} \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftharpoons}} \mathrm{RCOO^-} + \mathrm{H_2O}$$

Humic acids are soluble only in an alkaline medium and fulvic acids are soluble in both alkaline and acid media. Both of these humic substances contain a relatively large number of functional groups (OH, COOH, SH, C=O), having a great affinity for metal ions such as Cu and Zn. Humic acids are insoluble in an acid condition and dissolve gradually as pH increases (Lester, 1987). Fulvic acids mainly form chelates with Zn ions over a wide pH range, thus increasing the solubility and mobility of Zn Helmke and Naidu, 1996). In alkaline media they are completely soluble. Interaction between Zn and humic acids is strongly affected by pH, because the solubility of Zn and humic acids is pH dependent. In acid conditions most of the Zn is soluble, while humic acids are insoluble (Huang, 1995).

Simple organic compounds such as amino acids, hydroxyl acids and phosphoric acids are also effective complexing or chelating agents for Zn, thus increasing its mobility and solubility in soils (Marschner, 1995).

2.5. DESORPTION OF HEAVY METALS

Generally, sorption of metals seems to be more nearly reversible at low than at high pH (Hogg et al., 1993). Adsorption reaction is fast and probably diffusion controlled, whereas the desorption reaction step has a rate constant that may be as much as three orders of magnitude slower. Adsorption reaction is energetically favourable, desorption always requires an activation energy to at least overcome the adsorption energy (Krishnamurti et al., 1999a). Consequently, many chemisorption reactions have much higher activation energy in the reverse than in the forward direction. The commonly observed nonreversibility in metal adsorption may be the result of the long time period that could be required for desorption to be completed (McBride, 1994).

2.5.1. Soil

Metal availability is determined by its activity in the soil solution, which is controlled by both the solid and solution phase characteristics of the soil. Thus the metal availability varies depending on the nature of the adsorption desorption process in the soils. Heavy metal adsorption occurs by both specific and nonspecific process (Naidu et al., 1994). The nonspecific forms can be readily exchangeable with 0.01 M $Ca(NO3)_2$ solution.

The desorption of heavy metals from soils is considered to be an important process (Hogg et al., 1993; Dang et al., 1994; Pardo & Guadalix 1996; McLaren et al., 1998; Krishnamurti et al., 1999b). It is important to determine whether or not sorbed metal ions are readily released from soil surfaces and how release is affected by soil characteristics such as pH.

Swift and McLaren (1991) indicated that desorption is as important as sorption. It controls the amount and rate of release of ions into solution and hence their phyto availability It is often observed that desorption is a more difficult process than adsorption and that not all of the adsorbate is desorbed; the reaction appears to be irreversible. (Sparks, 1995). Desorption occurs at low pH values and for Zn the critical pH value is about 5. Experimental evidence and chemical theory suggest that metal sorption on Fe and Al oxides is an inner sphere complexation and that metals are unlikely to desorb. Herms and Brummer (1984) found big increases in the concentration of Zn and Cd in the equilibrium solutions of soils samples with decreasing pH.

Most studies involving heavy metal have been limited to soils of permanently charged surfaces having net negative charge. Many of the soils have the capacity to sorb relatively large amounts of metal ions (Alloway, 1995). In contrast, soil contains variable charge minerals that have low negative surface charge densities at low pH values. Such soils exhibit low affinity for heavy metals, especially at pH values closer to the point of zero charge (Naidu et al., 1994). In such soils metal adsorption depends on environmental factors such as pH determined by management practices, ionic strength of the soil solution and the presence of organic ligands. Soils with low negative surface charge densities generally have low affinities for metal ions and, particularly at pH values of 4 to 5 (Naidu et al., 1997) heavy metals may become mobile in such soils under certain conditions.

Information on desorption is required to predict the mobility and fate of contaminants in contaminated soils and to develop sound and cost effective remediation strategies. Some studies have been undertaken to assess the desorption of Zn for nonvolcanic soils (Dang et al., 1994). Variable charge soils are widely distributed in New Zealand, representing major volcanic soils. These soils have been used to study the behaviour of Cu and Cd (Bolan et al., 1999b; Hogg et al., 1993; Khan, 2001; McLaren et al., 1998), but there is little information on the behaviour of Zn in these soils.

2.5.2. Sludge

Most of the metals in sludge are associated with the particulate matter and the metal removal system is mainly one of solubilization (Sreekrishnan & Tyagi, 1996). Numerous studies have examined the sorption of heavy metals by sludge (Brown & Lester, 1982; Cheng et al., 1975; Nelson et al., 1981) a very few have examined the desorption process. The metal availability may vary depending on the nature of both the sludge and the adsorption-desorption process. The solubility of metal is governed primarily by pH, temperature, oxidation-reduction potential of the sludge, and the concentration of the metals and ligands (Volesky & Holan, 1995). The metal forms present in the solid phase can be transformed into soluble (mobile) forms which have generally been investigated by means of a chemical extraction technique to distinguish the metals contained in wastewater sludge as metal exchangeable, adsorbed, organic and inorganic bounded. Among these, strong acid extraction may be the most extensively studied method and also that providing the best results along with biological methods. Sreekrishnan and Tyagi (1996) reported that acid leaching is the fastest technique for metal removal from sewage sludges and is suitable for higher plant capacities. In any event, those techniques may influence the polluting power of acid treated sludge and modify the intrinsic sludge characteristics such as nutrient availability, solid content and pH.

Butter et al. (1995) used 1 M Na_2SO_4 to desorb Cd from the waste biomass successfully. However, there is very little literature available on desorption heavy metals from the activated sludge produced in the New Zealand.

2.6. MOVEMENT OF HEAVY METALS IN CONTAMINATED LAND

Once heavy metals have been introduced into cropland, they can be taken up by plants and subsequently become incorporated into the food chain. Although it has been assumed that these metals are immobile in managed agricultural soils (McBride, 1995) factors that enhance mobility could result in more plant uptake or leaching of the metals to the ground water.

Most of the knowledge on movement of heavy metals is based primarily on homogenized soil columns studies; under these conditions there is a strong bonding between the metals and the soil particles (Camobreco et al., 1996). Other field studies showed some leaching of metals through preferential paths where the movement depends on the chemical and biological characteristics of the particular soil type and the type of heavy metal (Camobreco et al., 1996; Sidle & Kardos 1977).

Soil analysis of sludge-amended sites reveals that repeated sewage sludge applications lead to the accumulation of substantial amounts of heavy metals in the soil profile. The deposited heavy metals are concentrated in the surface layer (0-10cm), with relatively high concentrations of heavy metals also present in the 10-20 cm layer (Cameron et al., 1994; Chang et al., 1984; Williams et al., 1980). Touchton et al. (1976), after 2 years and 8 months' addition of sludge found that Cu and Cd had moved into the 0-7.5 cm depths and Zn had moved into the 30 cm depth. Boswell (1975) reported Zn movement to a depth of 30 cm and Cd and Cu to 15cm after the application of 168 metric ton/ha during a 2 year study. Sidle and Kardos (1977) added

27 metric ton/ha of sewage sludge to a forest soil and after 17 months observed that 3.2% of the applied Zn had moved below 120cm in the soil profile.

Even though metals are tightly bound in the surface layers of soil, having only slight movements into the profile, without further addition of organic materials a gradual decomposition and loss of organic matter will take place in the soil. This loss could result in the reaching of high concentration of metals through sludge addition. A direct leaching of metals has been observed by Lamy et al. (1993) who also observed increased leaching of Cd from a sludge-treated forest soil. If waste contains significant quantities of metals in the form of simple inorganic salts, leaching to ground water is more likely to be a potential problem. Soil and sludge characteristics are important factors in controlling the retention and mobility of sludge metals. In particular, metal mobility might be enhanced if sludge and soluble organics reduce the soil pH. A very recent study (McLaren, 2002) reported that Ni and Zn, only a very small proportion of the metals applied in the sewage sludge were leached completely from the soil lysimeters (i.e., below 70cm soil depth).

Most researchers have found that total Zn either remains uniform or increases with depth, while extractable Zn decreases with depth in an uncontaminated soil profile. Korte et al. (1976) stated that Zn movement is controlled by soil texture, surface area, percent of free oxide and pH. Cation exchange capacity was not helpful in predicting movement because Presant and Tupper (1965), found Zn to be highest in the B-horizon where iron oxides are predominant. Copper and Pb form stronger complexes with surfaces and soluble organics than do Cd and Zn. This tends to make them less mobile in soils, but it also provides a greater opportunity for facilitated transport by soluble organics (if present). Numerous studies (Elliott et al., 1986; Tyler & Mc Bride, 1982) have shown that the relative mobility of these elements in soil is Cd>Zn>Cu>Pb.

Dowdy et al. (1991) mentioned the possibility that metals are transported to lower depth in the soil through cracks and macropores in a process they call *nonmatrix water flow* known as *preferential flow*. It has been shown to increase greatly the mobility and velocity of solute movement to the ground water (Steenhuis et al., 1995).

Another factor that could enhance metal mobility is transport of metals incorporated in soluble metal organic complexes-although metal organic complexation generally leads to decreased mobility. Metal-organic complexes can become soluble at pH greater than 7 (McBride, 1994). Also, as the organic matter in soil decomposes, it could release soluble metal organic complexes. Cadmium and Zn are not bound as strongly to organic matter and therefore would not be as greatly affected by sludge decomposition (Mc Bride 1995).

2.6.1. Factors influencing the transport of heavy metal

Transport of metal ions is controlled by both the soil solution composition and the metal ion concentration (Naidu et al., 1997). Chemical parameters such as pH, ionic concentration, index cations, ligands and so on that influence sorption processes control the concentration of metal species in solution and consequently their transport through the soil profile (Naidu et al., 1997). In addition, organic matter and hydrous oxides that provide highly charged sorptive surfaces significantly affect the mobility of metals (Camobreco et al., 1996).

2.6.1.1. Soil and Solution pH

Soil and solution pH have been repeatedly identified as the most important factors in determining heavy metal adsorption and desorption because they can affect the surface charge of layer silicate clays, organic matter and oxides of Fe and Al. (Christensen, 1984; Hornburg & Brummer, 1993; Naidu et al., 1994). In addition to the effect of sorption of cations, which increases with increasing pH, and complexation with organic matter, also influence the precipitation-dissolution reactions, redox reactions, mobility and leaching, dispersion of colloids, and the eventual bioavailability of the metal ions (Naidu et al., 1994).

Increased adsorption of metal ions with increasing values of pH is due to both increased negative surface charge density (Naidu et al., 1994) and the increased concentrations of the MOH^+ species in the soil system (Alloway, 1995; McBride, 1994). Generally, adsorption increases from <20 to 100% within the narrow pH range of 3-5 for all metals (Naidu et al., 1994) except those metals that form oxyanions.

However, the effect of pH on adsorption of heavy metals is dependent on the initial solution concentration, the nature of the soil constituents and the metal retention capacity of the soils (Naidu et al., 1996). In general, Zn has been found to be desorbed at pH 5 (Barak & Helmke, 1993).

Even though the variable charge allopanic soils selectively adsorb more Zn at a pH level below the point of zero charge, these soils may have low affinity for metal cations-especially when the metals are added with sewage sludge which may cause the soil to go below the point of zero charge because of the metal hydrolysis reaction and the decomposition of organic matter in sludge (Helmke and Naidu, 1996).

2.6.1.2. Organic and inorganic ligands

Interactions of organic ligands with metals and consequently their impact on transport are an important factor where metals are introduced into the soil environment (Harter and Naidu, 1995) through land application of sewage sludge. Highly mobile dissolved organic matter has the potential to enhance the chemical mobility of the complexed metals within the soil profile (Dunnivant et al., 1992; Guggenberger and Zech, 1994; Naidu et al., 1993). Naidu and Harter (1997) also showed that in soils with high negative surface charge densities, the presence of organic ligands significantly reduces sorption of Cd. Soluble or colloidal organics emanating from sewage sludge are able to mobilize metals adsorbed on soil or sludge particles (Del-Castilho et al., 1993; Christensen, 1985; Gerritse et al., 1982).

Significant concentrations of natural and synthetic ligands are present in many soils and aquatic systems. The ligand ions generally include Cl^-, SO_4^{2-}, PO_4^{3-} and NO_3^-. The nature and the amount of these inorganic anions have been found to affect the sorption of heavy metal cations by soil particles (Homann & Zasoski, 1987; Shuman, 1986). In temperate soils Cl^- and SO_4^{2-} have been shown to either have no effect or to reduce metal adsorption through the formation of metal-ligand complexes (Homann & Zasoski, 1987). Huangi (1991) and Naidu et al. (1997) showed that the presence of Cl^- ions decreases adsorption of Cd. This could be attributed to the presence of Cd chloro complexes, which have lower affinity for adsorption sites. The influence of ligand ions on the reaction of Cd^{2+} and Zn^{2+} can be quite complex and dependent on the soil type. The formation of metal-SO_4^{2-} complexes in soil solution may decrease the adsorption of metal ions (Bingham et al., 1984; McLaughlin et al., 1994; Roy et al., 1993).

Specific interactions of negatively charged ions like SO_4^{2-} and PO_4^{3-} with variable charged soils may increase the negative charge on soil surfaces and enhance adsorption of metal cations (Naidu et al., 1994). The specific sorption of inorganic anions is likely to increase the negative charge in soil particles and thereby increase the sorption of heavy metal (Bolan, 1999b; Bolland et al., 1977; Shuman 1986).

The presence of inorganic ligands in soil solutions can markedly affect the mobility of Cd and also of other metals. This is because such ligand ions can form stable Cd-ligand complexes. Kookana and Naidu (1996) studied the transport of Cd in an Oxisol in a repacked column in the presence of 0.01 M $Ca(NO_3)_2$ and 0.01 M $CaCl_2$, and found that Cd moved more quickly than did NO_3^- in the presence of Cl^-.

Therefore while the organic ligands have the ability to mobilize the metals adsorbed on soil or sludge particles, inorganic anions have the ability to either increase or decrease the mobility of heavy metal. This depends on the type of inorganic anion.

2.6.1.3. Redox Potential

The moisture content of soils influences their retention of trace metals through oxidation- reduction reactions (Adriano, 2001). In oxidized soils, the redox potential may range from about +400 to+700mV. In sediments and flooded soils, the redox potential may range from around –400 (strongly reduced) to+700mV (well oxidized) (Gambrell & Patrick, 1978). Under reducing conditions, sulfides of metals can form. These are insoluble, so that metal mobility and bioavailability are considerably less than would be expected under oxidized soils (Adriano, 2001).

When soil redox conditions change, the ratio of oxidized to reduced species in solution will also change. Two main types of chemical transformations may be responsible for lowering the mobility and the availability of trace metals under water-logging and reducing soil condition (i) Formation of insoluble sulfide (ii) Formation of discrete carbonate, metal oxide or hydroxide of low solubility.

Therefore, the redox potential is also an important soil factor in regulating the bioavailability of heavy metal.

2.6.1.4. Cation Exchange Capacity

The CEC of soils is largely dependent on the amount and type of clay, organic matter, and the oxides of Fe, Al and Mn (McBride, 1994). In general, the higher the CEC of a soil, the greater the amount of metals a soil can retain without potential hazards. Organic matter has both the cation exchange property and chealating ability (complexation). Trace metals in sludges are taken up less readily by plants when they are added than are they added to sludge as inorganic salts or trace metals added directly to soil in the same concentrations as present in sludge (Hooda & Alloway, 1993).

The adsorption of cations by soils is a competitive process. The degree to which any element is adsorbed depends on the concentration and identity of the other cations in the system. The presence of other divalent cations (Ca^{2+}, Co^{2+}, Cr^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+}) retards the adsorption of Cd by soils due to the competition between Cd and the other metal ions (Garcia- Miragaya & Page, 1976; Homann & Zasoski, 1987).

2.7. CONCLUSIONS

- It is clear from the review of literature discussed above that Cd, Cu, Zn and Ni are the most commonly occurring sludge-borne metals in New Zealand.

- Usage of phosphate fertilizer, agricultural farming system, metal working and painting are the major contributors of the above said heavy metals to the waste water and finally to the sludge in New Zealand.

- The bioavailability and toxicity of these heavy metals depends not only on the total concentration but also on their ability to form complexes with organic and inorganic ligands in the sludge-metal system. The release of heavy metals into the environment is based on the adsorption–desorption of metals from sludge.

Also, the literature suggests that Cu forms more stable complexes with organic ligands than do Cd and Zn.

- Based on the literature available on heavy metal dynamics in the environment it is apparent that complexed, exchangeable and organically bound metals from the labile pool would be bioavailable depending on the factors such as pH, Eh, CEC and organic and inorganic ligand concentrations.

- Variable charge soils, represented by major volcanic soils, are widely distributed in New Zealand. These soils exhibit low affinity for heavy metals at low negative surface charge densities. Some management practices such as sewage sludge application to this soil may create a soil condition, which may lead to lowering the negative surface charge of the soil. Also some environmental factors influencing the surface charge density of this soil such as pH, ionic strength and ligand concentrations have to be studied to predict the bioavailability of heavy metals in this soil since there is little information available in this soil.

- From previous studies it is clear that Cd and Zn are more mobile elements than are Cu and other toxic elements. There are enough studies about Cd and copper in New Zealand soils. But there is little information available on the behaviour of Zn in volcanic soil both nationally and internationally.

- Most of the leaching studies on heavy metals are based on homogenized soil columns, which are unlikely to represent field conditions.

- More than 66% of the total sludge generated in United States is disposed to the land. Australian Government has already banned the incineration and disposal of sewage in to the ocean. The addition of sewage sludge to land leads to leaching of heavy metals in to ground water and it might cause major ecological damage to the environment.

Therefore, there is a need to study (i) the adsorption-desorption of sludge borne metals in sludge and the selected soil environment. (ii) an *in situ* study on more potentially mobile heavy metal when it is applied with sewage sludge on the soil and the effect of commonly occurring nitrate and phosphate on the availability and mobility of such heavy metal in volcanic soil in New Zealand.

Chapter Three

MATERIALS AND METHODS

3.1. INTRODUCTION

This chapter outlines the methods and materials of this research, namely a) biosorption and b) sorption-desorption and movement of Zn from sewage sludge in soil. Different techniques (Chapter One) are available for the removal of heavy metal from industrial and municipal waste. The biosorption technique was used in the current studies (Sec.3.4) to understand the biosorption- desorption of Zn, Cd and Cu onto activated sewage sludge biomass and the factors influencing these processes. The process of heavy metal sorption- desorption was examined in relation to its effect on downward movement in volcanic Egmont soil using the materials and methods outlined in section 3.6 and 3.7 of this chapter.

3.2. SLUDGE AND SLUDGE ANALYSIS

3.2.1. Sludge

The activated sludge mixed liquor produced at the Kapiti Coast, Paraparamua, New Zealand wastewater treatment plant was collected from the aeration tank, because of its high heavy metal content compared to any other closer wastewater treatment plants to Massey University. Total solid content was 3000 mg/L. The characteristics of this sludge are shown in Table 3.1.

3.2.2. Sludge analysis

3.2.2.1. Total solids

A uniformly stirred sewage sludge sample was measured in a clean evaporating crucible (known weight). Then it was kept in an oven at 103-105°C for 1 h. Again, the crucible with residue was weighed (Eaton et al., 1995).

Table 3.1. Physical and chemical analysis of the activated sewage sludge collected from Kapiticoast wastewater treatment plant

Sludge Volume Index	245
Soluble BOD	0.5-2.5
Total solid (mg/L)	3000
pH	6.8-7.0
Total BOD	155-2000
Total N (mg/kg)	24000
Ammonia (mg/kg)	3500
Nitrate (mg/kg)	500
Total P (mg/kg)	12500
Ca (mg/kg)	22100
Mg (mg/kg)	5300
K (mg/kg)	700
Na (mg/kg)	1500
Total Zn (mg/kg)	194
Total Cd (mg/kg)	39
Total Cu (mg/kg)	148
Total Ni (mg/kg)	0
0.1 M $CaCl_2$ extractable Zn (mg/kg)	47
0.05 M EDTA extractable Zn (mg/kg)	126

3.2.2.2. Total suspended solids

A measured volume of uniformly stirred sewage sludge sample was filtered through glass fiber filter paper (known weight). Then the filter paper with residue was kept in an oven at 103-105°C for 1 h. The weight after drying was measured (Eaton et al., 1995).

3.2.2.3. Volatile suspended solids

A known volume of well mixed sewage sludge sample was filtered through glass fiber filter (known weight) paper. Then the filter paper, along with filtered residue, was kept in a muffle furnace at 550°C for 15 min. The ash was determined (Eaton et al., 1995).

3.2.2.4. pH

A well mixed (liquid) sewage sludge sample was taken in a beaker. Then the pH was measured with an Orion model 230-pH meter.

3.3. SOIL AND SOIL ANLYSIS

3.3.1. Soil

The soil used in this study was volcanic Egmont soil from Taranaki, New Zealand. This type of soil is widely distributed all over New Zealnd. Legume based permanent pasture is the major agricultural use for these soils. Phosphate and sulfate fertilizers are used regularly to enhance biological nitrogen fixation by the legume component. Suryaningtyas (1998) has described the profile characteristics of Egmont black loam as consisting of a moderately developed fine nutty structure- A horizon (0-15 cm); black (10YR 2/1) loam overlying brown (10YR 5/3-4/2) loam (gritty); some small creamy pieces of weathered pumice, and dark yellowish brown gritty silt loam C-horizon.

3.3.2. Soil analysis

3.3.2.1. Soil water content

The soil water content at the time of sampling must be ascertained so that the dryweight of soil being used for various studies is known and final results can be expressed on a dryweight basis. Identical procedures are used to determine the moisture content of different horizons of soil.

To determine soil water content, soil was weighed into a soil moisture can and dried for 24 h at 105°C. The soil was reweighed with the loss in weight being noted, which is gravimetric water content.

% gravimetric water content = (wet wt. soil- dry wt.soil)/(dry wt.soil) x 100

3.3.2.2 Soil pH

Soil pH was determined in soil: water (1:2.5) suspensions equilibrated by mixing for 16 h and determined (after settling soil particles) using a pH meter fitted with a glass electrode (Orion model 230 A).

3.3.2.3. Total soil Zn

The ratio of HNO_3 to HCl used varies amongst researchers, but in this study a ratio of 1:4 (69 % HNO_3 : 37 % HCl) was chosen (Zanders, 1998). Samples of air dried, finely ground soil (0.5 g) were weighed into 50 ml conical flasks and 10 mL of 6 % H_2O_2 were added. The conical flasks were then placed on a heating block and warmed gently, to prevent excessive foaming, until the reaction had finished. At this stage the heating block temperature was increased to around 85°C and all liquid evaporated off. After allowing the flasks to cool, 10 ml of HNO_3 : HCl mixture (1:4) was added to each Flasks, swirled and left to stand overnight with small glass funnels (stem down) placed in each flasks.

The solution was then refluxed until cessation of brown fumes (about 1.5 hour), at which stage the glass funnels were removed. The digestion was continued until samples reached near dryness, at which stage they were removed from the hot plate. Following cooling of the flasks exactly 20 ml of 1% w/v HNO_3 was added by pipette to each digested sample. The flasks were then covered and left overnight to soak. Mixing, settling and decanting of the solution into storage tubes took place the following day. One ml of aliquot was taken from each storage tube and the volume made up to 10 ml with 1 % HNO_3 for the determination of Zn.

3.3.2.4. Extractable soil Zn

3.3.2.4.1. EDTA extractable soil Zn

The method used by Beckett (1989) was adopted to determine the carbonate form of Zn in soil. Samples of air-dried 5 g soil were shaken with 20 ml of 0.01 M ethylene diamine tetra-acetic acid (EDTA) at pH 7 in 50 ml polypropylene centrifuge tubes on an end-over-end shaker at 20°C for 16 h. The samples were centrifuged at 2000 rpm for 15 min and the supernatant filtered through a Whatman No.42 filter paper. Zn in the filtrate was determined by AAS with an air- acetylene flame.

3.3.2.4.2. HCl extractable native Zn

Samples of airdried 5 g soil sample were shaken with 50 ml 0.1M HCl for 2 h and centrifuged at 2000 rpm for 15 min and the supernatant filtered through a Whatman filter paper No.42. Zinc in the filtrate was determined by AAS (Lombin, 1983; Agbenin, 1998).

3.3.2.4.3. Phosphorus retention capacity

Two grams of airdried soil was weighed into a stoppered, 50 mL polypropylene centrifuge tube and 40 mL of KH_2PO_4 (250 mg/L) was added. This was shaken for 16 h at 20°C. Then it was centrifuged at 2000 rpm for 15 min. The supernatant was analysed for remaining soluble phosphate by the ascorbic acid method (Eaton et al., 1995).

3.3.2.4.4. 2 M KCl-extractable soil nitrate

Five grams of field moist soil was taken into 200 mL plastic shaking bottles and 50 mL 2 M KCl was added and shaken in an end-over-end shaker for 1 h. Suspension was filtered through a Whatman 40 filter paper and stored at 4°C. Samples were analysed in an auto analyzer (Technicon Auto analyzer II) (Blakemore et al., 1987).

3.3.2.4.5. Olsen- soluble phosphorus

One g airdried soil was taken into a 50 ml centrifuge tube and 20 mL 0.5 M NaHCO3 extracting reagent was added and shaken for 30min in an end-over-end shaker. Suspension was filtered through No.42 (Whatman) paper. The aliquot was analysed by the ascorbic acid method. After development of blue colour after 10 min (but not more than 30 min) the absorbance of each sample was measured at 880 nm using reagent blank as the reference solution (Blakemore et al., 1987).

3.4. BIOSORPTION OF HEAVY METALS FROM ACTIVATED SLUDGE

3.4.1. Pretreatment of materials

Polypropylene tubes and all the glassware were soaked overnight at ambient temperature in 1+2+9: HCl+HNO_3 + Water, then rinsed three times in tap water, distilled water and deionised water with subsequent drying.

Activated sludge was washed with 0.145 N NaCl solution to prevent osmotic effect. Also 0.145 N NaCl solution was used as bulk solution throughout the biosorption study.

3.4.2. Experimental approach

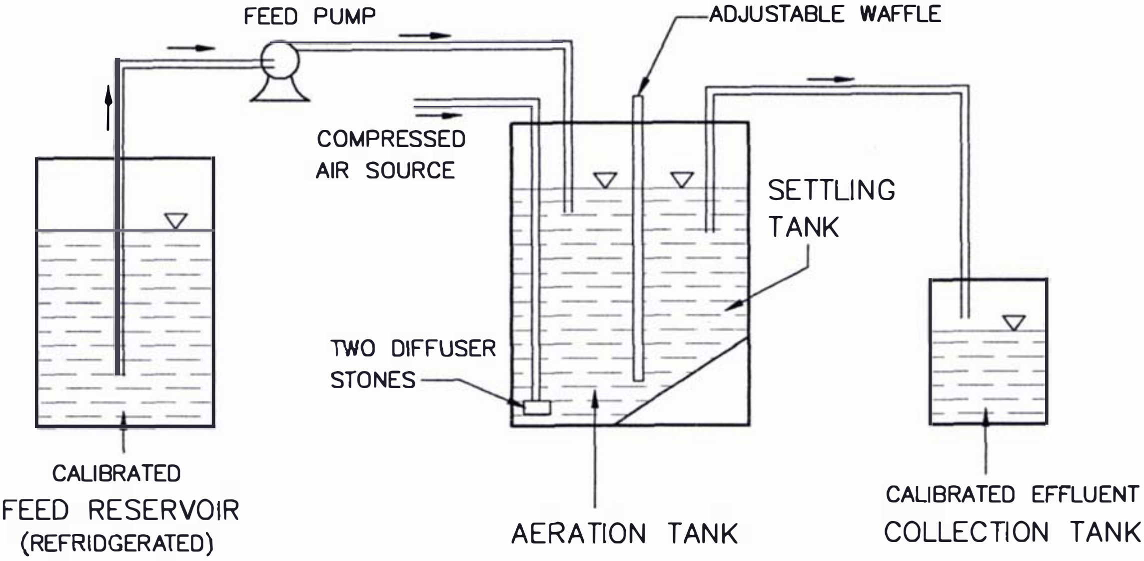


Figure 3.1. **Schematic diagram of the laboratory scale activated sludge**

The activated sludge obtained from the Kapiti Coast wastewater treatment plant was fed with Palmerston North wastewater treatment plant sewage effluent in a laboratory scale completely mixed reactor at 21 days' Solids Retention time (SRT). Concentration of sludge mass was optimized at 3000 mg/L. Over the duration of every batch experiment the sludge biomass was assumed to remain in a constant physiological state except for possible toxicity caused by metal addition. Cadmium, Cu, Zn and Ni were selected for experimentation because of their widespread industrial use and known toxicity to aquatic organisms. All experimental results were derived from batch shake flask experiments.

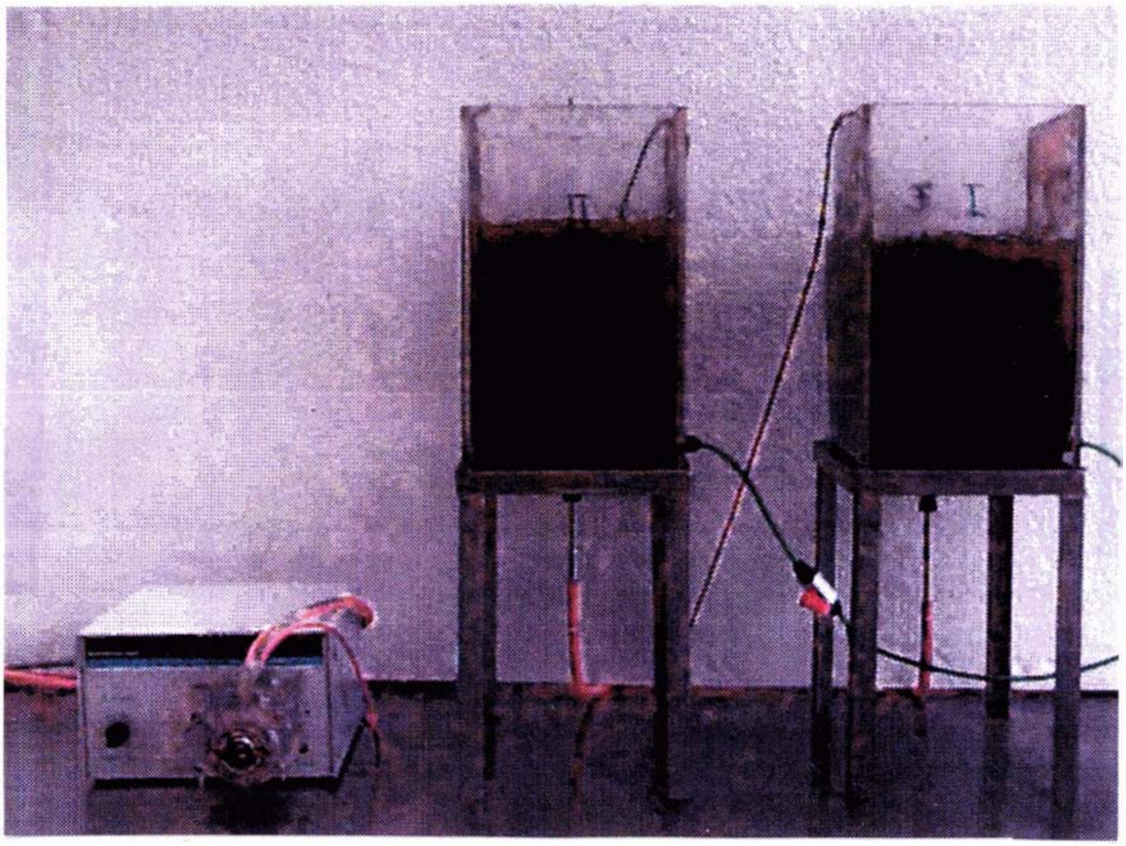


Plate 3.1. **Laboratory scale activated sludge unit.**

3.4.2.1. Cadmium

3.4.2.1.1. Equilibrium time study

Cadmium solutions of 5, 10, and 15 mg/L in, 0.145 N NaCl were studied with 0.5 % and 1 % wet weight of activated sludge in an incubator shaker at 250 rpm at 25°C (washed with 0.145 N NaCl). At 30 min., 2, 4, 6, 8, 10 and 24 h samples were withdrawn and filtered through 0.45 μm membrane filter paper (Whatman, type HA). The remaining Cd concentrations versus time were plotted and an appropriate equilibrium time was selected.

3.4.2.1.2. Isotherm study

Various amounts of sludge (0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 g wet weight) were transferred into 250 mL flasks. One Hundred mL of different initial metal concentrations of 5, 10 and 15 mg/L of Cd solution were added. After 6 h (equilibrium time) in an incubator shaker at 25°C, 250 rpm, mixed liquor was withdrawn and filtered through 0.45 µm membrane. The remaining Cd concentration was measured by using AAS.

3.4.2.2. *Copper*

3.4.2.2.1. Isotherm study

Various amounts of sludge (0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, and 2.0 g wet weight) were transferred into 250 mL flasks and 100 mL of Cu solutions of initial metal concentrations of 5, 10 and 25 in saline solution were added. The metal solutions were prepared by dissolving the $CuCl_2.2H_20$ in 0.145 N NaCl in deionised water. The pH was adjusted to 5.5-5.7 using 0.1 N NaOH and 0.1 N H_2SO_4. After 10 h of equilibrium time (Chareonsudjai, 1994) in an incubator shaker (250 rpm) at 25°C mixed liquor was withdrawn and filtered through 0.45 µm membrane. The Cu remaining in the liquor was measured by using AAS. A blank test was also performed without sludge to investigate the removal, which might occur via metal precipitation and adsorption onto the glass wall, and to estimate initial concentration of Cu^{2+} by dilution.

3.4.2.2.2. Sorption kinetics at varying temperatures

Pretreated biomass of 0.5 % wet weight was placed rapidly in 600 ml metal solutions in 2 L flasks. This point was taken as zero time. Flasks were kept at 25°C, 30°C and 40°C temperature levels at 250 rpm in incubator shakers. Samples were then drawn from the flasks at predetermined time intervals (equilibrium time), using clean plastic 6 ml syringes, and immediately filtered through 0.45 µm pore size syringe end filters thereby removing the biomass from the aqueous phase and terminating the biosorption reaction. Prior to analysis the filtrate samples were stored in plastic bottles. The metal uptake experiments were performed at pH 5.5. Effect of temperature on adsorption was studied to determine the initial uptake rate.

3.4.2.2.3. Analysis of samples to determine the rate of Cu uptake

After the biosorption was complete the Cu test solution and filtrate samples were analyzed using an atomic absorption spectrophotometer (AAS) to determine the Cu concentration. Before being measured by AAS the heavy metal solutions were appropriately diluted to ensure that the heavy metal concentrations in the samples were linearly dependent on the absorbance detected. The change in concentration between the initial Cu solution and the filtrates represented the uptake of Cu by biomass. The decrease in Cu concentration over the time sequence could be determined.

3.4.2.3. Zinc

3.4.2.3.1. Equilibrium time study

Zinc solutions of 10 mg/L and 25 mg/L in 0.145 N NaCl were studied with 0.6 % wet weight of activated sludge in an incubator shaker at 250 rpm at 25°C. The metal solutions were prepared by dissolving $ZnSO_4.7H_2O$ in 0.145 N NaCl in deionized water. The pH was adjusted using 0.1 N NaOH and 0.1 N H_2SO_4, to 6.8. At 0, 0.5, 2, 4, 6, 8, 10 and 24h, samples were withdrawn and filtered through 0.45 μm filter paper. The remaining Zn concentration in the filtrate was determined. The graph between remaining Zn concentrations versus time was plotted and an appropriate equilibrium time was selected.

3.4.2.3.2. Isotherm study

Various amounts of sludge (0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75 and 2.0g wet weight) were transferred into 250 ml flasks. One hundred ml of different concentration Zn solutions in saline solutions were added. The pH of the metal solutions was adjusted as mentioned in section 3.4.2.3.1. After 16 h (Equilibrium time) the mixed liquor was withdrawn and filtered through 0.45 μm membrane. The remaining Zn concentration was measured using AAS. A blank test was also performed without biomass.

3.2.2.5.3. Sorption kinetics

Kinetic study was carried out to determine the initial uptake rate of each metal. Pretreated biomass of 0.5 % wet weight was placed rapidly in 600 ml metal solutions in 2 L Flasks, this point being taken as time zero. Flasks were kept at 25°C and 40°C at 250 rpm in an incubator shaker. Samples were then withdrawn from the Flasks at predetermined time intervals using clean plastic 6 ml syringes and immediately filtered through 0.45 μm pore size syringe end filters.

3.4.2.3.4. Analysis of samples to determine the rate of Zn uptake

The Zn blank solution and the filtrate samples were analyzed using AAS to determine the Zn residual concentrations. The temperature of the flame used was 2300°C. The change in concentration between the initial Zn solution and the filtrate represented the uptake of Zn by the biomass.

3.4.2.3.5. Determination of Zn in the biomass after completion of biosorption

Metal sorbed biomass of 1.0 g was transferred to a 250 ml Pyrex beaker. Four ml concentrated nitric acid and 10 ml concentrated hydrochloric acid were added and covered with watch glass. The contents were heated on a hot plate and gently refluxed for 30 min. The digested content was transferred to a 100 ml volumetric flask and the supernatant was diluted appropriately and the Zn concentration in the biomass was estimated. (Sample preparation procedure for Spectrochemical Determination of Total Recoverable Elements, Method 200.2)

3.4.2.4. Nickel

3.4.2.4.1. Isotherm study

Various amounts of sludge (0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 g wet weight) were transferred into 250 ml Flasks. One hundred ml of different initial concentrations of 10, 15 and 30 mg/L nickel solutions in saline solutions were added. Metal solutions were prepared by dissolving $NiCl_2.6H_2O$ in 0.145 N NaCl in deionized water. The pH of the metal solution was adjusted to 6.6. After 24 h, which is more than ample time for adsorption equilibrium, mixed liquor was withdrawn and filtered through 0.45 μm membrane. The remaining Ni concentration was measured using AAS.

3.4.2.4.2. Sorption kinetics

Pretreated biomass of 0.5 % wet weight was placed rapidly in 600 ml metal solutions, in 2 L flasks. This point was taken as time zero. Flasks were kept at 25°C at 250 rpm in an incubator shaker. Samples were then withdrawn from the flasks at predetermined time intervals using clean plastic 6 ml syringes and immediately filtered through 0.45 μm pore size syringe end filters and blank solution and filtrate samples were analyzed using AAS without any dilution.

3. 5. DESORPTION OF HEAVY METAL FROM ACTIVATED SLUDGE

After the biosorption experiment, the metal loaded activated sludge was taken from the metal solution by centrifuging. Again it was washed with distilled water. The distilled water was measured for metal concentration and discarded. A known weight (3.5 g) of metal loaded sludge was taken in 100 ml of distilled water, 0.1 M Na_2SO_4, 0.1 M K_2SO_4, 0.1 M Na citrate and 0.1 M Na_2CO_3 eluant (desorbing agent) of conical flasks. Flasks were incubated at 25 ± 2 °C with shaking (100 rpm). The pH of the contents was maintained at 5.74, 5 and 4. Samples were withdrawn after 1, 2, 3, 6 and 24 h and the desorbed Zn and Cu were estimated using AAS. There are number of literatures available on Cd desorption in New Zealand soils. Therefore Zinc and Cu were taken for the desorption study.

3.6. ADSORPTION OF ZINC IN SOIL

3.6.1. Soil sampling and preparation for adsorption study

3.6.1.1. Soil sampling

Soil for batch experiments was excavated from the same site, but the soil was ground to break up any aggregates. Also, similar depth soil samples of three different soil pits were mixed to reduce soil heterogeneity. All samples were air dried then sieved through a 2 mm stainless steel sieve and stored in sealed plastic bags.

3.6.1.2. Preparation of soil samples for adsorption (batch) study

Field soil samples were airdried and coarsely ground using a porcelain mortar and pestle until they passed through a 2 mm sieve. They were then stored in plastic sealed plastic bags at room temperature. Subsamples for total elemental analysis were ground fine using the same mortar and pestle and similarly stored. The solution : soil ratio of Zn adsorption study was 50 : 1 which was used by many researchers (Agbenin, 1998; Ahumada et al., 1997)

3.6.2. Adsorption of Zn in volcanic Egmont soil

3.6.2.1. Equilibrium adsorption study

Zinc solutions of 100 mg/L of 110 ml made up with deionized water were shaken with 2.2 g air dried soil and samples were withdrawn at 15 min, 0.5, 1, 1.5, 2, 4, 6, 8,10, 16 and 24 h and filtered through Whatman 42 filter paper. The remaining concentration versus time was plotted and an appropriate equilibrium time was selected. Identical procedures were used for both horizon soils.

3.6.2.2. Isotherm study

Zinc adsorption by volcanic Egmont soil was measured by shaking 1g air dried soil with 50 mL Zn solution containing 0-200 (25, 50, 75, 100, 125, 150, 175, 200) mg Zn/L as $Zn(NO3)_2$ made up in deionized water, 0.1 M KNO_3 and 0.1 M KH_2PO_4. The soil Zn solution suspensions were shaken for 18 h, and then filtered through a No. 42 filter paper. Zinc and Fe concentrations were measured in the filtered equilibrium solutions by flame AAS. The pH of the equilibrium suspension was also measured.

3.6.2.3. Effect of pH in Zn sorption by volcanic Egmont soil

The method used by Barrow and Whelan (1998) was adapted to determine the effect of pH in Zn sorption by volcanic Egmont soil. The soil required 30 mmol of calcium carbonate ($CaCO_3$) to raise the pH of 1kg soil by 0.7 pH units. This was examined at the beginning of the study. One sample of topsoil (0-20 cm) was taken as control having pH level of 5.7. Four more topsoil samples were added with different amounts of finely powdered $CaCO_3$ to maintain the pH levels of 6.0, 6.5, 7.0 and 7.5. Diluted nitric acid was added to one more topsoil sample to maintain the pH level of 5.3. All these six soil samples were moistened with deionized water to near field capacity (60.7% w/w). One sample of subsoil (20-32cm) was taken as control having native pH level of 6.5. Different amounts of finely powdered $CaCO_3$ were added to two subsoil samples to maintain the pH levels of 7.0 and 7.5. Different amounts of diluted nitric acid were added to three subsoil samples to maintain the pH levels of 5.3, 5.7 and 6.0. These six subsoil samples were moistened with deionized water to near field capacity (48.1 % w/w). All these twelve samples were incubated at 60°C for 24 h. This increases the rate of reaction with acids and alkalis (Barrow & Cox, 1990) and there is little further change in pH.

Subsamples of all pH treatments were mixed with $Zn(NO_3)_2$ solutions of 100, 200, 300, 400 mg/L Zn at solution : soil ratio of 10:1 and shaken for 24h at 25°C and the Zn concentrations in the supernatant were measured.

3.6.2.4. Effect of phosphate and nitrate on Zn sorption by volcanic Egmont soil

The method used by Agbenin (1998) was adapted to determine the effect of phosphate and nitrate on Zn sorption by allophanic soil. One hundred g each of topsoil and subsoil samples were incubated in plastic containers with 0, 500, 1000 mg P/kg soil for 3 weeks in triplicate. These 18 soil samples were maintained at field capacity at 30°±2°C. The containers were loosely covered to ensure aeration and weighed regularly to determine moisture loss, which was not allowed to exceed 40% of field capacity. After 3 weeks, the samples were air dried and screened to pass through such that a 2-mm sieve for Zn adsorption studies. Potasium dihydrogen phosphate (KH_2PO_4) was used as the Phosphorus source. An identical procedure was used to study the effect of nitrate on Zn sorption. Soil samples were added with 0, 500, 1000 mg nitrate/kg soil. Potasium nitrate (KNO_3) was used as nitrate source.

A known weight (2.2 g) of each soil with phosphate treatment and nitrate treatment and control were equilibrated in triplicates with the solution concentration of 100 mg Zn /L. Samples were withdrawn at 0, 0.5, 4, 6, and 24 h, and the filtrate was analysed for Zn by AAS. The amount of Zn sorbed was the difference between Zn added and Zn in solution.

3.7. DESORPTION OF ZINC IN SOIL

3.7.1. Preparation of soil for desorption study

3.7.1.1. Zinc addition to the soil

Three hundred ml of 100 mg/L Zn solution was added to 6 g soil of both A and B horizons (top and sub) soil samples. The contents were shaken in an end-over-end shaker for 3 h. The supernatant was analyzed for residual Zn content. Then the soil was centrifuged with 100 ml distilled water to remove the Zn in the soluble stage. Next the soil was airdried at ambient temperature and left for 40 days, thus allowing slow reactions to occur and providing more realistic conditions. Total concentrations in the inorganic Zn applied topsoil (A horizon) and subsoil (B horizon) were 1000 mg/kg and 1100 mg/kg respectively.

3.7.2. Desorption of Zn in volcanic Egmont soil

Generally the desorption rate is slower than adsorption rate and may be as much as three orders of magnitude slower than adsorption. Therefore, 10:1 solution:soil ratio was used for this desorption study.

After removing the entrained Zn, 5 g of the Zn loaded soil was shaken on a horizontal shaker with 50 ml of 0.1 M KNO_3, 0.1 M KH_2PO_4 and distilled water for a predetermined reaction time (0.5, 3, 5, 7, 16 and 24 h). At the end of the reaction period the soil suspension was centrifuged at 2000 rpm for 10 min and an aliquot was measured for Zn concentration.

3.8. COLUMN LEACHING STUDY

3.8.1. Soil core Sampling

Seven undisturbed soil columns were hand excavated randomly. Each lysimeter core was 10 cm in diameter and 32 cm in length. The main features of the sampling method involved placing the lysimeter casing on the soil surface and digging a small trench around it to expose a small depth of soil monolith below the casing cutting edge. The casing was gently pushed down over the exposed depth of soil and the process repeated until the casing was full. The columns were sealed in polythene bags and stored in a refrigerator at 4°C, prior to the column experiments.

3.8.2. Loading of Zn in sewage sludge for soil application

For loading with Zn the sludge was incubated for 40 hours in 1 L Flasks in a rotary shaker at 25°C after addition from 100 mg/L stock solution of zinc nitrate solutions. Where addition of zinc nitrate solution caused acidification below pH 6. Adjustment was made using 4 M sodium hydroxide to raise pH to 6.5. The volume change due to addition of NaOH was negligible.

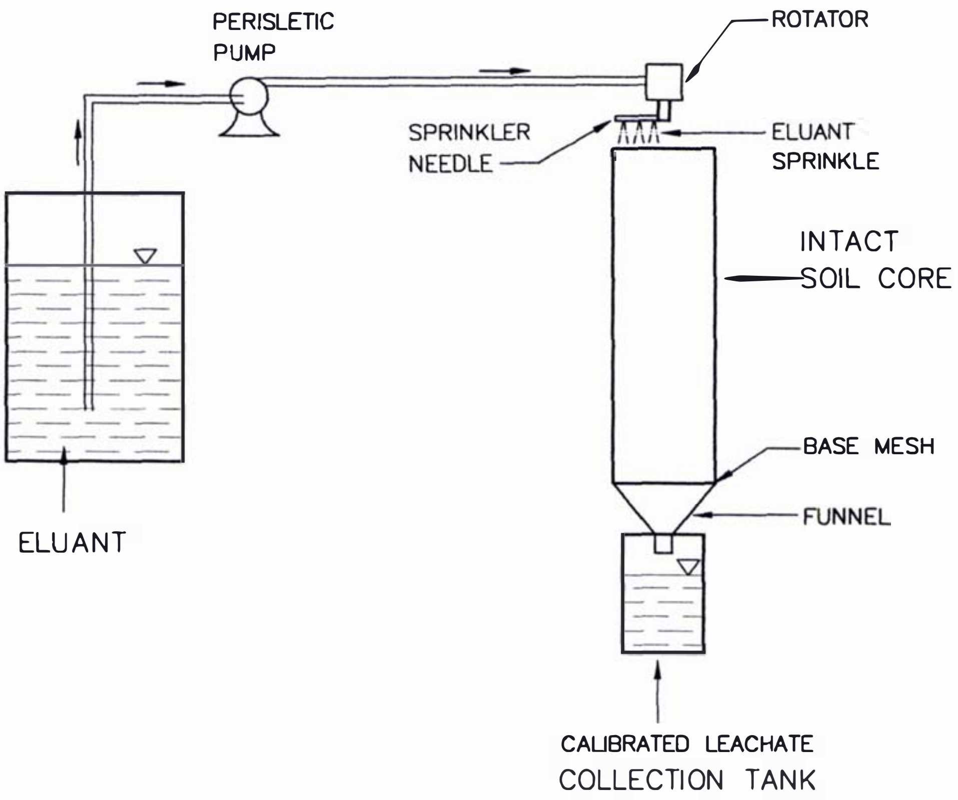
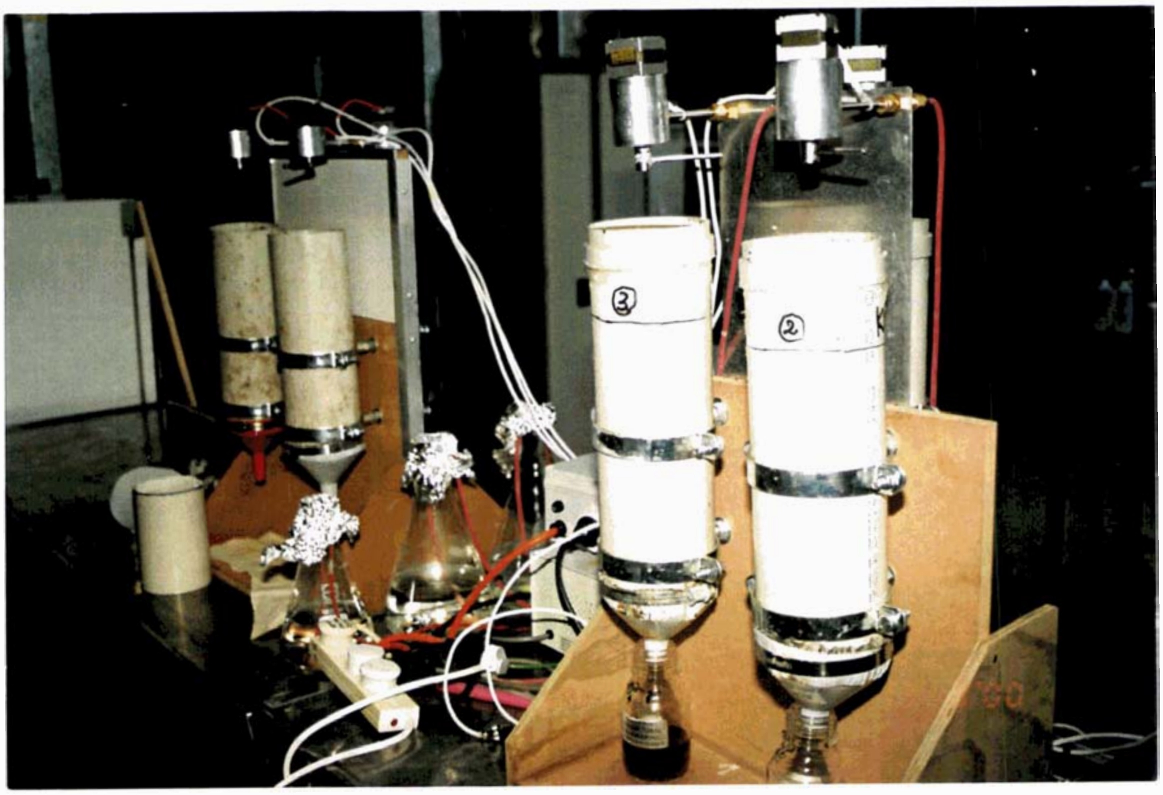


Figure 3.2. **A schematic diagram of the experimental set-up for the intact core leaching experiments**

The solids concentration of the Kapiti Coast activated sludge was 3300 - 4200 mg/L. Zinc nitrate was chosen as the Zn source since NO_3 is not likely to have any interaction with Zn for specific sorption compared to sulphate, chloride and phosphates.

After the loading samples of the sludge was analysed for total and soluble Zn. Supernatant was removed and the sludge was dewatered by centrifugation. The dewatered sludge was airdried and incubated at 25°C for 2 weeks before soil application.



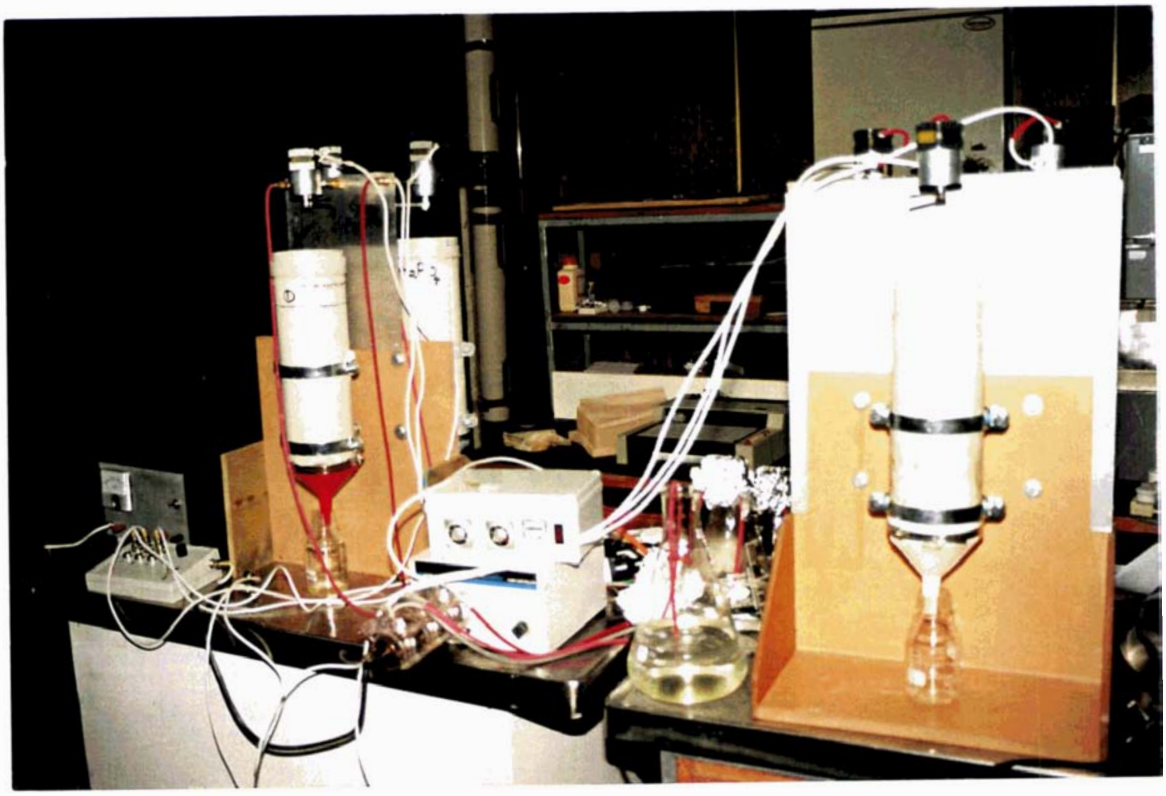


Plate3.2. **Experimental set-up for the core leaching experiments**

3.8.3. Treatments of soil columns

Seven undisturbed soil columns were used for this experiment. All of them were prepared by extracting undisturbed soils in the field (Sec. 3.8.1). These columns were saturated with deionized water. Then six columns were treated with 0.1 M KNO_3, 0.1 M KH_2PO_4 and distilled water in duplicates and the seventh column was used as a control column witout any treatments throughout the experimental period. The KNO_3, KH_2PO_4 solution and distilled water were stored in separate reservoirs and applied using peristaltic pumps at a flow rate of 1 mL/min. The respective solutions were applied until the concentrations of these anions in the effluent reached that of the input solutions. At that point application of the solution with added $Zn(NO_3)_2$ was done with a hand spray on the top of three columns to which 0.1 M KNO_3, KH_2PO_4 and deionized water had been applied previously. The other set of three columns, to which 0.1 M KNO_3, 0.1 M KH_2PO_4 and deionized water had been applied previously had an airdried equivalent amount of Zn amended sludge applied to the top of each column.

3.8.4. Leaching of soil columns and leachate collection

These six columns were leached with deionized water at an application rate of 5 cm /day using a distributor. Each distributor had one moving needle with 3 holes, with a uniform flow rate. There was, however, some variation in the amount of deionized water intercepted by each column. The leaching continued for up to 4-5 months. Sludge incorporated soil columns took 5 months and the Zn applied (sprayed) soil columns took 4 months to pass the required pore volumes. Over 15 pore volumes of effluent were collected and the effluent solutions were analysed for Zn, phosphate and nitrate as described above.

Column leachates of 1000 ml were collected in individual glass flasks every day. Sampling was done every day. After measuring the pH the samples were acid preserved and frozen within an hour of sampling for later analysis. After passing through 15 pore volumes of water (16-20 weeks time) the soil cores were pushed out of the PVC pipe and cut into 6 sections at the following depths (cm); 5, 10, 15, 20, 25. After air drying and passing through a 2 mm sieve these soil samples were stored in polythene bags for Zn analysis.

3.9. FRACTIONATION OF HEAVY METALS

3.9.1. Soil sample preparation

Soil samples were taken from the intact soil core used to study the effect of anion on the mobility of Zn from both Zn amended sludge applied columns and inorganic Zn applied columns after passing through 15 pore volumes of deionsized water. The soil was partitioned into 6 depths. Each sample was analysed in duplicate. Samples were air dried at 25°C. Each depth of soil was coarsely ground with a pestle and mortar and sieved to less than 2mm. All samples were then stored in plastic bags until analysed.

3.9.2. Fractionation scheme

Step1: Exchangeable and water-soluble. (Ex)

Extractant solution: 0.1 M $CaCl_2$

Method:

A 10 g sample was weighed into a 100 mL centrifuge tube, 30 mL extractant was added, as explained in the fractionation scheme and the tubes stoppered and shaken for 16 h. Stoppers were removed, and the tubes centrifuged at 2000 rpm for 10min. Supernatant was filtered through Whatman No.42 filter paper. Zinc in the filtrate was determined by AAS with an air-acetylene flame. To determine the watersoluble form of Zn again 10 g soil sample was shaken with 30 mL of deionized water for 2-3 h. And similar procedure was followed as indicated above. The shaking time to get watersoluble form of Zn was 3 h because of its ease release into the soil solution.

Step2: Organically bound (OR)

Extractant solution: 3 % NaOCl, adjusted to pH 8.5 immediately before use with 50 % HCl.

Method:

Whole soil (not subjected to $CaCl_2$ extraction) was used to determine the remaining heavy metal fractions. Therefore, the organic fraction was derived from the quantities extracted by NaOCl, less the quantities extracted by $CaCl_2$. A 5 g topsoil sample and a10 g subsoil sample were weighed into 100 mL centrifuge tubes seperately. Forty ml extractant was added to the topsoil sample, and 20 mL extractant to subsoil sample. Solution: soil ratio of top and sub soil samples were kept as 40:5 and 20:10 since the organicmatter content top soil is greater than subsoil. The tubes were placed in a boiling waterbath for 30 min and stirred/shaken occasionally. After removal from the waterbath, the tubes were cooled and weighed. The samples were centrifuged at 2000 rpm for 10 min., filtered (Whatman No.42) and weighed. The extraction process was repeated, and the tubes again weighed after the bath. Zinc in the filtrate was determined by AAS with an air-acetylene flame. Organically bound metals were calculated to be the sum of the metals in the two extractions, less any water soluble and exchangeable forms (from Step 1). This experiment was triplicated.

The soil was washed with 10 mL deionized water, centrifuged and the water discarded. Samples were oven dried at 60°C for 2 days, and weighed. Then the soil was finely ground to prepare it for the next step.

Step3: Oxides bound

Extractant solution: Acid oxalate ascorbic acid solution -
[0.2 M ammonium oxalate ($(COONH_4)_2 . H_2O$),
0.2 M oxalic acid ($(COOH)_2 .2H_2O$) and
0.1 M ascorbic acid adjusted to pH 3 with 50% NaOH]

Method:

A 2 g washed sample from the previous step was weighed into a 100 mL centrifuge tube, and 50 mL extractant was added. The tubes were placed in a boiling water bath for 30 min, and stirred occasionally. The tubes were then removed from the bath, allowed to cool, and weighed. Samples were centrifuged at 2000 rpm for 10 min and filtered (Whatman No.42) and Zn in the filtrate was determined by AAS with an air-acetylene flame.

Step4: Carbonate form of Zn

Extractant solution: 0.05 M Na_2 –EDTA solution

Method:

A 2 g washed sample from the step 2 was weighed into a 50 mL centrifuge tube, and 20 mL of extraction solution was added and to the tubes. It was shaken on an end-over-end shaker at 20°C for 16 h. The samples were centrifuged at 2000 rpm for 15 min and the supernatant filtered through Whatman No.42 filter paper and Zn in the filtrate was determined by AAS with an air-acetylene flame.

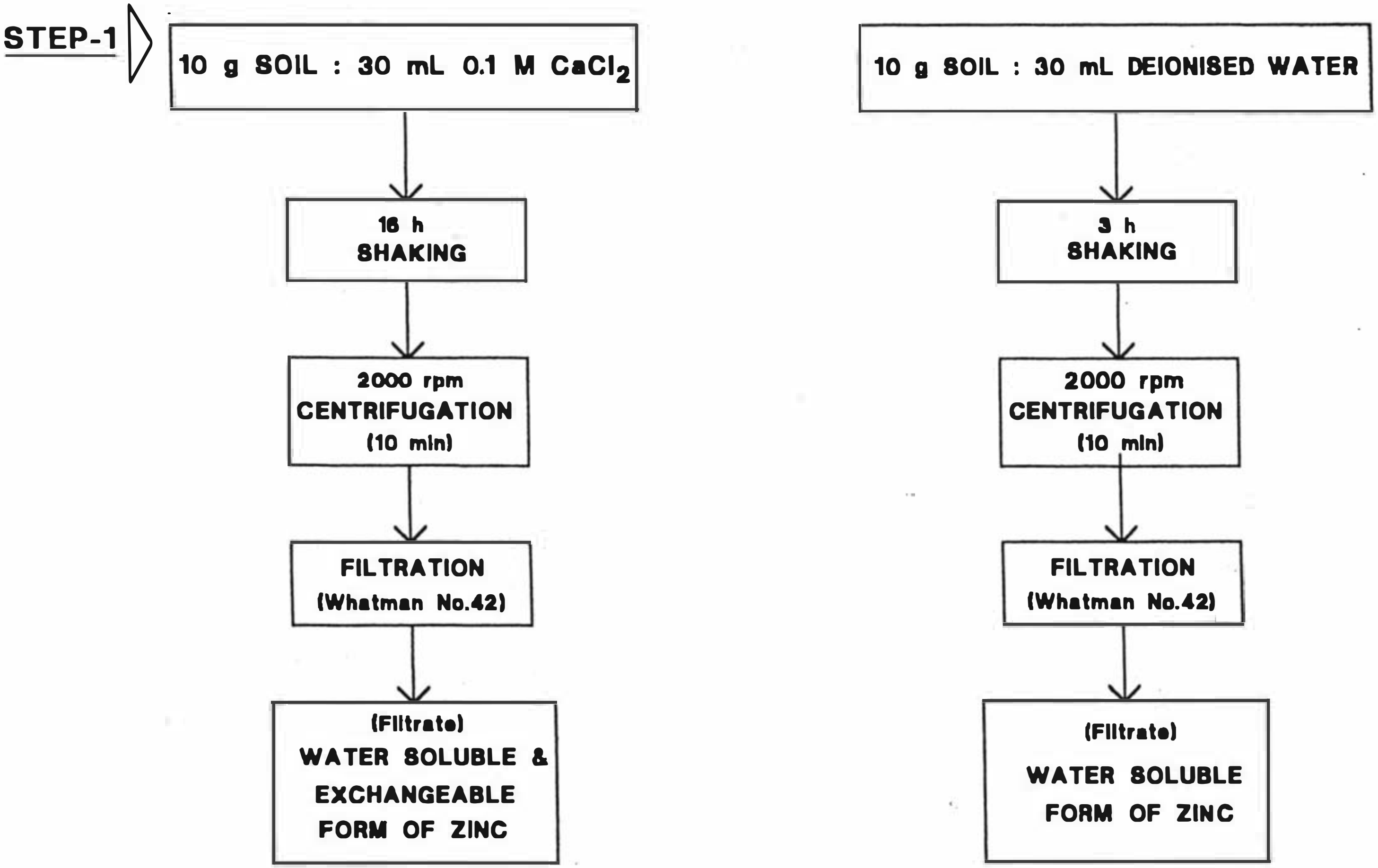


Figure 3.3. Schematic diagram of the fractionation scheme - Step-1 (Water soluble and exchangeable form of zinc extraction)

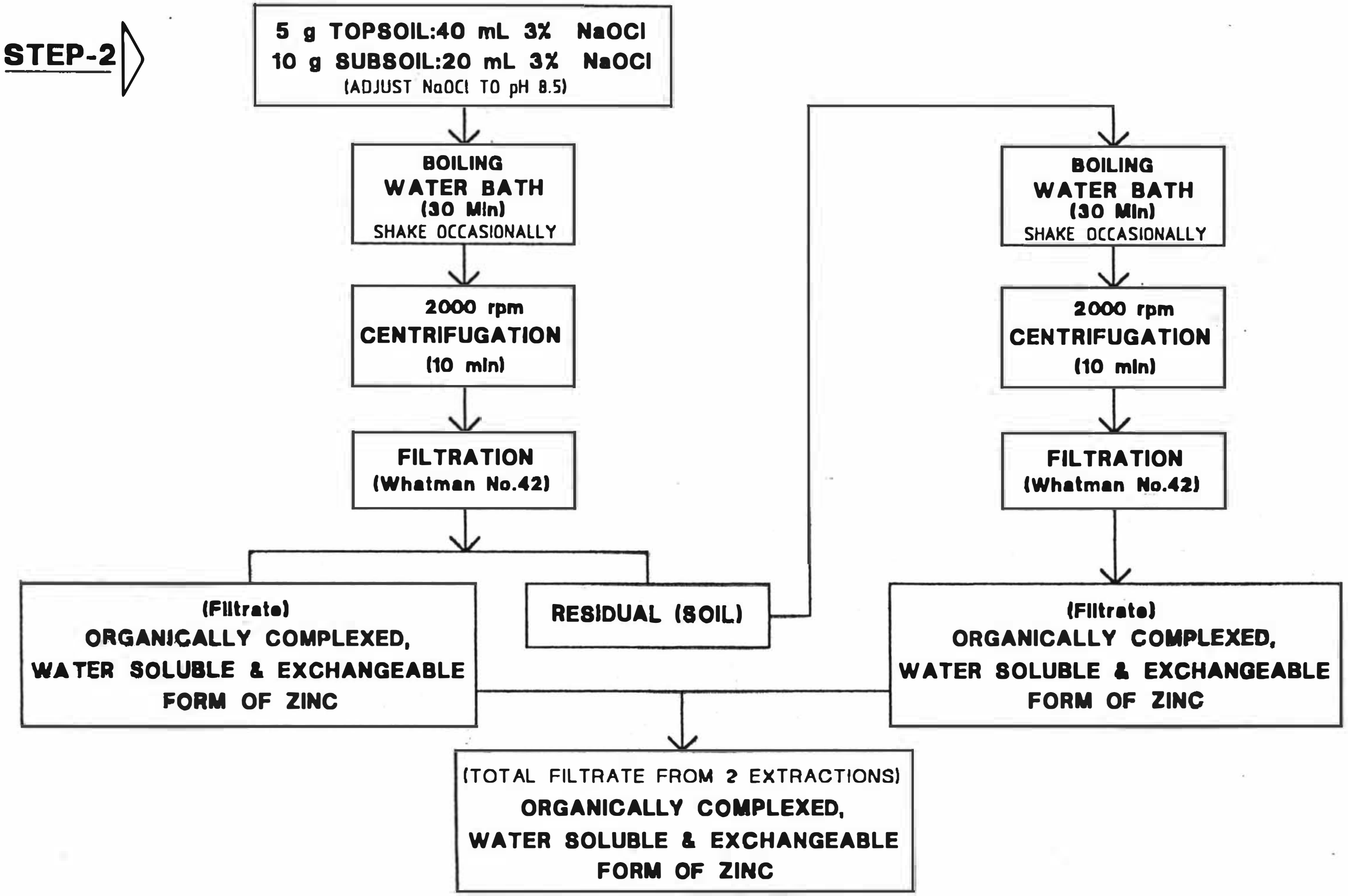


Figure 3.4. Schematic diagram of the fractionation scheme - Step-2 (Organically complexed form of zinc extraction)

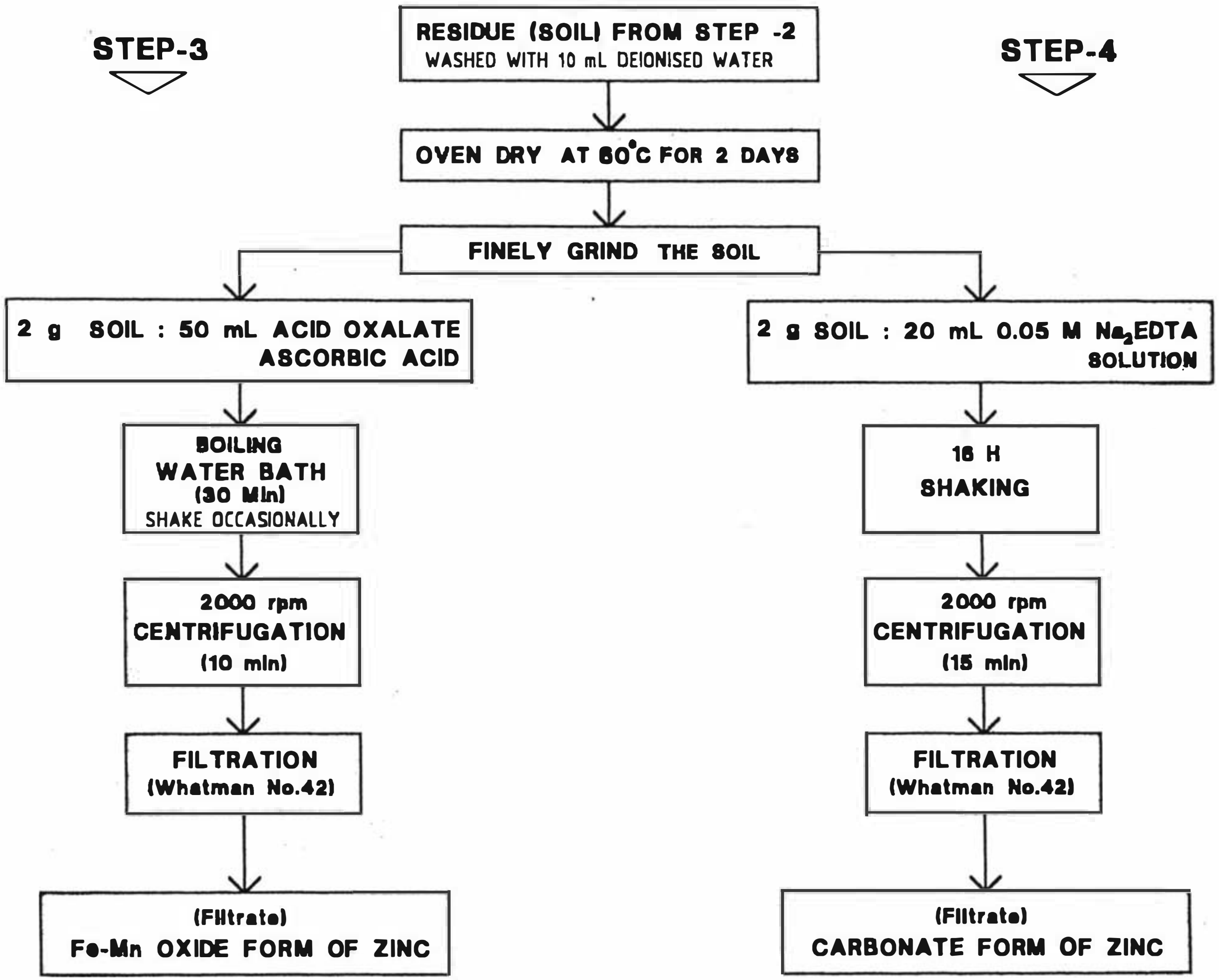


Figure 3.5. Schematic diagram of the fractionation scheme - Step-3 & 4 (Fe-Mn oxide and Carbonate form of zinc extraction)

Chapter Four

BIOSORPTION AND DESORPTION OF HEAVY METALS ON ACTIVATED SEWAGE SLUDGE

4.1. INTRODUCTION

Many municipal activated sludge plants receive combined domestic and industrial wastewater containing heavy metals. These metals typically include Cu, Zn, Ni and Cd and originate predominantly from industrial discharges. Knowledge about the physical-chemical interactions between the activated sludge process and soluble metal ions is limited. This study was undertaken to investigate the ability of sludge to remove soluble metal species from wastewater and the affinity of the biological mass with selected heavy metals.

4.2. GENERAL DESCRIPTION OF ACTIVATED SLUDGE

Activated sludge obtained from the Kapiti Coast wastewater treatment plant was fed with primary treated sewage from Palmerston North city wastewater treatment plant in a laboratory scale completely mixed reactor at 21 days Solid Retention Time (SRT). Concentration of the sludge was maintained at 3000 mg/L. Over the duration of every batch experiment the sludge biomass was assumed to remain in a constant physiological state except for possible toxicity caused by metal addition. Activated sludge was pretreated with 0.145 N NaCl solution to prevent the occurance of an osmotic effect prior to use in further experiments.

4.3. EQUILIBRIUM TIME

The time required for equilibrium of Cd, Zn and Cu biosorption by activated sludge is shown in Figure 4.1 where the deionized water was used as background electrolyte. Half of the total Cd was bound by activated sludge in 30 min. and this was followed by a much slower step, which reached equilibrium after 10 h. It adsorbed 65 % of the total cadmium when equilibrium was reached. A similar trend in cadmium removal was reported by Brown and Lester (1982) with activated sewage sludge. Nelson et al.

(1981) reported that adsorption of heavy metals on activated sludge solids occurred within first hour of contact. However, with 0.145 N NaCl solution used as an adsorption medium, significant adsorption of Cd was not observed - as shown in Figure 4.2.

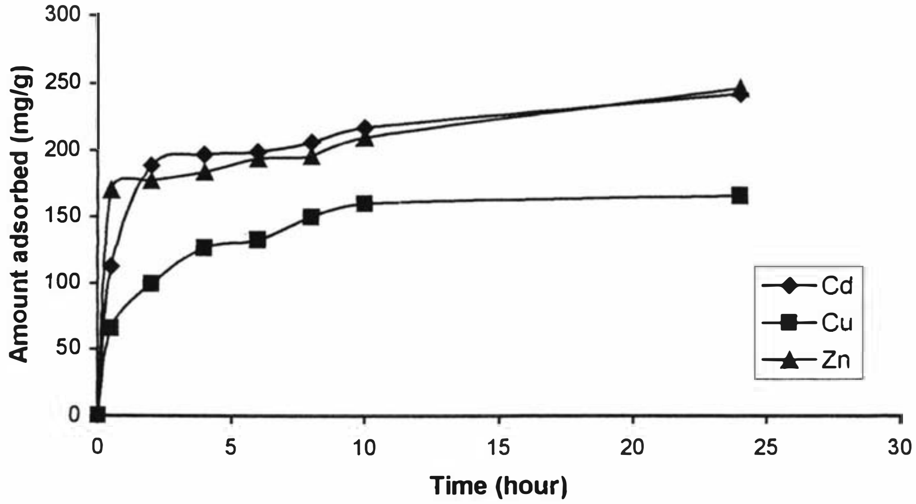


Figure 4.1. **Time dependent biosorption of Cd, Cu and Zn on activated sludge**

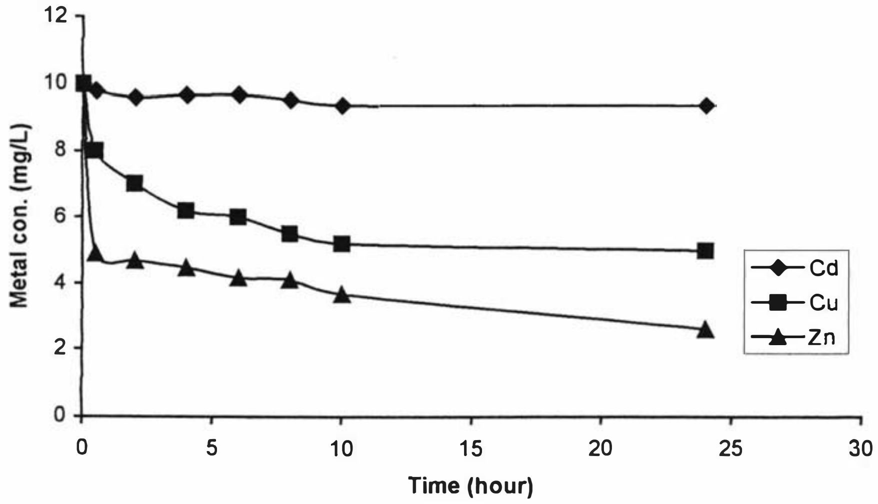


Figure 4.2. **Time dependent biosorption of Cd, Cu and Zn in 0.145 N NaCl solution on activated sludge**

The biosorption process (Fig. 4.1) can be divided into two phases. The first step is believed to be because of the adsorption on the cell surface. This is followed by a much slower step, implying that the adsorption and desorption take place simultaneously. The equilibrium adsorption time was observed to be in the range reported by Chareonsudjai (1994) who reported that the system reached equilibrium after 6 h for Cu. Neufeld and Hermann (1975) found that the system had approached almost complete equilibrium after 3 h for Zn and Cd. However who indicated that 2 weeks were required for complete equilibrium to be achieved. The relative affinity of the sites of activated sludge biomass to Cd and Zn may be poor. Also, this slow sorption could be attributed to the pore size of the surface of the activated sludge biomass in relation to the molecular size of the cadmium (Kipling, 1965). Adsorption of simple molecules onto a solid surface normally takes place rapidly if the solution is not viscous.

Adsorption was observed to be biphasic because of its different uptake rates. The first stage, which is thought to be surface adsorption on the cell walls, is a reversible reaction also called *passive uptake* (physical adsorption or ion exchange at the cell surface). The second stage (*active uptake*) could be due to metabolic activity and involves transport of the metal ions into the cytoplasm of the cell.

The equilibrium sorption of cadmium may be affected by the ionic strength of the bulk solution. It could be due to either Na^+ or Cl^-. There is little literature on the effect of Na^+ on cadmium adsorption. Also, Cd^{2+} ions are more selective than Na^+ ions for cation exchangers. Therefore the interference is more likely due to Cl^-. This will be discussed further in section 4.4.

The time required for equilibrium of copper biosorption by activated sludge is shown in Figure 4.1. Copper was adsorbed by activated sludge rapidly in the initial stage. Within 30 min less than half of the total amount was sorbed by sludge; this was followed by a much slower step, which reached equilibrium after 5-6 h. This equilibrium time is similar to the results obtained by Chareonsudjai (1994). There was no significant difference observed on Cu sorption equilibrium between 0.145 N NaCl and distilled water used as bulk solution of the adsorption medium. This implies that Cl^- did not interfere with the Cu biosorption onto the activated sludge. Wong et al.

(1993) reported that the presence of anion such as borate, carbonate, chloride and sulphate did not affect Cu uptake by *Pseudomonas putida*. This is similar to what is observed in copper uptake by activated sludge in this study.

Zinc and Cd showed a similar trend of time dependance in adsorption behaviour with activated sewage sludge biomass compared to copper. Both Zn and Cd relatively more readily absorbed than is Cu in activated sludge.

4.4. EQUILIBRIUM ISOTHERMS OF BIOSORPTION

4.4.1. Cadmium

From the experimental data obtained from equilibrium sorption of Cd at three different concentrations (5,10 and 15 mg/L), isotherms were developed. The isotherms looked like S and L shapes, as can be seen from Figures 4.3 and 4.4. “S” and “L” types are the two main classes of isotherms (Patricia et al., 1984). For the “L” type curve-as more solute is adsorbed-there is progressively less chance of adsorption sites being available, whereas an “S” type isotherm indicates that adsorption was enhanced as the concentration of metal increased. Rudd et al. (1984a) also observed “S” shaped curves when studying Cd sludge interactions. It was suggested by Forster (1976) that “S” shape curves were produced by polysaccharides of activated sludge. As shown in Figure 4.3 the steep slope of the middle portion of the Cd-sludge isotherm indicated a very high affinity at the lower metal concentration. The plateau region of Figure 4.4 may be a reflection of complexation or saturation indicating that once this value reached no further adsorption occurs.

However, when the experimental data were applied to adsorption models such as those of Langmuir and Freundlich, the data were found to fit both the Langmuir and Freundlich models reasonably well (see Table 4.1).

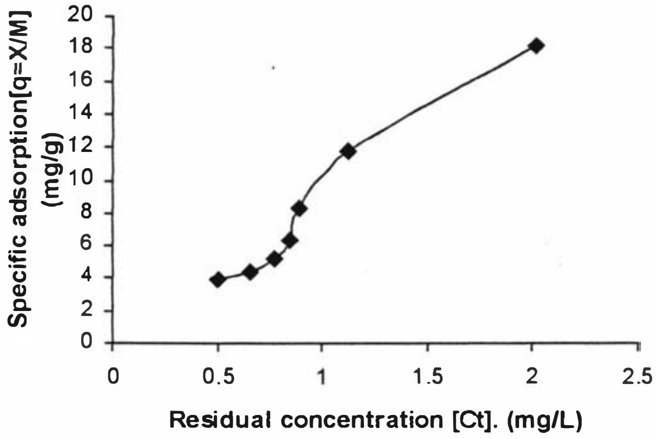


Figure 4.3. **'S shape'Cd adsorption isotherm (initial metal concentration 5mg/L)**

Table 4.1. Constants and correlation coefficients for Freundlich's and Langmuir's equilibrium adsorption equation for Cd

Initial Cd Concentration (mg/L)	Langmuir			Freundlich		
	Qmax (mg.metal/ g.bio mass)	b (Langmuir constant)	R^2	K (Freundlich constant)	n- Sorption intensity	R^2
5	35.7	0.18	0.92	8.34	0.80	0.93
10	38.9	0.34	0.90	11.26	2.13	0.85
15	44.8	0.53	0.97	15.73	2.33	0.93

Conditions for the application of the Langmuir adsorption isotherm require that the solution from which adsorption occurs must be dilute and the solute must have limited solubility in the solvent. There should be no competition from other components in the soluble phase, adsorption should be physical and only a monolayer formed, the surface of the adsorbent should be energetically homogenous and-finally-there should be no lateral interaction between the adsorbed molecules. Freundlich isotherm is based on the assumption that the adsorbent has a heterogeneous surface composed of different adsorption groups. Each group of adsorption sites follows Langmuir equation. In this system, it is unlikely that the surface of the adsorbent is energetically homogenous. Even though the Freundlich isotherm is of an empirical nature and the Langmuir isotherm theoretical the two can be shown to coincide over a narrow range of concentrations (Kipling, 1965; Patricia et al.1984). Sidle and Kardos (1977) and Aksu and Yener (1998) fitted adsorption (on soil) data to both Freundlich ($R^2 = 0.955$) and Langmuir ($R^2 = 0.921$) adsorption isotherms.

Linear transformation of the data using the Langmuir model gave Q_{max} and values of constant b, where b, equals a ratio of adsorption rate constant to a desorption rate constant. It is related to energy of adsorption through the Arrhenius equation, which also gives an indication of the affinity of the metal for binding sites on the biosorbent (Volesky & Holan, 1995). Values of the Langmuir parameters are summarised in Table 4.1. These data show the Q_{max} value for Cd ranges approximately between 36-45 mg/g biomass. Gould and Genetelli (1984) reported that the results of Cd binding with anaerobically digested sludges was 36.3 mg/g biomass at pH 5.0 and 23.7 mg/g at pH 7.2-7.6 using 0.01 M metal solution.

Therefore, it appears that there is not much difference in the binding of Cd between anaerobic and aerobic sludges. Ronald and Angelidis (1988) reported that, in general, the trend of metal chemical partitioning was similar for both aerobic and anaerobic sludges.

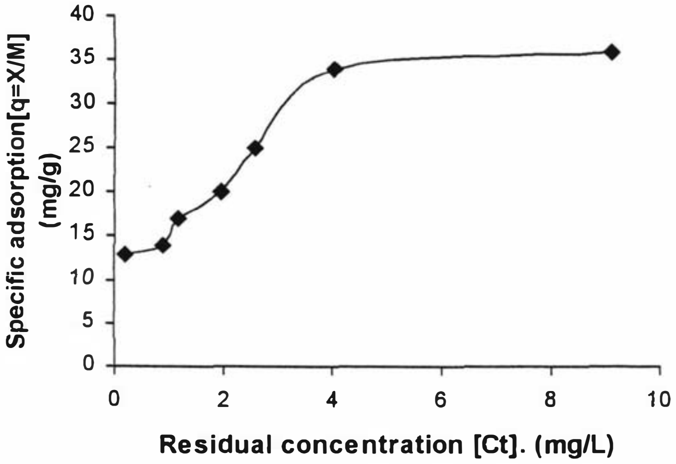


Figure 4.4. 'L shape' Cd adsorption isotherm (intial metal concentration 15mg/L)

Cadmium is a soft Lewis acid and therefore, reacts and complexes most readily with soft Lewis bases such as the chloride and hydroxyl groups (Adriano, 1986). However, being a soft acid acceptor in coordination reactions, it prefers soft donor atoms such as sulphur and nitrogen. So Cd should interact strongly with –SH group such as in cysteine. Activated sludge including amino acid, amino sugar, polysaccharide, hydroxyl and carboxylic acids of aliphatic and aromatic nature contains suitable donor atoms for complex formation with Cd.

4.4.2. Copper

From the experimental results obtained from equilibrium sorption of Cu of three different concentrations (5, 10 and 25 mg/L) isotherms were produced. The shape was 'S' at 10 mg/L as the initial copper concentration. As concentration increases it is no longer sigmoid (Figure 4.5, and Figure 4.6). The experimental data were fitted to adsorption models of Langmuir and Freundlich (Fig. 4.5).

Linear transformation of data using the Langmuir model gave Q_{max} 14.1, 17.2 and 27 mg/g biomass when initial metal concentrations were 7.5, 10 and 25 mg/L and this equilibrium, pH 5.7, was maintained in each system. Freundlich constant ranged from 8-12.2 when the initial metal concentration increased from 7.5 to 25 mg/L. Adsorption intensity increased from 2.1-4.2 when the initial metal concentration increased from 7.5-25 mg/L. Some researchers have reported that the sorption of Cu (Chareonsudjai, 1994; Sidle & Kardos, 1977a) could be better explained by the Freundlich model than the Langmuir model.

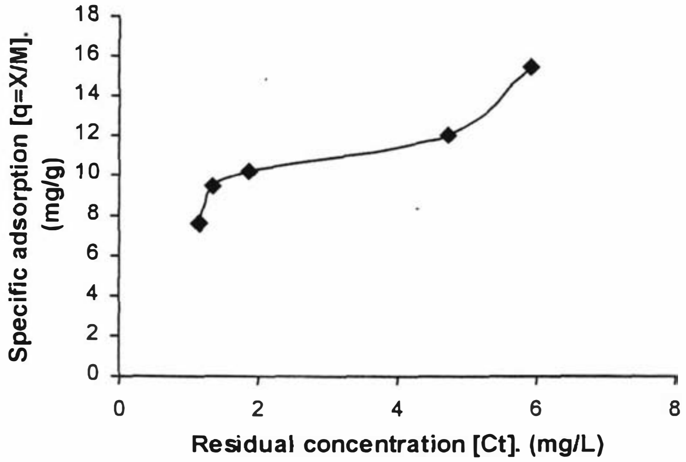


Figure 4.5. **Copper adsorption isotherm (Initial metal concentration 10 mg/L)**

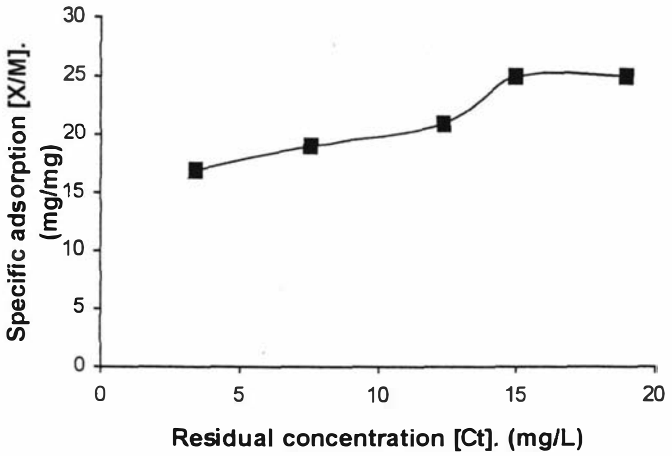


Figure 4.6. **Copper adsorption isotherm (Initial metal concentration 25 mg/L)**

When the initial Cu concentration was 10 mg/L a sigmoid isotherm was obtained. However when the initial metal concentration increased the shape was likely to change to "L" shape. This could be due to the reduction in the number of available binding sites as metal concentration increases, such that the proportion of total metal bound at the higher concentration decreases.

Table 4.2. Constants and correlation coefficients for Freundlich's and Langmuir's equilibrium adsorption equations for Cu

Initial Cu Concentration (mg/L)	Langmuir			Freundlich		
	Qmax (mg.metal/ g. biomass)	b (Langmuir constant)	R^2	K (Freundlich constant)	n-Sorption intensity	R^2
7.5	14.14	1.42	0.91	8.06	2.1	0.93
10	17.24	0.75	0.89	7.90	2.96	0.88
25	26.40	0.49	0.81	12.2	4.2	0.90

4.4.3. Zinc

In sewage sludge Zn is more common and found in a high concentration than Cu and Cd. Therefore, 10, 50 and 100 mg/L concentrations of initial Zn solutions were used to study the equilibrium isotherms. Isotherms were produced from the experimental data obtained from equilibrium sorption of Zn at three different concentrations (10, 50 and 100 mg/L). Activated sludge biomass adsorbed more than 60% of the initial 10mg/L concentration similar to Cd. However, when the initial metal concentration increased from 25 mg/L, over 70% of the initial metal concentration was adsorbed. The fit of the Langmuir equation showed in every metal concentrations of 10, 50 and 100 mg/L. When the initial metal concentration was 10 mg/L and the fresh biomass concentration was 1 g/100 mL, the adsorption constant was 24mg/g biomass in deionized water solution. The maximum adsorption constant increased (57.5 to 60 mg/g) with increasing initial metal concentration from 10 to 50 mg/L. Gould and Genetelli (1978) reported that 80 mg Zn^{2+}/g dry biomass was achieved at pH 7.5. This suggests that the metal concentration increases the driving force, which could have enhanced the metal uptake by the sludge.

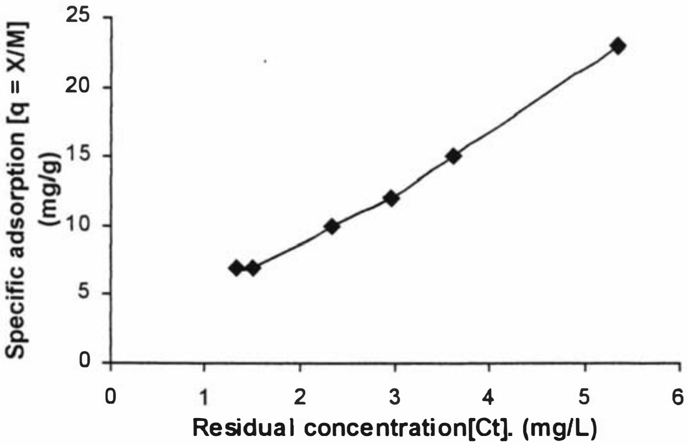


Figure 4.7. **Zinc adsorption isotherm (initial metal concentration 10 mg/L)**

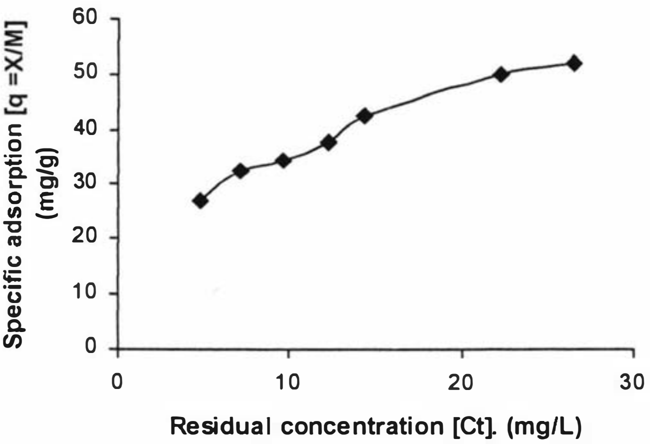


Figure 4.8. **Zinc adsorption isotherm (initial metal concentration 50 mg/L)**

Table 4.3. Constants and correlation coefficients for Freundlich's and Langmuir's equilibrium adsorption equations for Zn

Initial Zn Concentration (mg/L)	Langmuir			Freundlich		
	Qmax (mg.metal/ g. biomass)	b (Langmuir constant)	R^2	K (Freundlich constant)	n- Sorption intensity	R^2
10	57.5	0.10	0.97	5.0	1.15	0.98
50	59.9	0.16	0.94	14.79	2.56	0.99
100	59.5	0.02	0.94	6.47	2.42	0.90

4.5. FACTORS AFFECTING THE EQUILIBRIUM ISOTHERM

4.5.1. pH

Hydrogen ion concentration or pH is the single most important factor influencing metal adsorption on both inorganic and organic surfaces (Nelson et al., 1981). They stated that the optimum pH range for Cd adsorption with activated sludge is 5.5-7.5. Adsorption was studied at two pH values (pH5 and pH7). The sorption was significantly higher when solution pH was close to 7 as shown in Table 4.4

Table 4.4. Effect of pH on biosorption of Cd sorption. Data are means ± SE, *n*=3

pH	Residual Cd (mg/L)	Initial Cd (mg/L)
4.6-5	6	10
6.8-7	1.2	10

The pH dependence of heavy metal uptake may be largely related to the various functional groups on the microbial cell surface and also chemistry of the metal solution. The functional groups involved are generally –COOH groups (Fourest & Roux, 1992), which are protonated at low pH values. So the concentration of hydrogen ions effectively competes for binding sites, resulting in a reduced uptake capacity. As the pH increases, more functional groups are dissociated and become available for Cd^{2+} binding. There is also much less competition from hydrogen ions in solution. A plateau would be reached when the functional groups are completely dissociated. The surface complex formation model theory also explains that as pH increases, there is less competition between proton and metal species for the surface sites; a decrease in positive surface charge results in a lower repulsion by the sorbing metal.

4.5.2. Chloride ion concentration

During the course of the biosorption study 0.145 N NaCl was used as bulk solution to eliminate osmotic effects. When this ionic strength was used, the Cd biosorption data did not fit either the Langmuir or Freundlich sorption model and the sorption was very low. When distilled water was used as bulk solution it was observed that activated sludge biomass adsorbed reasonable quantities of Cd as described earlier. As can be seen in Tables 4.5a, 4.5b and 4.5c, washing with 0.01 N $NaNO_3$ and 0.145 N NaCl did not affect the specific sorption of Cd. However 0.145 N NaCl has been found to interfere with the sorption of Cd almost 3.8 times when it was used in the Biosorption study.

Lee et al. (1998) studied the effect of ionic strength on the removal of Cd, Cu and lead by apple residue. They pointed out that increasing ionic strength over 0.1 N of NaCl resulted in a dramatic decrease in metal ion removal. This could be attributed to the higher ionic strength of the surface of the activated sludge biomass decreasing the access of Cd ions to the surface for binding.

Another reason may be the formation of cadmium chloro-complexation. Huangi (1991) mentioned that Cd removal capacity in NaCl is hindered significantly at pH less than 5-6 and when the ionic strength is 0.05 M. He attributed this to the formation of Cd-chloro complexes, which are not adsorbed. In this experiment even though the pH was 6.5-7, the Cl^- ionic strength was around 3 times greater than the chloride concentration used by Huangi (1991). It can be concluded that increased Cl^- might have resulted in the formation of Cd-chloro complexation even above the 5-6-pH range. Naidu et al. (1997) suggested that Cd- Chloro complexation is the active process in reducing Cd^{2+} retention and its adsorption on soil colloids, when the soil pH exceeds 7.5. Therefore, the actual pH range that influences the formation of Cd-Chloro complexation in the presence of Cl^- is not clear.

The stable complexes of Cd with Cl^- ligand are highly mobile and unadsorbable (Alloway, 1995). Moore and Ramamoorthy (1984) also supported the finding mentioned above that chlorides are more selective than many organic complexing agents in their interaction with Cd. Evans et al. (1991) found that the reduction in metal adsorption in the presence of Cl^- was Zn<Pb<Cd<Hg, and this was directly related to the ability of the metals to form complexes with Cl^-.

For this biosorption study $CdCl_2.2.5H_2O$ was used to make metal solution. This cadmium compound itself contains Cl^-. Each mg of Cd in solution contains 0.63 mg of Cl^-. This Cl^- also would have affected the sorption of Cd together with the 0.145 N NaCl. Volesky and Holan (1992) reported that the type of anionic counterparts in the solutions of salts used could influence the sorption of Cd cations.

Hahne and Kroontje (1973) reported that the chloride ion concentration determines the degree of complexation and also differentiates heavy metals markedly depending on their affinity for such complex formation. They examined the distribution of different chloride complexes of Zn and Cd at different chloride concentrations and found that the formation of $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ begins before the formation of $ZnCl^+$, $ZnCl_3^-$ and $ZnCl_4^{2-}$. Naidu et al. (1994) indicated that $CdCl^+$ decreased the sorption of Cd onto soil particles.

Table 4.5a. 0.01 N $NaNO_3$ washed sludge (0.6 g/L) and deionized water bulk solution

Replicates	C_0-C_t (mg/l)	X/M (mg/g)
1	10.27	15.7
2	10.14	15.7
3	9.70	14.8

Table 4.5b. 0.01 N $NaNO_3$ washed sludge (0.6 g/L) and 0.145 N NaCl bulk solution

Replicates	C_0-C_t (mg/L)	X/M (mg/g)
1	2.65	4.0
2	2.19	3.3
3	2.54	3.8

Table 4.5c. 0.145 N NaCl washed sludge (0.6g/L) and 0.145 N NaCl bulk solution

Replicates	C_0-C_t (mg/L)	X/M (mg/g)
1	2.43	3.7
2	2.45	3.7
3	2.51	3.8

4.5.3. Initial metal ion concentration

Table 4.6. Effects of initial metal concentrations on Cd adsorption: Initial pH; 7.2, T; 25°C; agitation 150 r/min.; Adsorption yield is defined as (mg adsorbed Cd / g biomass) at equilibrium/mg metal/L solution) at initial time x100

C_0 Initial metal Concentration of Cd (mg/L)	Q_{max} (mg/g)	b Adsorption affinity	K Freundlich adsorption constant	n Sorption intensity	Adsorption Yield = Q/C_0 (L/g)	Biosorption Efficiency= C_0-C_t/C_0 (%)
5	35	0.18	8.34	0.80	7	90
10	39	0.34	11.26	2.13	3.9	91.4
15	44	0.53	15.73	2.33	2.9	98.7

The Q_{max} and b (affinity of metal for binding sites) increased when the initial metal concentration of Cd increased from 5 mg/L to 15 mg/L (See Table 4.6). Freundlich adsorption constant (K) and n also increased when the initial Cd concentration was increased from 5 to 15 mg/L. However, the adsorption yield reduces as the initial metal concentration increases (Table 4.6). The enhancement obtained in metal sorption could be due to an increase in electrostatic interaction (relative to covalent interaction) involving sites of progressively lower affinity for metal ions (Al-Asheh & Duvnjak, 1995). When the initial Cu concentration increased from 7.5 to 25 mg/L, the adsorption capacity increased from 14.14 to 26.4 mg/g (Table 4.2). When the initial Zn concentration increased from 10 to 50 mg/L the adsorption capacity and the freundlich constants increased from 57.5 to 59.9 and from 5 to 14.79. Conversely when the initial Zn concentration increased to 100 mg/L the freundlich adsorption capacity decreased from 14.8 to 6.47 mg/g. It could be because of the relatively higher concentration of Zn and the saturation of binding sites. Equilibrium sorption isotherm studies shows that metal uptake by activated sludge biomass can be a chemically equilibrated and saturable mechanism. Thus, there was an increase in metal uptake as long as binding sites were unsaturated. Similar results were obtained by Puranik and Paknikar (1999) recently on Cd biosorption with a citrobacter strain. Cheng et al. (1975) reported initial Cd concentrations of 2.08, 10.3 and 25.5 mg/L after 10 min of metal sludge contact time; the amounts of Cd uptake were 86, 84 and 74 %. These results clearly indicate that only the equilibrium sorption mechanism is related to filling the unsaturated binding sites with increased metal concentration.

4.5.4. Temperature

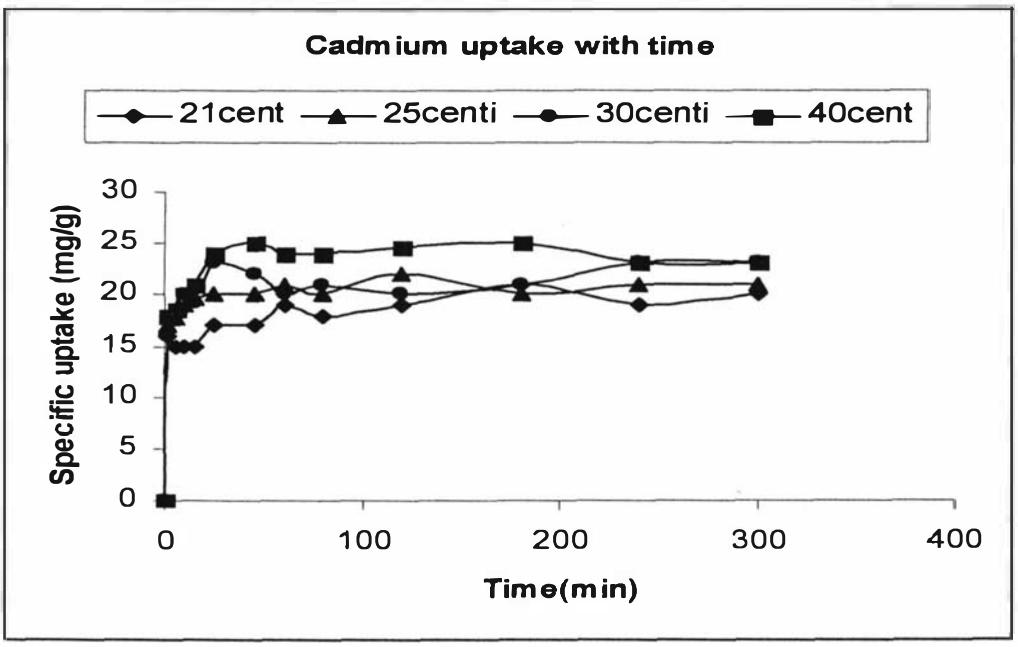


Figure 4.9a. **Specific uptake of Cd with time at different temperatures**

The initial Cd uptake rate was affected by the temperature in the range of 21°C - 40°C (Figure 4.9a). At 21°C uptake was more rapid than in other systems operated at 25°C, 30°C and 40°C. And the initial adsorption rate increased from 21-30°C and again decreased at 40°C; Calculated initial adsorption rates were 0.07, 0.13, 0.27 and 0.17 mg/g/min. at 21°, 25°, 30° and 40°C respectively (Figure 4.9b). Initial adsorption rates were calculated from the initial slope obtained from 4.9a. The slope of the initial adsorption rates at different temperature are shown in figures 4.10 a, b, c & d.

A similar effect of temperature on initial adsorption rates of 5 different metals; Cu, Zn, Fe, Cr and Pb was observed by Aksu and Kutsal (1990) when the initial metal ion concentration was 100 mg/L and biomass was 0.75 g/L at an agitation rate of 150 rpm for microbial biomass.

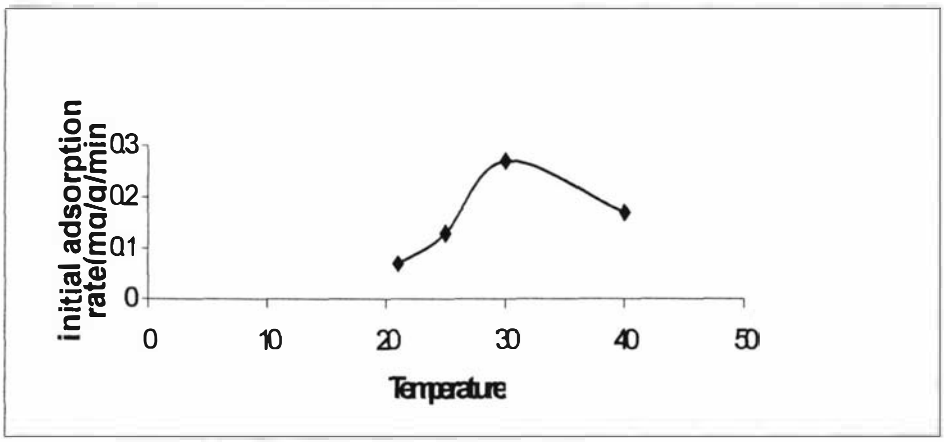


Figure 4.9b. **Effect of temperature on initial adsorption rate of Cd**

Selective adsorption generally decreases with rise in temperature. This is the expected effect for an exothermic process. It can be due to the reduction in magnitude and specificity of van der Waals forces between the solute and solid surface (and between adjacent adsorbed solute molecules) as the temperature increases (Kipling, 1965). However, Rao (1935) observed that there was no significant change with temperature in the magnitude of selective adsorption and he pointed out that chemisorption does not change with temperature variation. There is limited literature on the effect of temperature on the removal of Cd through biosorption on activated sludge solids.

Temperature in the range of 25-45°C did not produce any significant difference in Zn^{2+} adsorption at pH around 7.

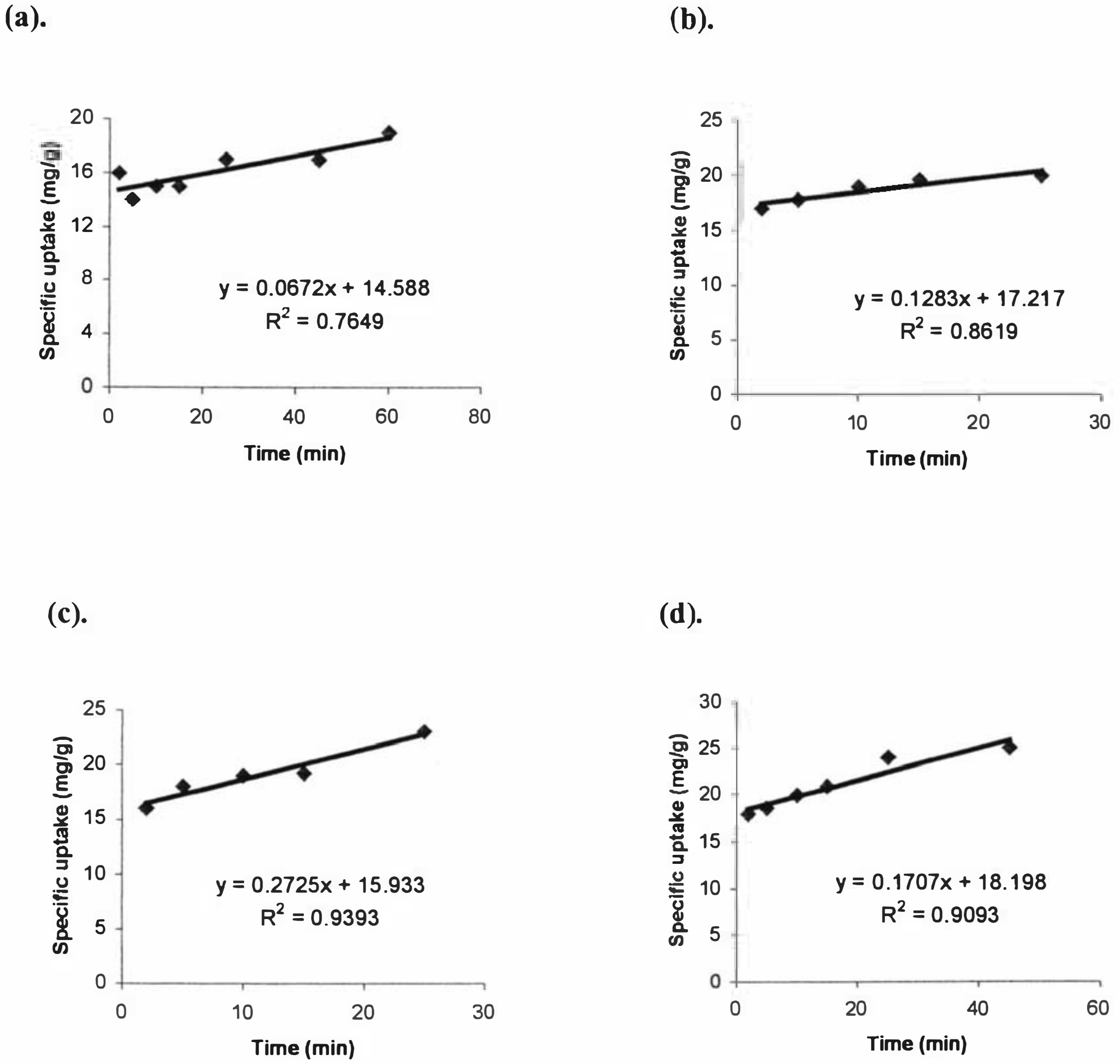


Figure 4.10. **Effect of temperature on initial adsorption rate of Cd: (a) 21°C, (b) 25°C, (c) 30°C, (d) 40°C.**

4.6. KINETICS OF BIOSORPTION

4.6.1. Cadmium

Cadmium uptake data when plotted as a function of time at optimum pH (Figure 4.11) showed that uptake was rapid in the first 25- 45 min of contact, accounting for 60-65% of initial Cd.

The rate of uptake during the first 45 min was 0.27 mg/g/min at 30°C reaching equilibrium in about 4 h.

Nelson et al. (1981) studied the kinetics of metal ion uptake by activated sludge in a batch reactor over a 20 h period. They found that adsorption occurred swiftly and nearly completelywithin the first hour of contact with a minimal subsequent uptake. Neufeld and Hermann (1975) observed that the initial uptake of Cd tends to level off after about 3 h of contact between metal and biomass.

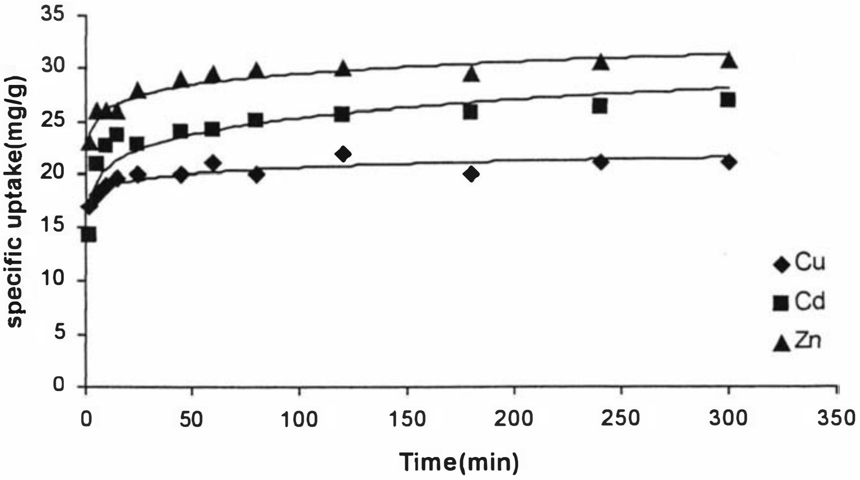


Figure 4.11. **Specific uptake of Zn, Cd and Cu with time**

It is known that the rate of metal uptake is influenced by factors affecting mass transfer from bulk solution to binding sites. Various steps of metal transfer from bulk solution to binding sites have been reported in the literature (Webber, 1985). The first step is bulk transport of metal ions in solution phase, which is usually rapid because of mixing and advective flow. The second step is film transport, which involves diffusion of metal through a hydrodynamic boundary layer around the biosorbent surface. The third step, actual adsorption of metal ions by active sites of the biomass, is considered to be rapid (Webber, 1985). Since the experimental condition provided a good mixing of biomass with Cd solutes, it is likely that the kinetics of the process were influenced only by the metal transfer from solution to the binding sites. Different types of binding sites have different affinities for the metal ions; sites with a high affinity become saturated first, while those with a lower affinity become involved later in the reaction. The specific uptake immediately after the contact was 15 mg/g and it reached 23 mg/g in 25 min. Therefore, a major proportion of metal removal is probably due to the passive adsorption mechanism including complexation by extracellular polymers.

4.6.2. Copper

Copper was initially sorbed by activated sludge rapidly, but less rapidly than Cd and Zn. Within 30 min, half of the total Cu of 10 mg/L was bound by sludge biomass, and reached equilibrium in 5-6 h. The initial adsorption rate increased from 25° to 30°C. The adsorption rates were found to be 0.22 and 0.29 mg/min at 25° and 30° C respectively.

4.6.3. Zinc

Zinc was initially sorbed by activated sludge rapidly. Zinc showed a trend similar to that of Cd (Figure 4.11). The initial adsorption rate was found to be 1 mg/g/min. This rate was maintained for 15 min. Then it started to decline to 0.2 m/g/min at 25 min.

4.6.4. Nickel

Activated sewage sludge biomass did not adsorb much Ni. Therefore no further studies were carried out in Ni.

4.7. DESORPTION OF COPPER AND ZINC

Among the five desorbing agents (eluants) tried for desorption of Zn and Cu from the loaded activated sludge biomass, Zn was desorbed more easily than Cu in all cases. This could be attributed to the fact that Cu bonded more strongly than did Zn with the biomass surfaces. Zero point one N Na_2SO_4 resulted in 16.5 % (88 μg) of Zn in 90 min. Desorption was not tried with any acid or EDTA. Ahuja et al. (1999) tried the Zn desorption with EDTA, HCl and H_2SO_4 and found that a maximum of 64.7 % Zn was desorbed with EDTA. In this study distilled water recovered 12.8 % (68μg) of Zn in 90 min. In a further 24 h again the data showed readsorption of Zn onto the biomass. This could be attributed to a very weak bonding of Zn on the activated sewage sludge biomass surface.

Table 4.7. Desorption of Cu and Zn with time using different eluants (***n***=3)

Eluant	Heavy metal	% of desorption at		
		30min	60min	90min
Deionized water	Cu	3.6	3.8	3.8
	Zn	12.12	12.37	12.81
Na_2SO_4 0.1 N	Cu	3.2	3.2	3.2
	Zn	16.1	16.43	16.54
K_2SO_4 0.1 N	Cu	3.85	3.85	3.85
	Zn	10.63	10.65	10.66
Na citrate 0.1 M	Cu	4.5	4.42	4.5
	Zn	12	12	12.12
Na_2CO_3 0.1 M	Cu	0.07	0.2	0.2
	Zn	1.27	1.34	1.34

4.8. CONCLUSIONS

- Activated sludge effectively removed more Cd, Zn and Cu than Ni. This could lead to accumulation of these toxic heavy metals in the biosorbed sludge unless the sludge is treated to recover them. The extracellular material present in activated sludge may play a significant role in the removal of these metals.

- The equilibrium time of biosorption was found to be 6-10 hours.

- Adsorption capacity of Cd on the activated sewage sludge ranged from 36 - 45 mg/g dry biomass.

- Adsorption capacity of Cu on activated sludge biomass was less and ranged from 14-27 mg/g dry biomass.

- Adsorption capacity of Zn with activated sewage sludge biomass decreased slightly with increasing initial metal concentration. It ranged from 54.9-60.6 mg/g.

- Cadmium and Cu showed “S” and “L” shape isotherms. It suggests that Cd and Cu had a high affinity with sewage sludge biomass at lower metal concentrations and had a low affinity at higher metal concentrations.

- Chloride ion interfered with the adsorption of Cd more than with the adsorption of Zn and Cu. This could be due to cadmium chloro complexation, which is more mobile.

- Percentage removal of Cd and Cu increased with metal concentration. However the percentage removal of Zn decreased with metal concentration. This may be because of the higher initial metal concentration used in the Zn sorption study.

- An increase of pH from 5 to 7 doubled the rate of Cd adsorption.

- Increasing the initial metal ion concentration decreased the adsorption capacity in Zn from 60.6-54.9 mg/g. Increasing the initial metal ion concentration increased the adsorption capacity of Cd but decreased the adsorption yield.

- Zinc was desorbed more than Cu from the activated sludge.

Chapter Five

ADSORPTION AND DESORPTION OF ZINC IN VOLCANIC EGMONT SOIL

5.1. INTRODUCTION

There has been increasing concern about the accumulation of Zn in soils due to the application of industrial sewage sludge and various chemical fertilizers containing high levels of Zn. Its subsequent movement to ground water and surface water is largely controlled by their extent of sorption and desorption between the aqueous and solid phases in soils (Swift & McLaren, 1991). The sorption may represent the combined effect of ion exchange, specific adsorption, and precipitation and surface complexation on the transfer of ions from the aqueous phase to the solid phase. Although numerous researchers have studied the adsorption process by soil, only a few have examined desorption. Desorption is also affected by soil pH, ionic strength and the nature and the amount of inorganic cations and anions in soils (Naidu et al., 1994).

Until recently, New Plymouth has been one of the cities in New Zealand that has received high levels of Cu, Zn and Ni in its wastewater in excess of the proposed guideline values (*New Zealand Guidelines for the Beneficial use of Biosolid,* 2001). Most of the information available on adsorption and desorption of Zn has been obtained from non-volcanic soils. Variable charge soils are widely distributed in New Plymouth, New Zealand, representing major volcanic soils which contain large amounts of aluminum and iron oxide and of allophonic constituents which show strong affinity for heavy metals (Wada, 1989). Soil pH and the presence of anions (nitrate and phosphates) appear to be two of the most important properties that determine metal sorption in variable charge soils (Bolan et al., 1999b). These soils have been used to study the behaviour of Cu and Cd. But there is little information available on the behaviour of Zn in these soils. Therefore, the adsorption and desorption of Zn in volcanic ash soil were studied, along with the effects of pH and anions (phosphate and nitrate) which-besides inorganic fertilizers-are the basic nutrients present in the sewage sludge.

5.2. ADSORPTION STUDY

5.2.1. General description of soil

The volcanic Egmont soil was collected from a site at Whareroa, Taranaki, New Zealand. This soil is classified as dark brown loam (New Zealand classification) and Andisol (US classification). Legume-based permanent pasture is the major agricultural use for these soils. Phosphates and sulfate fertilizers are used regularly to enhance biological nitrogen fixation by the legume component. It has heterogeneous porous media that consist of aggregates and macropores between the aggregates and a moderately developed fine nutty structure- A horizon (0-15cm); black loam overlies brown loam (gritty) and, some creamy pieces of weathered pumice exist throughout the profile. Dark yellowish brown gritty silt loam occurs in C horizon (New Zealand Soil Bureau, 1968).

5.2.2. Soil properties

The soil was slightly acidic with pH values of 5.7 and 6.3 for A horizon (top soil- 0-15 cm) and B horizon (sub soil- 15-32 cm) soils respectively (Table 5.1.). The organic carbon contents of top and sub soils were 10.5% and 2.7% respectively. The EDTA extractable Zn and the total Zn content were 13.8, 108 and 6.56, 92 mg Zn/kg in top and sub soils respectively. These contribute to unique chemical and physical properties such as variable charge, high phosphate retention, low bulk density, notable friability, and weak stickiness. The data presented in Table 5.1. indicate that the soil had a large amount of Olsen phosphorus (49.6 mmol/kg).

Table 5.1. Soil physical and chemical properties of volcanic Egmont soil

Parameters	Topsoil (A-horizon)	Subsoil (B- horizon)
Physical parameters		
Soil classification	Dark-brown loam	Yellow-brown loam
Particle size (g/kg)		
Sand	550	650
Silt	230	260
Clay	220	90
Particle density (g/cm^3)	2.3	2.5
Bulk density (g/cm^3)	0.74	0.79
Field capacity (w/w)	60.70	48.10
Total porosity (%)	67	69
Chemical parameters		
Organic carbon %	10.5	2.7
Soil pH (1:2.5)	5.7	6.3
Olsen P (mmol/ kg)	49.7	53.1
SO_4 (mg/ kg)	4	10.5
CEC (cmol/ kg)	33	16.2
K (cmol/ kg)	0.71	0.21
Ca (cmol /kg)	11.5	3.3
Mg (cmol /kg)	4.7	1.67
Na (cmol/ kg)	0.6	0.2
Acid oxalate:		
C (%)	10.5	2.7
N (%)	0.82	0.3
Al (%)	3.54	4.28
Fe (%)	1.63	3.42
EDTA extractable Zn (mg/ kg)	13.84	6.56
Total Zn (mg/ kg)	108	92

5.2.3. Zinc sorption as a function of time

The methodology used for sorption and desorption of Zn is given in chapter 3 section 3.6-3.7 and the results are described below.

Initially Zn sorption by the soils was rapid; 2.5-3.1 mg/g soil of Zn sorbed within the first 5 h. This is double the amount of Zn sorption reported by Pardo & Guadalix (1996) in volcanic soils (Andepts). This was followed by a very small increase in the amount of Zn sorbed. More than half of the total Zn was sorbed by the soil in the first hour followed by a much slower rate of sorption. Equilibrium was attained after 10 h (Figure 5.1). The equilibrium time in this study was shorter than the 18 h reported by Pulford (1986) who studied in volcanic soil. The allophonic constituents of volcanic Egmont loam soil show strong affinity for heavy metals (Wada, 1989). The soil used in this study from both the A (0-15 cm, pH-5.7) and B (15-32 cm, pH-6.3) horizons showed a slight difference in the affinity of adsorption. Both the horizons contained iron oxides and the Zn sorption onto these oxides could have resulted from chemisorption (McBride, 1989). However the physical and chemical properties for these two horizon soils are different (Table 5.1).

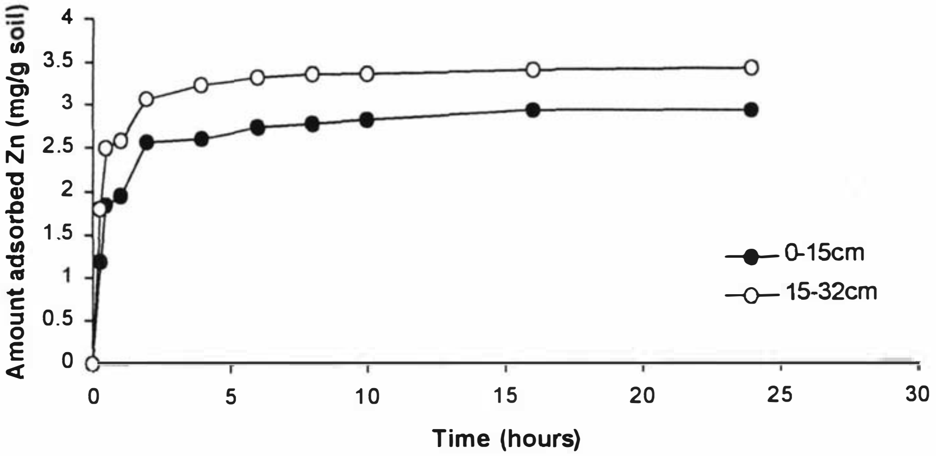


Figure 5.1. **Equilibrium time for adsorption of Zn by volcanic Egmont soil from different depths**

5.2.4. Adsorption isotherm for volcanic Egmont soil

Zinc adsorption isotherms at natural soil pH (5.7 and 6.3) for the A (0-15 cm) and B (15-32 cm) horizons of volcanic Egmont soils are shown in Figures 5.2a and 5.2b. The solution Zn concentration used in determining the isotherms was higher than would exist in the soil solution under normal field condition. These high concentrations were used to ensure accurate characterization of the adsorption and desorption process. The pH was not monitored and controlled in this experiment.

The data were fitted to the Freundlich isotherm. Although the experimental data fit well to both Langmuir and Freundlich equations (see section 4.4), based on the literature observations, only Freundlich isotherm will be used for further research.

$$Y = KC_t^{1/n}$$

Where, Y is the amount of Zn sorbed (mg Zn/g soil), C_t is the final concentration of Zn (mg/L) in the solution, and K and n are constants. K is termed as the Freundlich unit-capacity coefficient, and n is a measure of energy associated with a particular sorption process. Both K and n are used to characterize Zn sorption by soils.

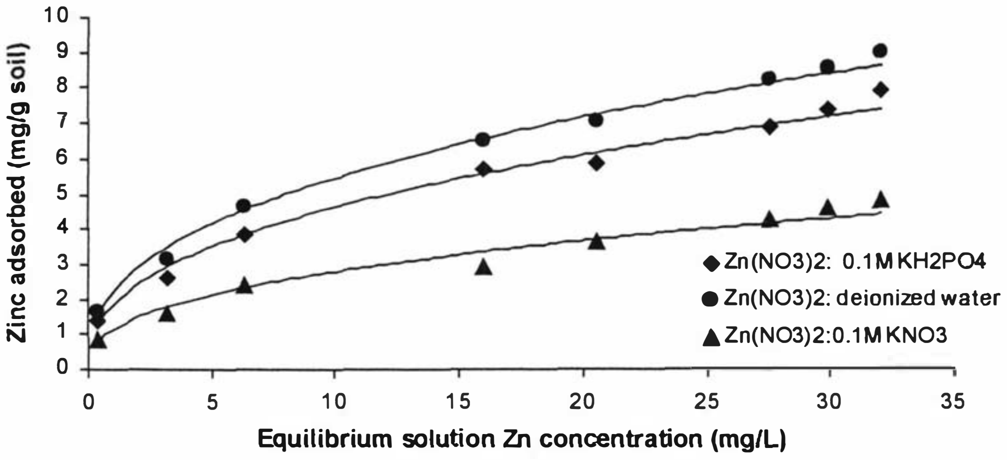


Figure 5.2a. **Zinc adsorption isotherm for the A horizon (0-15 cm) of volcanic Egmont soil with different background electrolytes**

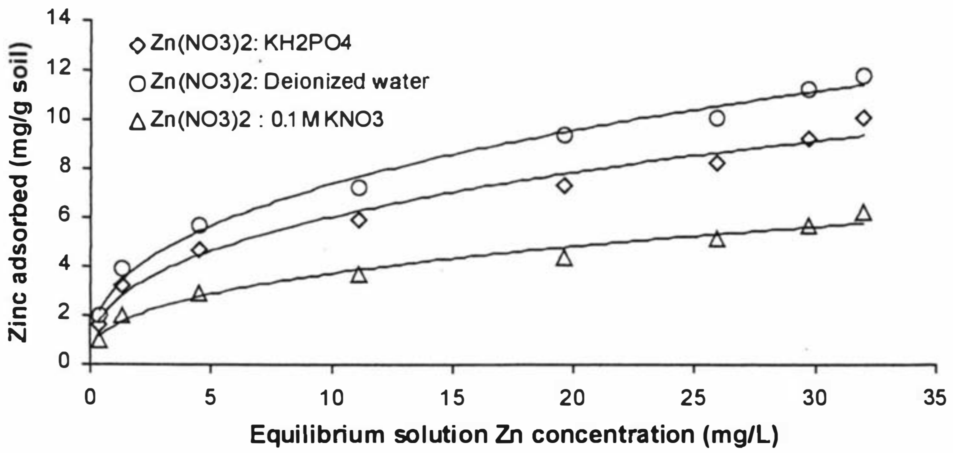


Figure 5.2b. **Zinc adsorption isotherm for the B horizon (15-32 cm) of volcanic Egmont soil with different background electrolytes**

Figures 5.2a and 5.2b shows the adsorption isotherms for the top and sub soil using Zn $(NO_3)_2$ as the source of Zn, and using deionized water, 0.1 M KH_2PO_4 and 0.1 M KNO_3 as the supporting electrolyte. Considerable differences were found in adsorption from phosphate and nitrate solutions. The salt solutions were used as ionic strength buffers and to provide a cation at much higher concentrations than that of Zn, so that ion exchange sites would be saturated with K^+ in both adsorption systems where 0.1M KNO_3 and 0.1M KH_2PO_4 were used. But in the experiment where deionized water was used as supporting electrolyte, Zn is held by ion exchange sites. Therefore a greater adsorption constant was obtained in the experiment where deionized water was used. Freundlich adsorption capacity coefficient (K) values showed (Table 5.2) a significant increase for the Zn adsorbed in KH_2PO_4 solution over that adsorbed in the KNO_3 solution. It is clearly seen that the sorption of Zn is higher in the presence of phosphate than nitrate. Bolan et al. (1999b) reported that Cd sorption was higher in the presence of phosphate than nitrate and this difference in Cd sorption between the different anion background media was less for the Manawatu soil (silt loam) than for the volcanic Egmont soil.

Table 5.2. Freundlich equation describing the adsorption of Zn at various electrolyte concentrations

Electrolite	Freundlich equation for Zn adsorption	
	(0-15cm) Top soil	(15-32cm) Sub soil
De ionized water	$Y=2.23\ C_t^{0.39}$ $R^2 = 0.99$	$Y=3.09\ C_t^{0.37}$ $R^2 = 0.98$
0.1 M KH_2PO_4	$Y=1.85\ C_t^{0.40}$ $R^2 = 0.99$	$Y=2.54\ C_t^{0.38}$ $R^2 = 0.98$
0.1 M KNO_3	$Y=1.14\ C_t^{0.39}$ $R^2 = 0.98$	$Y=1.57\ C_t^{0.37}$ $R^2 = 0.98$

5.2.5. pH dependent adsorption isotherms for different horizons of volcanic Egmont soil

Zinc sorption isotherms measured at different pH levels ranging from 5.3-7.5 for the volcanic Egmont soil of top and sub soils are presented in Figure 5.3a and Figure 5.3b. In both top and sub soils, Zn sorption increased with increasing pH. Freundlich constant (K) values increased with increasing soil pH in both top and sub soils (Table 5.3.). This result of pH effect on sorption of Zn is consistent with the results obtained in many previous studies in variable charge soils (Barrow & Whelan 1998; Basta & Tabatabai, 1992; Bolan et al., 1999b; Brummer et al., 1986; Naidu et al., 1994). Three possible reasons may be identified for the increase in heavy metal sorption with increasing pH (Bolan et al., 1999b). Firstly, in variable charge soils, an increase in pH causes an increase in surface negative potential, resulting in an increase in cation sorption. Secondly, an increase in soil pH is likely to result in the formation of hydroxy species of metal cations, which are sorbed preferentially over the metal cation. Thirdly, precipitation of Zn is likely (Zn hydroxide) to result in greater retention. But the sorption curve presented in figures 5.3a and 5.3b that fit Freundlich isotherm, the precipitation of Zn is not evident. But the sorption curve presented in figures 5.3a and 5.3b that fit Freundlich isotherm, the precipitation of Zn is not evident.

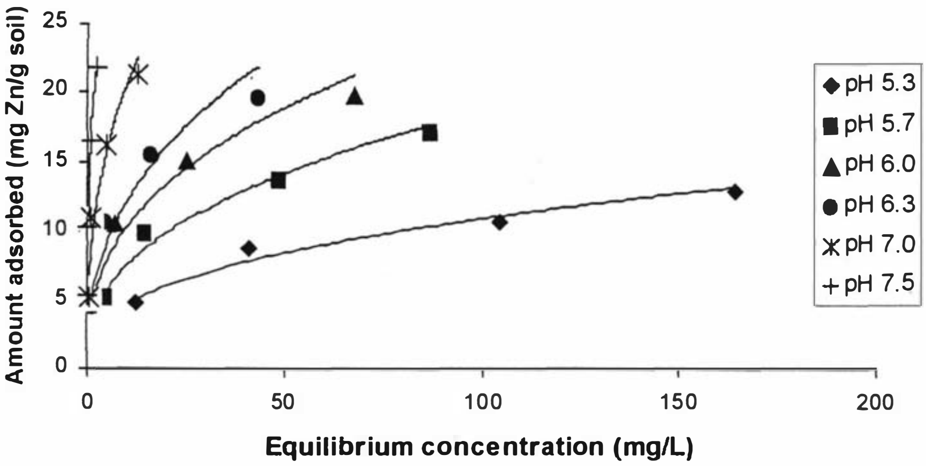


Figure 5.3a. **Zinc adsorption on the A horizon (0-15 cm) of volcanic Egmont soil at different soil pH**

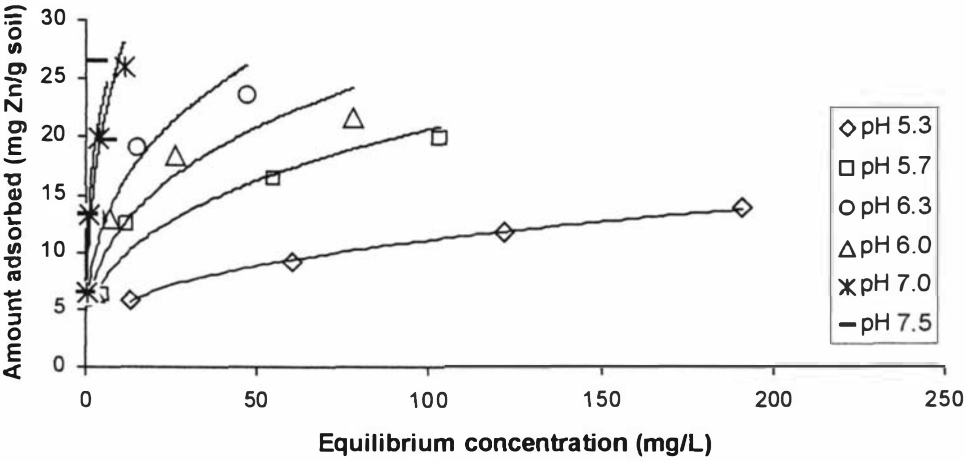


Figure 5.3b. **Zinc adsorption on the B horizon (15-32 cm) of volcanic Egmont soil at different soil pH**

Pulford (1986) also reported a role for a precipitation mechanism involving Zn and Fe, which is independent of pH. This mechanism may be important in the selected volcanic soil where amorphous iron oxides, associated with large amounts of ferric ions in solution, are important matrices accommodating Zn. Whatever the mechanisms involved, the sorbed Zn has to be identified whether it is strongly bonded to the soil or loosely held by any exchangeable mechanisms.

Table 5.3. Freundlich equation describing the adsorption of Zn at various pH levels in different horizonc of volcanic Egmont soil

Soil pH	Freundlich equation for Zn adsorption	
	(0-15cm) Top soil	(15-32cm) Sub soil
5.3	$Y=1.97\ C_t^{0.37}$ $R^2=0.97$	$Y=2.53\ C_t^{0.32}$ $R^2=0.99$
5.7	$Y=3.01\ C_t^{0.40}$ $R^2=0.98$	$Y=4.25C_t^{0.34}$ $R^2=0.89$
6.0	$Y=4.29\ C_t^{0.38}$ $R^2=0.95$	$Y=5.44\ C_t^{0.34}$ $R^2=0.89$
6.3	$Y=4.76\ C_t^{0.41}$ $R^2=0.94$	$Y=7.09\ C_t^{0.34}$ $R^2=0.92$
7.0	$Y=8.76\ C_t^{0.37}$ $R^2=0.84$	$Y=11.43\ C_t^{0.37}$ $R^2=0.93$
7.5	$Y=17.23\ C_t^{0.29}$ $R^2=0.99$	$Y=18.17\ C_t^{0.63}$ $R^2=0.88$

5.2.5.1. Distribution coefficients from the pH dependent experiment

Distribution coefficient (K_d) is generally used to express the mobility of the heavy metals in soil (Anderson & Christensen, 1988; McBride et al., 1997). A large K_d value represents high soil affinity for Zn and a low mobility; whereas a low K_d value indicates a high mobility and low retention in soils.

$$\text{Distribution coefficient } (K_d) = \frac{\text{equilibrium metal concentration in soil}}{\text{equilibrium metal concentration in solution}}$$

The slope of the linearised isotherms was used to calculate the K_d values in different pH of the A and B horizon soils.

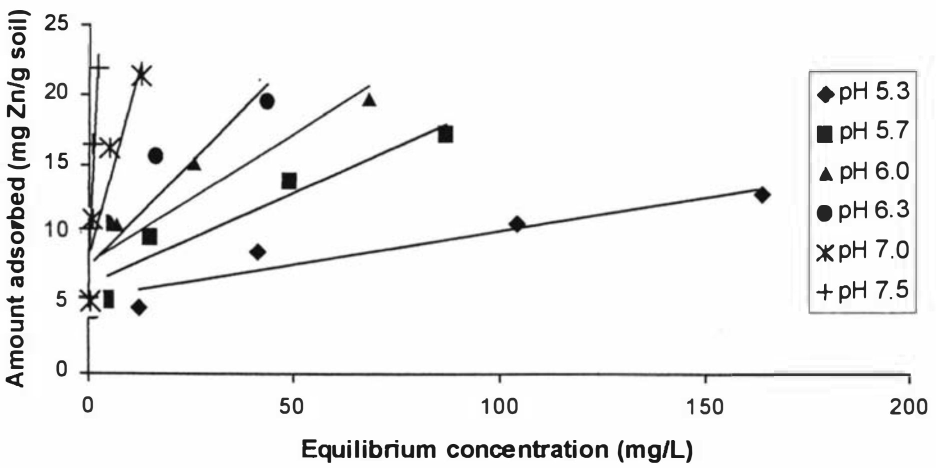


Figure 5.4a. **Linearised isotherm for the A horizon of volcanic Egmont soil at different soil pH**

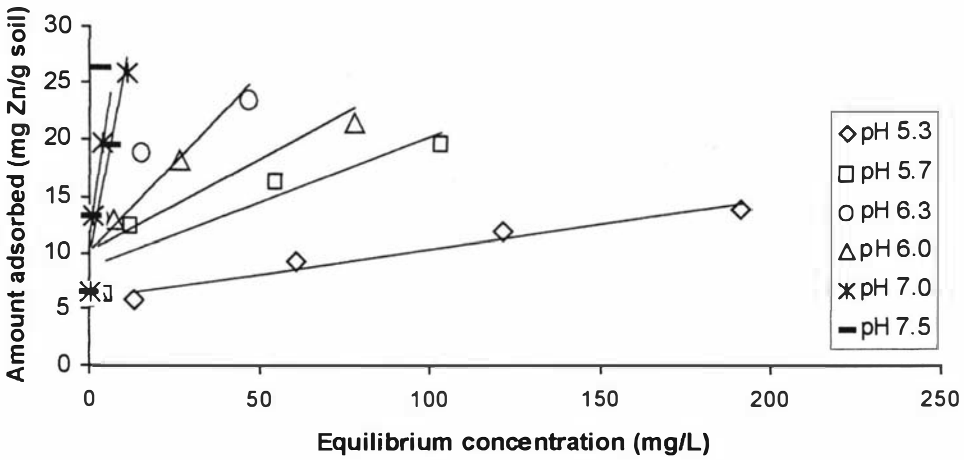


Figure 5.4b. **Linearised isortherm for the B horizon of volcanic Egmont soil at different soil pH**

The distribution coefficient increased with increasing pH (Figure 5.5) indicating stronger sorption of Zn at higher pH levels. Anderson and Christensen (1988) reported that pH – rather than either the Fe-Mn oxide on soil organic matter content – was the most influential factor in determining the distribution of Zn in soils.

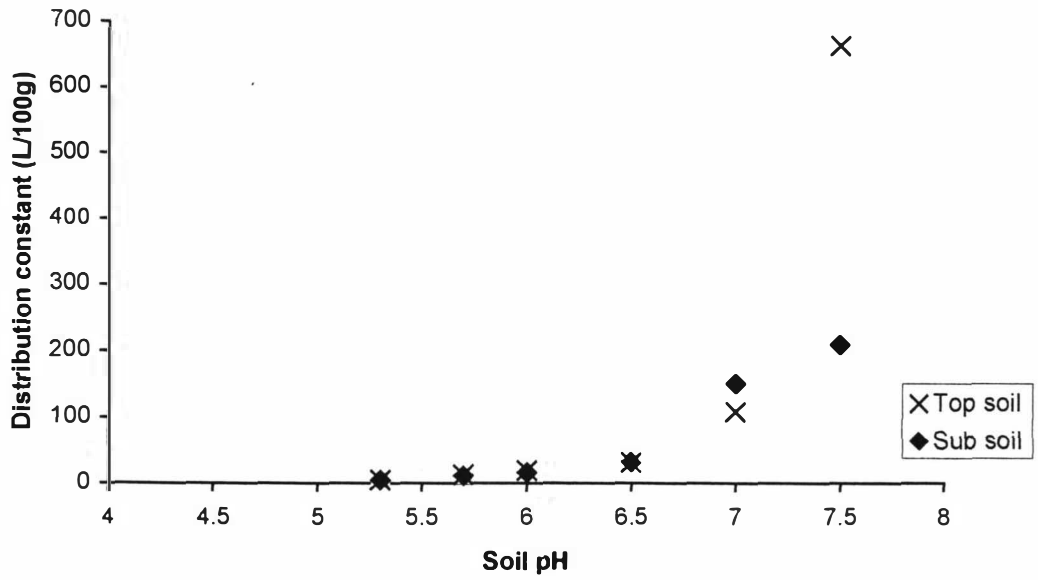


Figure 5.5. **Distribution coefficient value (Kd) of Zn sorption at different soil pH for the A and B horizons of volcanic Egmont soil**

5.2.5.2. Behaviour of Zn sorption in different horizons of volcanic Egmont soil

When the data for Zn adsorption isotherms for the topsoil (0-15 cm) and subsoil (15-32 cm) were fitted to the Freundlich equation, the subsoil showed a higher Freundlich adsorption capacity than the topsoil in all cases (Tables 5.2 and 5.3). The topsoil (0-15 cm) has greater organic matter content than the subsurface soil. Also, it has a much higher percentage of cation exchange capacity than does subsoil (B horizon). Subsoil contains significantly higher percentage of allophane (topsoil 36-40 %, subsoil 66-75 %) (New Zealand Soil Bureau, 1968). This marked difference in the adsorption capacity of the same soil could be attributed to the presence of a higher percentage of allophane.

5.2.6. Effect of adsorbed phosphate and nitrate on Zn adsorption

Volcanic Egmont soil sorbed more Zn (2.23-3 mg/g) compared to other volcanic soils (maximum of 0.9-1 mg/g soil) reported by Pardo & Quadalix (1996). This higher Zn adsorption capacity is attributed to the presence of high amount of allophanic clay and the high organic matter content (Zachara et al., 1992) in both A and B-horizons. The sorption of Zn was higher in the presence of phosphate than it was either in the presence of nitrate or in the control sample. It may be attributed to the increase in net negative charge on the soil surface resulting from $H_2PO_4^-$ and HPO_4^{2-} adsorption (Bolan & Barrow 1984; Naidu et al., 1990b). Phosphorus-induced Zn retention was related to pH increase associated with specific adsorption of phosphate. The presence of pH increment increases the hydrolysis of Zn.

Zinc retention increased linearly with increasing phosphate concentration: 0, 500, and 1000 mg. P/kg soil (Figures 5.6a and 5.6b). Phosphate application of 500 and 1000 mg P/kg soil increased the amount of Zn adsorption significantly compared to the control. The effect of phosphate on the sorption of Zn was more pronounced in sub soil than in topsoil (Figure 5.1).

The sorption of anions such as phosphate and nitrate showed that phosphate adsorption was greater than nitrate adsorption (Mott, 1981). It has often been observed that phosphate is sorbed mainly through a specific sorption process and nitrate is sorbed mainly through a nonspecific sorption process (Mott, 1981). While non-specific anion sorption occurs only at positive sites, specific sorption occurs even when the surface is net negatively charged or neutral (Barrow, 1983) because these soils carry only a small amount of positive charge. Therefore, the sorption of nitrate is considerably less than that of phosphate (Bolan et al., 1999a)

Several mechanisms can be advanced to explain the positive effect of phosphate on Zn sorption. These include (1) increase in net negative charge on the soil surface resulting from $H_2PO_4^-$ and HPO_4^{2-} adsorption (Bolan & Barrow, 1984; Naidu et al., 1990b). (2) cosorption of $H_2PO_4^-$ and metal as an ion pair, and (3) surface complex formation of metal on the phosphate compound. The enhanced sorption of a number of heavy metals have been demonstrated via increased surface charge in the presence of $H_2PO_4^-$ ions (Bolan et al., 1999a) both much work is still needed to provide conclusive evidence for mechanisms (2) and (3) (Bolan et al., 2003).

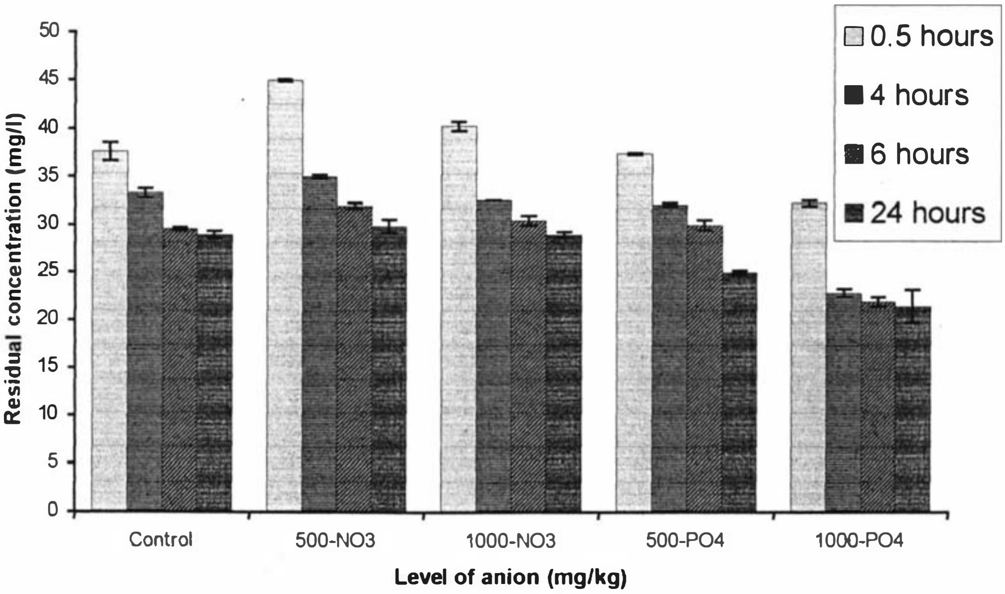


Figure 5.6a. **Effect of phosphate and nitrate on the residual concentration of Zn solution in topsoil (Error bar indicates Std. Error)**

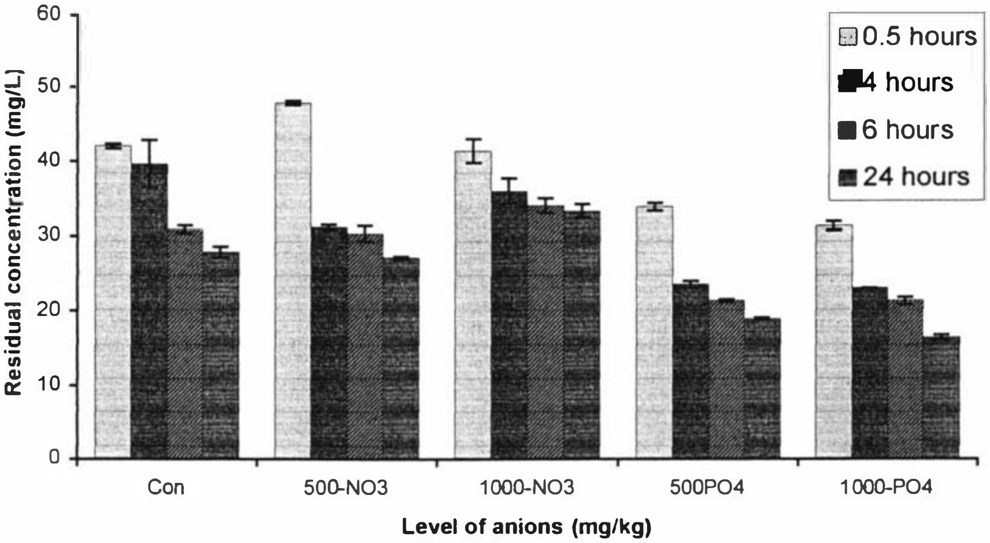


Figure 5.6b. **Effect of phosphate and nitrate on the residual concentration of Zn solution in subsoil (Error bar indicates Std.Error)**

5.3. DESORPTION OF ZINC FROM ZINC ADDED VOLCANIC EGMONT SOIL

The metal concentrations in soil solution, metal bioavailability and toxicity are most likely to becontrolled by adsorption and desorption reactions at the surfaces of soil colloidal material (Swift & McLaren, 1991). Compared with the numerous sorption studies on soil, there are relatively few that examine desorption. Most of the desorption studies on Zn (Kuo & Mikkelsen, 1980; Dang et al., 1994) used complexing agents EDTA (ethylenediamine tetra acetic acid), DTPA (diethylene triamine penta acetic acid or sodium citrate to desorb metals from the soil. Although it can be argued that natural complexing agents play an important role in solubilizing metals in soil, the use of relatively high concentrations of synthetic complexing agents to stimulate desorption is likely to produce enhanced amounts of desorption and faster desorption rates than would occur under normal soil conditions. Therefore, in this study the weak solutions of 0.1 M KNO_3, 0.1 M KH_2PO_4 and deionized water were used to see the desorption of Zn into natural soil solution.

5.3.1. Desorption of amended Zn

Both A (topsoil) and B horizon (subsoil) soil samples were incubated for 40 days with 1000 mg Zn/kg soil thus allowing slow reactions to occur and providing more realistic conditions. The cumulative amounts of Zn desorbed in 24 h time in A horizons of soil were 22.2 %, 6.3 % and 3.1 % in KNO_3, KH_2PO_4 and deionized water respectively. The cumulative amount of Zn desorbed in 24 h in B horizons of soil were 19.7 %, 5.1 % and 2.6 % in KNO_3, KH_2PO_4 and deionized water respectively (Figure 5.7). These results are in agreement with the results reported by Pardo and Guadalix (1996) who obtained relatively higher desorption (30 %) by using 0.1 M $NaNO_3$ as a desorbing agent.

During reaction periods from 0.5 to 24 h with 0.1 M KNO_3 and deionized water desorption of Zn from A and B-horizons of volcanic Egmont soil increased with time. Desorption patterns were generally characterized by an initial fast reaction followed by a slower continuing reaction (McLaren et al., 1998). This experiment was carried out only once since it is widely reported in the literature that desorption continues through for several months after reaching a plateau (Hogg et al., 1993; Dang et al., 1994). The percentage of the total Zn desorbed was significantly higher with KNO_3 extractants than with KH_2PO_4 and deionized water.

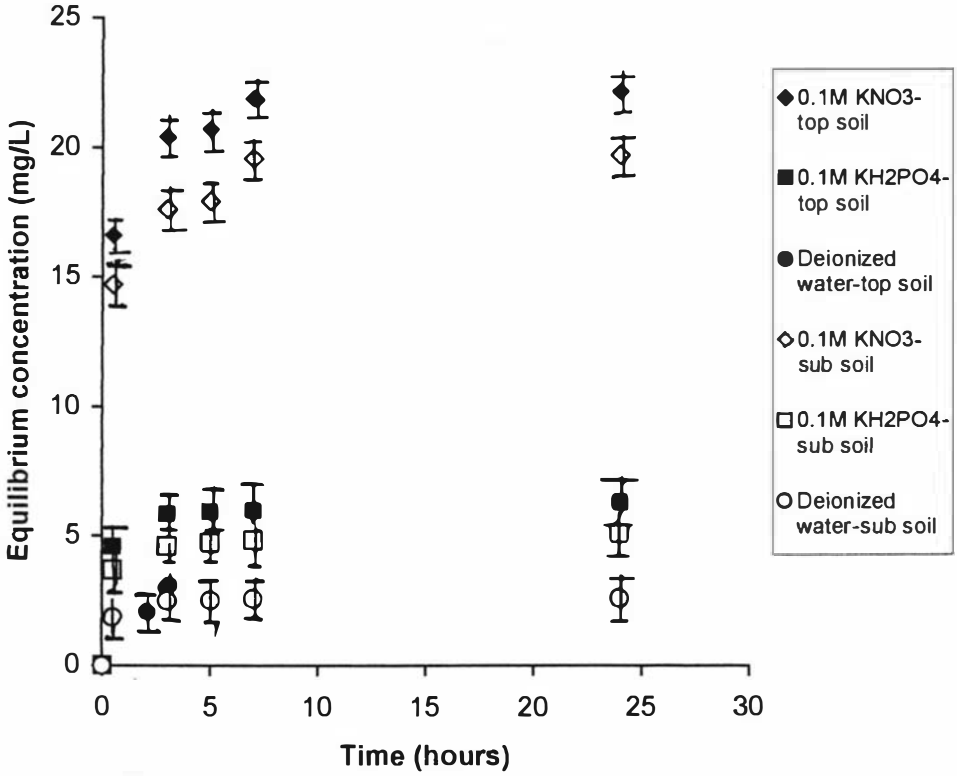


Figure 5.7. **Desorption of Zn from volcanic ash soil using different electrolytes (Error bars indicates Std. Error)**

5.3.2. Zinc desorption at varying pH levels

Zinc desorption in volcanic Egmont soils at two pH levels are illustrated in Figures 5.8a and 5.8b. The cumulative percentages of desorption in a 24 h period were 37 % in topsoil (A horizon) and 33 % in sub soil (B horizon) at pH 5.3. The cumulative percentages of desorption at 24 h were 14.3 % in topsoil (A-horizon) and 12.2 % in sub soil (B-horizon) at pH 7.5. Pardo and Guadalix (1996) examined the Zn sorption and desorption by volcanic ash soil by volcanic ash soil under most acidic conditions in 0.01 M $NaNO_3$ and found that 50 % of the sorbed Zn was recoverable. The results show an increase of cumulative desorption at pH 5.3 and the desorption decreased with an increase in pH of volcanic Egmont soil.

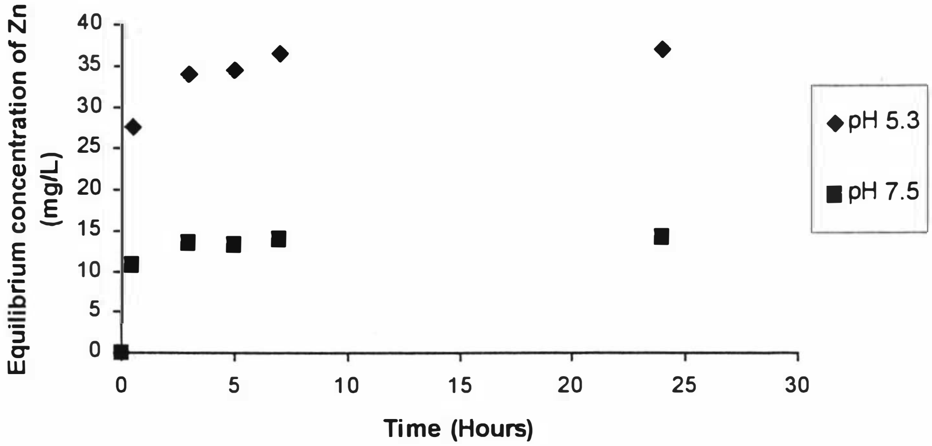


Figure 5.8a. **Desorption of Zn from volcanic Egmont topsoil at different pH**

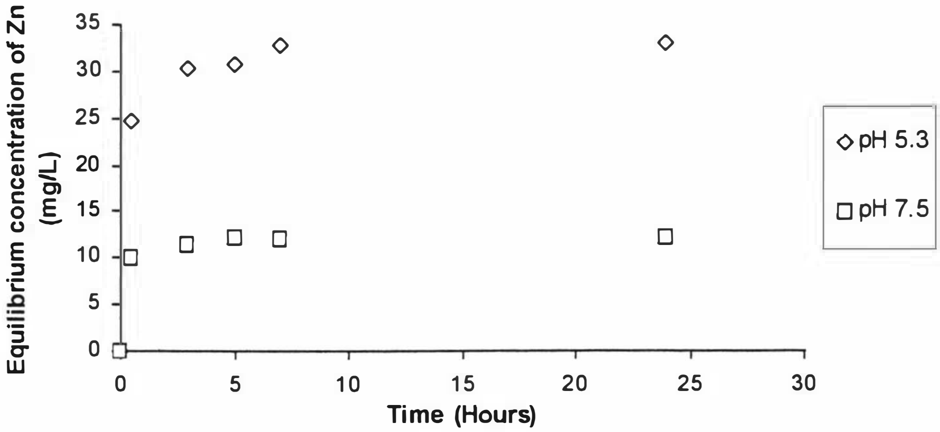


Figure 5.8b. **Desorption of Zn from volcanic Egmont subsoil at different pH**

5.4. CONCLUSIONS

- Zinc was immediately sorbed in this volcanic ash soil, reaching near maximum levels within 3-4 hours and equilibrium was attained in 6-10 hours.

- The Freundlich equation adequately described the Zn adsorption data.

- The highest value (2.23 and 3.09 mg/g soil in topsoil and subsoil respectively) of adsorption constant (K) for Zn was observed in deionized water as electrolyte in the original field pH (5.7) and least value (1.13 and 1.57 mg/g soil in top and subsoil respectively) was observed in the 0.1 M KNO_3 as electrolyte.

- Zinc sorption increased with an increasing pH level from 1.97 and 2.50 mg/g at pH 5.3 to17.23 and 18.17 mg/g at 7.5 for top and sub soil respectively.

- The proportion of Zn desorbed was higher in 0.1 M KNO_3 than in deionised water, and when 0.1 M KNO_3 was used as an eluant it was 22.2 % and 20 % in top and sub soils respectively.

- The desorption was 37% (at pH 5.3) and 14% (at pH 7.5) of the sorbed Zn and 33% and 12% for top and subsoils respectively.

Adsorption and desorption reactions are likely to be the major factors controlling the availability of Zn in the soil. In chapters four and five, a basic description of the types of surfaces that will adsorb Zn is provided and the relative amounts of Zn retained under given conditions are detailed.

There has been increasing concern about the transport of Zn present in sludges which are unchelated in the soil, therefore more mobile and move to ground water and surface water. This is affected by soil pH, ionic strength and the nature and the amount of inorganic anions in soil. Zinc concentration in sewage sludges in some treatment plants goes up to 49,000 mg/kg (Sommers, 1977). Also many of the leaching studies conducted to date either on Zn or Cd examined the movement in repacked soil columns. The repacked soil column may underestimate the heavy metal transport since it provide an ample chances for the contacts between the percolating water and soil particles.

Therefore, laboratory study with intact cores was conducted to see the mobility of Zn after the application of sewage sludge and inorganic Zn volcanic Egmont soil and to see the effect of most commonly available anions on the mobility of Zn. This will be presented in next chapter.

Chapter Six

MOBILITY AND MOVEMENT OF ZINC IN UNDISTURBED VOLCANIC EGMONT SOIL

6.1. INTRODUCTION

The application of sewage sludge to land is an effective disposal method if the metals contained in the sludge are immobile in agricultural soil. Factors such as the quantity and type of soil binding sites, pH, the concentration of complexing anions (organic and inorganic) and competing cations in soil solution that enhance mobility could result in more plant uptake or leaching of metals to the ground water.

Most of the knowledge on the movement of heavy metals is based on homogenized soil column laboratory studies. The repacked soil columns may not necessarily reflect the true conditions. Information from a few field studies suggests that metals leach through preferential paths and that this movement is influenced by the presence of anions (Dowdy & Volk 1983; Giordana & Mortvedt 1976; McBride et al., 1997).

Many recent studies indicate that Zn is a highly mobile element among the sludge-borne heavy metals (Basta & Sloan 1999; Leeper 1972; McLaren 2002). However, there are limited field studies (in situ) in New Zealand on the movement of sludge-born Zn (McLaren, 2002). Therefore, there is a need to undertake in situ studies on the movement of Zn and assess how the presence of anions influences this movement.

The behaviour of Zn in sewage sludge and in organic Zn applied soil was studied using intact soil columns (32 cm depth) in laboratory conditions. Some recent studies indicate that the effect of phosphate on the sorption of cadmium was more pronounced in volcanic Egmont soil than in alluvial Manawatu soil in New Zealand (Bolan, 1999b). To examine the influence of most common soil anions on Zn movement some columns were pretreated with phosphate and nitrate.

6.2. NITRATE AND PHOSPHATE PRETREATMENTS

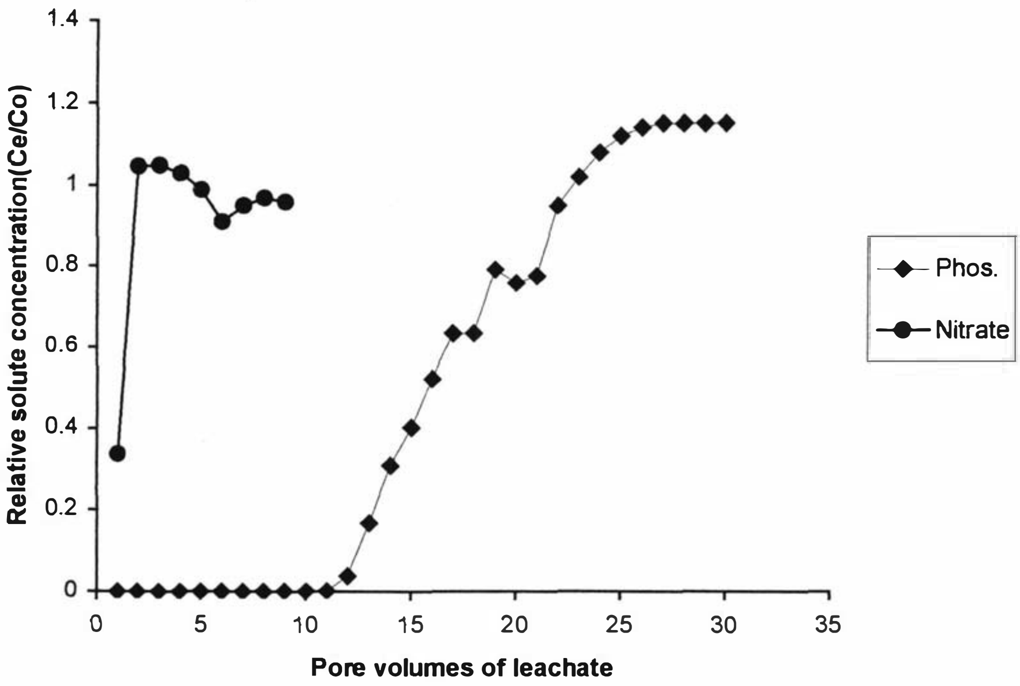


Figure 6.1. **Breakthrough curves for nitrate and phosphate for volcanic Egmont soil**

Breakthrough curves for nitrate and phosphate for volcanic soil are given in Figure 6.1. Nitrate appeared in the leachate after passing through the first pore volume of 0.1 M KNO_3 solution and reached its peak level of relative solute concentration after passing through the second pore volume. Phosphate appeared much later (after passing through 10 pore volumes of 0.1 M KH_2PO_4 solution) in the leachate than did nitrate and started to increase its relative solute concentration gradually from 10th pore volume and reached its peak level after passing through 23 pore volumes of 0.1 M KH_2PO_4 solution. The shape of the undisturbed soil breakthrough curves suggests a flow pattern in which there was only one plateau. This confirms that either these undisturbed columns do not appear to have a significant network for preferential flow or maybe the macro pores closed during the course of the run. Calculated pore volumes, flow velocities and moisture content for the six (T1 to T6) undisturbed soil columns are shown in Table 6.1. The moisture content was obtained by dividing the pore volume calculated by the total volume of each column. Velocities were calculated using the formula:

$$\mathbf{V = QL/Pv}$$

Where

V = velocity, cm/day

Q = average flux of water through columns, ml/day

L = column length, cm

P_v = pore volume, ml

The average flux of water through each column was obtained by dividing the total throughput volume by the duration of the experiment.

Pore volume was calculated by using particle density of the soil and the bulk density of each column using the formula:

$$1-(\rho_b/\rho s) = \mathbf{V_f/V_t}$$

ρ_b _ bulk density

ρ_s _ Particle density

V_f - Pore volume

V_t _ Bulk volume

It is confirmed from the breakthrough curve that volcanic soil's phosphate sorption capacity is much higher than its nitrate sorption capacity. The breakthrough curves also suggest that these columns were saturated with these anions.

Table 6.1. Undisturbed columns calculated pore volumes, flow velocities and moisture contents.

Column	Pore volume (mL)	Flow velocity (cm/day)	Moisture Content
T1	1903.0	3.81	0.712
T2	1805.8	3.96	0.676
T3	1785.3	3.92	0.668
T4	1802.0	4.77	0.716
T5	1700.0	5.16	0.676
T6	1730.6	5.07	0.688

Note: T1- No anion treated sludge applied soil column. T2–Nitrate treated sludge applied soil column. T3 – Phosphate treated sludge applied soil column. T4 –No anion treated inorganic Zn applied soil column. T5 – Nitrate treated inorganic Zn applied soil column. T6 – Phosphate treated inorganic Zn applied soil column.

6.3. MOBILITY OF ZINC IN VOLCANIC EGMONT SOIL

6.3.1. Zinc leaching

The leachate analysis data obtained from the sewage sludge applied columns showed that Zn concentration in the initial leaching aliquot (pore volume) was notably greater than that observed in the final leachate (Figure 6.2). The relatively high initial Zn in leachate concentration may be associated with the translocation of the water-soluble fraction of the sewage sludge, which is more mobile (Sposito et al., 1982). The initial leachate was highly coloured (yellow/brown) in the sludge treated column, which was preadsorbed with phosphate solution. This coloured leachate could be due to the extraction of the organically bound iron from some amorphous inorganic substances as well as from horizons of accumulation of Fe--organic matter complexes. Zinc also complexed with the water-soluble organic fraction would have also been transported with the leaching medium, resulting in high initial leachate concentration. However, once the readily water-soluble organic matter was removed from the soil solution, Zn concentration would decline in the leachate. This may explain the high initial concentration of Zn and iron in the leachate of the sludge applied phosphate treated column. The total Zn recovered in leachate from the sewage sludge applied columns were 0.11, 0.17 and 0.26% of the total recovered Zn for no anion, nitrate and phosphate treated columns respectively.

The leachate analysis data obtained from the inorganic Zn applied column showed that an increased initial Zn concentration appeared in the initial leachate collected from both nitrate and phosphate pretreated columns (Figure 6.3). The Zn concentration in the leachate of nitrate and phosphate treated columns was notably higher than that in the untreated (no anion treated) column leachate. Otherwise, no significant loss of Zn to the leachate occurred for any of the different anion treated column leachates. The total Zn recovered in leachate from the Zn spiked columns were 0.12, 0.45 and 0.41% of the total recovered Zn for no anion, nitrate and phosphate treated columns respectively. The lowest percentage of Zn in the no anion treated column is in agreement with the general effect of increasing ionic strength on Zn adsorption in the solid phase (Garcia-Miragaya & Page, 1976; Naidu et al., 1994).

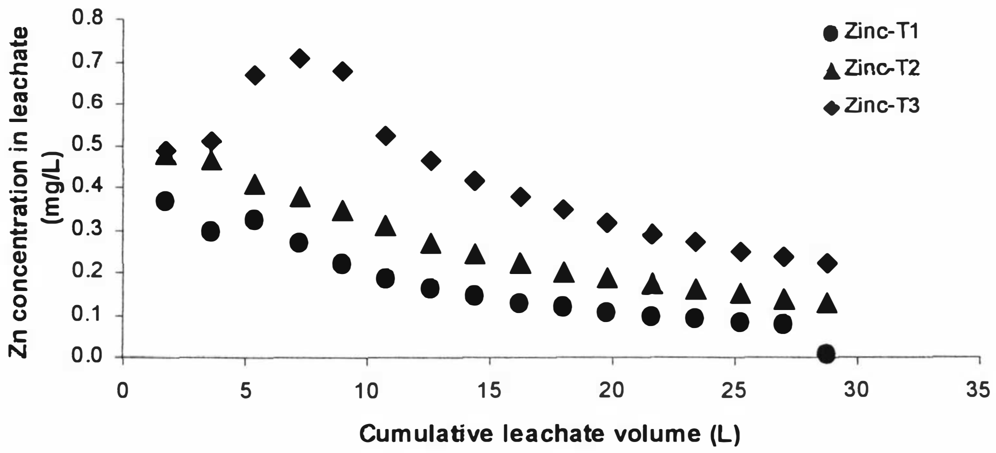


Figure 6.2. **Concentration of Zn in leachate from sewage sludge applied columns leached with deionized water. T1- No anion treated sludge applied soil column. T2– Nitrate treated sludge applied soil column. T3 –Phosphate treated sludge applied soil column.**

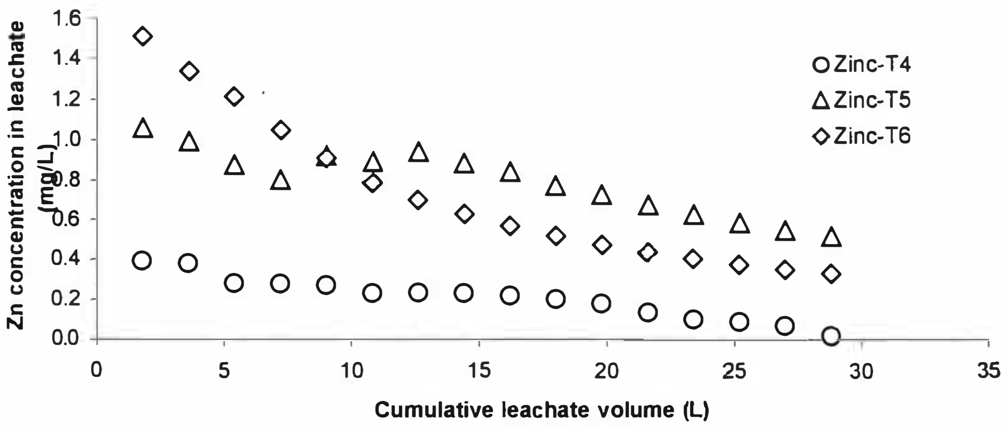


Figure 6.3. **Concentrations of Zn in leachate from inorganic Zn applied columns leached with deionized water. T4 – No anion treated inorganic Zn applied soil column. T5 – Nitrate treated inorganic Zn applied soil column. T6 – Phosphate treated inorganic Zn applied soil column.**

6.4. MOVEMENT OF ZINC IN VOLCANIC EGMONT SOIL

6.4.1. Zinc movement in sewage sludge and inorganic Zn applied columns

Soil analysis of the sewage sludge applied soil columns revealed that a higher rate (180 tons/ha) of sewage sludge application has resulted in the accumulation of substantial amounts of Zn in the top layer (0-5 cm depth) of the soil profile (Table 6.2a). These findings are consistent with observations by Cameron et al. (1994), Chang et al. (1984) and Williams et al. (1980) who reported the accumulation of heavy metals in the surface layer of soils after sewage sludge application. These researchers found little heavy metal accumulation beyond the zone of sludge incorporation. In this study a considerable amount of Zn was found even in 32 cm soil depth, which is markedly greater than in the same depth of the control soil column. Therefore it can be concluded that Zn has moved in every treatments compared to the control.

Table 6.2a. Total acid digestible Zn in sewage sludge applied soil columns in relation to soil depths.

Soil Depth	No anion treated (T1) Total acid digestible Zn		Nitrate treated (T2) Total acid digestible Zn		Phosphate treated (T3) Total acid digestible Zn	
cm	mg	%	mg	%	mg	%
0--5	2378.84	57.0	2349.87	57.5	2653.54	60.3
5-10	1438.50	34.5	1447.27	35.4	1545.05	35.1
10-15	284.14	6.8	242.61	5.9	187.71	4.26
15-20	46.15	1.1	27.62	0.7	8.64	0.19
20-25	17.30	0.4	11.31	0.3	3.90	0.08
25-32	9.75	0.2	10.34	0.2	2.99	0.07
0--32	4174.68	100	4089.02	100	4401.83	100

The soil Zn content at various depth was calculated by subtracting the amount of the total acid digestible Zn in the control soil column from the total acid digestible Zn in sewage sludge or inorganic Zn treated soil columns at different soil depths. Determination of these values reveals that a high percentage of the Zn accumulated in the top layer 0-5 cm (57-60 %) of the sewage sludge applied columns (T1, T2 & T3). At the depth of 5-10 cm also they had a remarkable increase of 34.5-35.4 % of Zn (Table 6.2a). Also the data showed that 8.5, 7.1 and 4.6 % of the total Zn derived from the sludge had moved from the top 0-10 cm depth to the rest of the column of no anion, nitrate and phosphate treated soil columns, respectively. At the deepest (25-32 cm) soil layer 9.75 mg (0.2 %), 10.34 mg (0.2 %) and 2.99 mg (0.07 %) of Zn was detected in no anion, nitrate and phosphate treated columns respectively. The phosphate treated column showed a slightly slower movement of Zn than the no anion and nitrated columns. A similar study conducted in New Zealand soil recently by McLaren (2002) strongly supports the results of this study on Zn transport in undisturbed soil columns. He observed a significant Zn movement below the layer of incorporation. The level of Zn application in his study was one-tenth of that used in this study. In a field study Dowdy et al. (1991) observed a loss (movement) of half of the total Zn from the top of soil profile after three years of application of sewage sludge. However, the portion of Zn moved from the top of soil profile was only 5-

8.5% in this particular study. The rain fall rate is one sixth of the rain fall received by the Dowdy's experimental plot.

Table 6.2b. Total acid digestible Zn in inorganic Zn applied columns in relation to soil depths.

Soil Depth	No anion treated (T4)		Nitrate treated (T5)		Phosphate treated (T6)	
	Total acid digestible Zn		Total acid digestible Zn		Total acid digestible Zn	
cm	mg	%	mg	%	mg	%
0--5	3400.21	70.2	3477.79	72.1	3817.57	77.2
5-10	802.20	16.6	738.40	15.3	705.43	14.2
10-15	509.04	10.5	472.84	9.8	341.69	6.9
15-20	93.45	1.9	88.90	1.8	59.30	1.2
20-25	24.10	0.5	29.75	0.65	15.85	0.33
25-32	12.33	0.3	16.70	0.35	8.05	0.17
0--32	4841.33	100	4824.38	100	4947.89	100

An equivalent amount of Zn used in sewage sludge application was applied in the form of inorganic Zn (zinc nitrate) to no anion, nitrate and phosphate treated soil columns (T4, T5 & T6). Analysis of the total acid-digestible Zn in each layer reveals that most of the total acid digestible Zn (70-77 %) accumulated in the top (0-5 cm) layers of T4, T5 and T6. Between 14 and 16 % of Zn was found in the 5-10 cm depth. Also the data show that 13.2, 11.7 and 8.61 % of the total Zn moved below 10 cm depth of no anion, nitrate and phosphate treated soil columns, respectively. At the deepest (25-32 cm) soil layer 0.17-0.3 % (8.05 – 12.33 mg) of Zn was detected (Table 6.2b). The phosphate treated column showed slower movement of Zn than did the other two columns.

Table 6.3a. Speciation of Zn in sewage sludge applied volcanic Egmont soil columns as affected by anions

Treatment	Speciation of Zn in soil depths						Amount of exchange anion in soil depths	
Anion	Depth (cm)	Water soluble (mg)	Exchangeable form (mg)	Oxide form (mg)	EDTA extractable (mg)	Organic form (mg)	Exchang. Nitrate (mg)	Exchang. Phosphate (mg)
No anion (T1)	0-5	26.15	409.64	157.80	688.65	869.68	26.94	38.70
	5-10	15.95	249.97	26.20	437.67	570.77	17.28	9.42
	10-15•	6.46	101.22	1.41	94.43	14.31	17.10	9.96
	15-20•	0.27	4.26	1.68	31.00	3.77	14.76	7.47
	20-25•	0.22	3.61	1.34	7.78	1.00	11.49	4.50
	25-32•	0.11	1.66	1.04	3.72	0.45	13.38	5.46
Nitrate (T2)	0-5	27.40	429.34	163.60	708.28	870.18	9.51	49.20
	5-10	16.80	263.58	26.55	425.63	586.77	22.68	29.80
	10-15•	5.69	89.16	2.02	92.23	7.26	26.19	11.25
	15-20•	0.26	4.04	1.20	15.40	2.42	15.78	7.42
	20-25•	0.19	2.90	1.09	5.68	0.10	10.74	1.14
	25-32•	0.11	1.71	0.84	4.17	0.05	34.20	9.60
Phosphate (T3)	0-5	32.00	501.41	221.60	742.82	878.64	25.4	237.6
	5-10	19.40	303.79	34.08	419.14	583.77	16.3	390.0
	10-15•	4.10	61.85	1.12	71.03	6.01	16.9	332.4
	15-20•	0.17	2.61	0.55	1.70	0.77	15.2	336.0
	20-25•	0.052	0.81	0.99	0.78	0.05	9.8	307.2
	25-32•	0.009	0.61	0.74	0.42	0.26	11.7	316.5

Inorganic sources of Zn equivalent to amounts supplied by sludge

•Distance in soil column below treated soil

The analysis reveals that a considerable proportion of Zn moved from the top (0-5 cm) layer to the lower depths in all six columns. Inorganic Zn applied columns showed higher mobility of Zn than did in sewage sludge applied columns. The effect of phosphate treatment on the movement of Zn was more prominent in the inorganic Zn applied soil columns and it had a limiting effect on the movement of Zn compared to nitrate treated soil columns. It will be discussed under the section "Factors influencing the downward movement of Zn".

Table 6.3b. Speciation of Zn in inorganic Zn applied volcanic Egmont soil columns as affected by anions

Treatment	Speciation of Zn in soil depths						Amount of exchange anion in soil depths	
Anion	Depth (cm)	Water soluble (mg)	Exchangeable form (mg)	Oxide form (mg)	EDTA extractable (mg)	Organic form (mg)	Exchang. Nitrate (mg)	Exchang. Phosphate (mg)
No anion	0-5	147.80	1089.35	523.48	1282.44	24.04	2.3	3.69
(T4)	5-10	33.40	242.15	109.21	316.99	12.51	5.1	3.43
	10-15	9.40	116.78	62.46	262.73	0.81	4.7	4.37
	15-20	0.84	24.81	15.38	35.26	0.67	3.6	2.60
	20-25	0.59	4.09	4.99	7.38	0.30	2.4	1.01
	25-32	0.39	1.28	2.19	1.72	0.50	3.8	1.67
Nitrate	0-5	157.10	1185.96	570.57	1249.57	24.24	5.7	4.20
(T5)	5-10	37.40	230.85	107.98	281.15	11.26	13.4	3.70
	10-15	10.43	93.82	60.31	249.07	1.26	13.3	4.20
	15-20	0.74	30.39	7.62	31.22	1.37	12.9	1.80
	20-25	0.43	10.95	4.16	5.73	0.65	9.5	0.92
	25-32	0.31	7.30	1.69	0.72	0.85	12.3	1.01
Phosphate	0-5	159.30	1494.49	586.78	1217.62	25.60	3.2	95.40
(T6)	5-10	36.70	244.82	94.12	266.10	9.80	6.3	204.40
	10-15	8.20	77.62	46.37	167.63	0.71	5.1	218.40
	15-20	0.28	10.32	4.10	28.28	1.07	3.7	268.32
	20-25	0.104	3.93	1.17	5.08	0.20	2.7	237.60
	25-32	0.018	1.55	0.74	0.62	0.65	3.3	351.10

Inorganic sources of Zn equivalent to amounts supplied by sludge

•Distance in soil column below treated soil

6.4.2. Factors influencing the downward movement of Zn

6.4.2.1 Soil pH

The determination of soil pH levels with depth of the sewage sludge amended soil umns revealed that pH reduced in the first four depths of 0 -20 cm then increased in all three soil columns, while the control soil was showing an increasing pH with depth (Figure 6.4). There was an increase in soil pH from 0-10cm depths of all three columns compared to control soil. This could be because of the basic cations in the sewage sludge. Tsadilas et al. (1995) mentioned that the control soil having initial soil pH ranging from 4.9-6.5 showed a raised soil pH because of the addition of sludge. The lowered soil pH from 10-20 cm depths compared to the control could be attributed to a high amount of water added into the columns (over a period of 20 weeks) and release of organic acids from sewage sludge applied to the surface soil. These results are in agreement with the work of other researchers (Al-Wabel, 1998; Bevacqua & Mwllano, 1994; Del-Castilho et al., 1993; Tester, 1990.). Tsadilas et al. (1995) indicated that a high sludge application rate could lower the soil pH due to increased nitrification. This lowered soil pH could have also contributed to the transport of Zn down to this depth.

The comparison of soil pH levels with the soil depth of the inorganic Zn applied soil columns reveals that soil pH was showing an increasing trend from the top to the bottom of the treatment columns and a higher level than control soil pH. The phosphate treated column showed a remarkable increase over other treatments (Figure 6.5). This higher increase of soil pH in the phosphate treated column could be attributed to the phosphate induced increase in negative charge. Bolan et al. (1999b) indicated that this phosphate-induced increase in negative charge was higher for the Egmont soil than for the Manawatu soil. Increase in pH increased the adsorption capacity of the soil and therefore it prevents the metal leaching in the phosphate treted soil column.

6.4.2.2. Organic colloids

The addition of sewage sludge increased the amount of Zn complexed with organic matter in the soil. However, the water-soluble fraction of sewage sludge could be reactive to trace metal cation (Sposito et al., 1982). Therefore, the water-soluble organic matter fraction of sewage sludge could have enhanced the Zn solubility with an increased metal concentration in the soil solution. A large quantity of water soluble and exchangeable fraction of Zn was observed down the sludge treated columns (Table 6.3a) leaving 9.75 mg, 10.34 mg and 2.99 mg of total digestible Zn at the lowest depth of the T1, T2, and T3 columns respectively (Table 6.2a). This movement of Zn could be due to the water-soluble organic matter fraction of sewage sludge. Also, there was a large amount of the organically complexed form of Zn observed below the sewage sludge incorporated layer of the soil columns. This indicates that some organic colloidal material could have translocated with the soil solution through the soil columns.

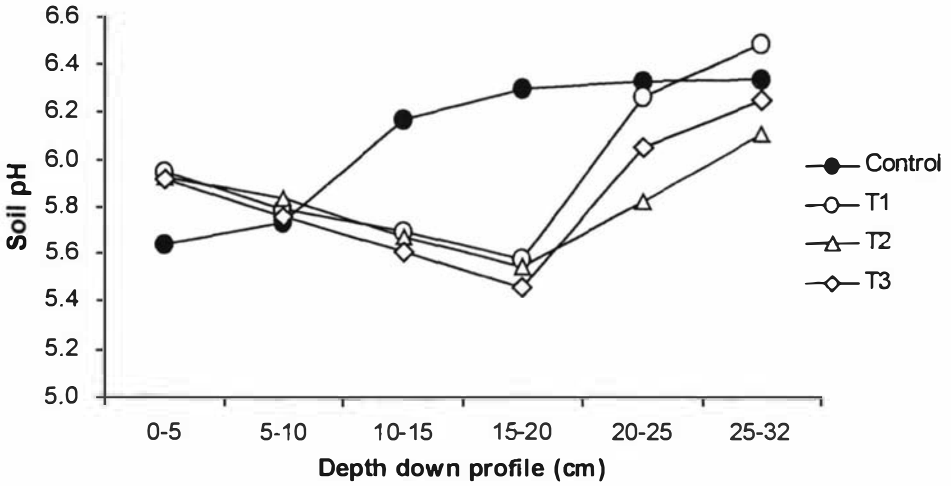


Figure 6.4. **Variation of pH in sewage sludge amended soil columns. T1- No anion treated sludge applied soil column. T2–Nitrate treated sludge applied soil column. T3 –Phosphate treated sludge applied soil column.**

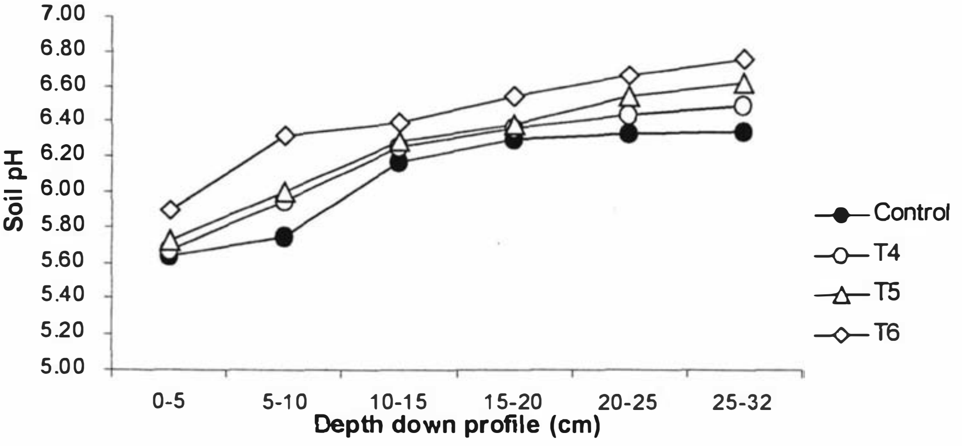


Figure 6.5. **Variation of pH in inorganic Zn treated soil columns. T4 –No anion treated inorganic Zn applied soil column. T5 – Nitrate treated inorganic Zn applied soil column. T6 – Phosphate treated inorganic Zn applied soil column.**

6.4.2.3. Extractable soil nitrate (2 M KCl)

The extractable soil nitrate (2M KCl extractable) in different depths of the sewage sludge treated soil columns increased significantly compared to the control column. These results reveal an increased rate of nitrification for the higher rate of sewage sludge application (Figure 6.6). Nitrate treated soil columns had only 19 mg of 2M KCl extractable soil nitrate more than the no anion treated sludge applied column. This is attributed to the high leaching rate of nitrate anion in the soil column in which 15 pore volumes of the deionised water passed through. Nitrate treated soil columns showed relatively greater mobility of Zn compared to other treatments. These results are in agreement with the results of Bolan et al. (1999b) who concluded that Cd leaching was higher in the presence of nitrate. This may be due to the fact that nitrate is more leachable and the sorption affinity of nitrate is very low.

6.4.2.4. Extractable soil phosphate (Olsen P)

The extractable soil phosphorus in different depths of the sewage sludge treated soil columns increased markedly compared to control soil (Figure 6.7). However, the phosphate treated columns showed greater phosphate accumulation compared to other treatments. This is due to the slow leaching of phosphate anion from the soil column. Volcanic soil had a high phosphorus sorption capacity (86-100 % phosphate added). This higher phosphate sorption capacity limited the downward movement of Zn through the phosphate-induced Zn retention (Bolan et al., 1999b; Bolan et al., 2003). This is more evident (Tables 6.3a and 6.3b) from the results of the inorganic Zn applied columns than from the sewage sludge incorporated columns. Phosphate markedly increased the exchangeable form of Zn and the oxide form of Zn in the layer (where inorganic Zn was applied) compared to no anion treated columns. Also, the downward movement of the water-soluble and exchangeable form of Zn in that particular soil column was low compared to no anion and nitrate previously adsorbed column. This observation is in agreement with the results of Ahumada et al. (1997)

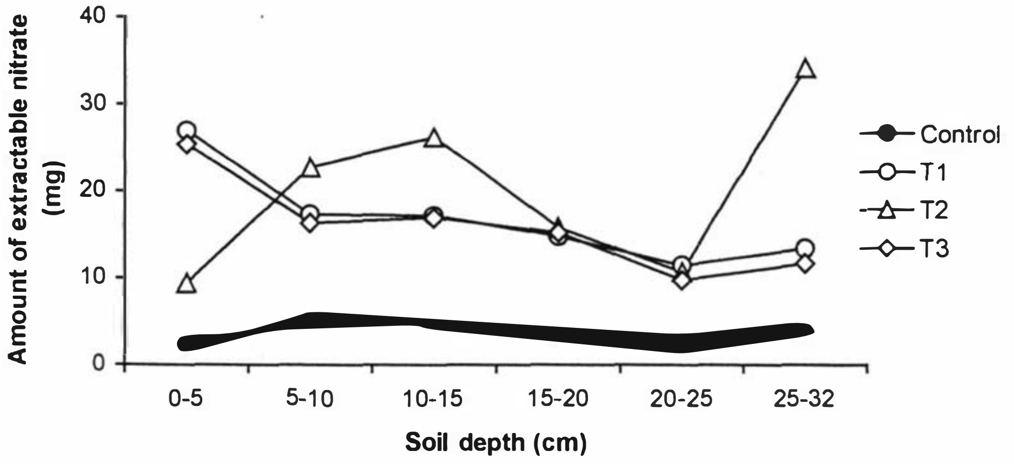


Figure 6.6. **Extractable soil nitrate (2M KCl) in sewage sludge treated columns in comparison with control soil columns. T1- No anion treated sludge applied soil column. T2–Nitrate treated sludge applied soil column. T3 –Phosphate treated sludge applied soil column.**

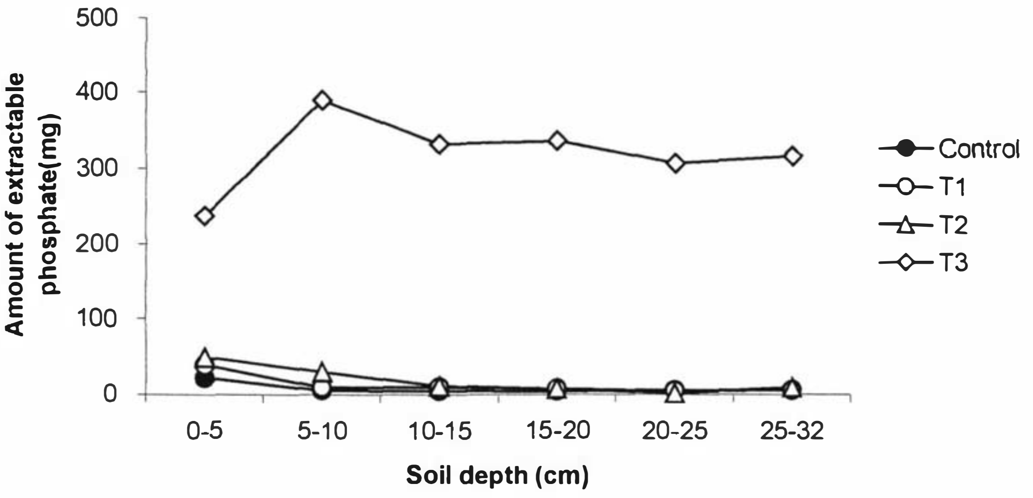


Figure 6.7. **Extractable soil phosphate (Olsen P) in sewage sludge treated columns in comparison with control soil columns. T1- No anion treated sludge applied soil column. T2–Nitrate treated sludge applied soil column. T3 –Phosphate treated sludge applied soil column.**

who reported that phosphate influences the distribution of extractable Zn fractions in Andosol (volcanic soil) by increasing the exchangeable Zn form-whereas in inceptisol and vertisol pretreatment with phosphate had no effect. In the volcanic soil used in this study, phosphate pretreatment increased the exchangeable form Zn and the oxide form of Zn. However, the exchangeable form of Zn was increased even more markedly compared to the oxide form. This could be due to the increased cation exchange capacity and an increase in the negative surface charges and to the creation of specific sorption sites as a result of phosphate sorption. This supports the results of Schalscha et al. (1981) who reported that the effect of added phosphate on Zn retention in allophonic can be explained by the increase of CEC. Retaining Zn in an exchangeable form rather than in an oxide form makes it more potentially bioavailable (Ahumada et al., 1997). Therefore, this exchangeable form of Zn may become readily available when the soil solution condition changes in volcanic soils.

The increased Zn retention could be due to an increased negative surface charge and the creation of specific sites as a result of P sorption. Schalscha et al. (1981) reported that phosphate sorption by volcanic soil could be due to the presence of allophonic clay and increased CEC which thus explained the effect of added phosphate on Zn retention.

6.5. MASS BALANCE OF ZINC

The total indigeneous Zn content of the soil was estimated from three small cores taken from around the location where the large intact soil cores were excavated for experiments. The total amount of Zn in each sludge treated column was calculated by adding the value of added Zn to the column with the mean value of total indigeneous Zn in the un treated small cores.

The recoveries of total Zn extracted from the inorganic Zn applied and sludge applied columns ranged from 97.1 %-99.5 % and 83 %-87.5 % respectively (Tables 6.4 and 6.5). The low level of recovery from the seweage sludge treated soil may be due to the oils and fats, which are present in the sample of sludge could limit the access of the extractants (Beckett, 1989).

Table 6.4. Recovery of Zn in the sludge Zn applied soil columns

Treatment	Initial +added (mg)	Recovered (mg)	Difference (mg)	Recovered (%)
No anion with sludge Zn (T1)	219.2 + 5080	4394.15 +4.9	900.15	83.01
Nitrate with sludge Zn (T2)	218.9 + 5080	4408.49 + 7.7	882.71	83.34
Phosphate with sludge Zn (T3)	216.1 + 5080	4621.30 +12.2	662.60	87.49

Table 6.5. Recovery of Zn in the inorganic Zn applied soil columns

Treatment	Initial+added (mg)	Recovered (mg)	Difference (mg)	Recovered (%)
No anion with inorganic Zn (T4)	217.45+5000	5060.80 + 6.1	150.55	97.11
Nitrate with inorganic Zn (T5)	219.40 +5000	5043.85 +22.9	152.65	97.07
Phosphate with inorganic Zn (T6)	212.70 + 5000	5167.36 +21.1	24.24	99.53

6.6. CONCLUSIONS

- Phosphate adsorption capacity is very high in volcanic Egmont soil.
- The maximum amount of Zn recovered in the leachate was 12.2 mg and 22.9 mg in sewage sludge and inorganic Zn treated columns respectively. These are only 0.26 % and 0.45 % of the total recovered Zn in sewage sludge and inorganic Zn applied columns respectively. This confirms the fact that the sorption capacity of volcanic Egmont soil is high - which could be because of the presence of aluminum and iron oxide and allophonic constituents in it.

- A maximum of 13.2 % and 8.5 % of the total recovered Zn moved below 10 cm depth in inorganic Zn applied and in sewage sludge applied soil columns respectively.

- Inorganic Zn applied soil columns showed higher Zn movement than did sewage sludge applied soil columns.

- When Zn was added after the phosphate and nitrate saturation, the increase in negative charge due to phosphate sorption resulted in an increase in Zn sorption and limited the downward movement of Zn in phosphate treated soil columns. This effect of phophate on Zn movement was more pronounced in the inorganic Zn treated column.

- Treatment of soil with phosphate influenced the distribution of 0.1 M $CaCl_2$ extractable Zn fractions in volcanic Egmont soil, increasing the exchangeable Zn form and decreasing the Fe-Mn oxide form.

Mobilty (leaching and movement) of Zn in the undisturbed soil columns was discussed in this chapter in terms of anion and a different Zn sources (sewage sludge, inorganic Zn).

The availability of Zn (redistribution) in the soil profile can be examined by a fractionation technique. Therefore, a fractionation technique was used to determine the species of Zn in sewage sludge and Zn applied soils of different depths. The effect of anion on the fractionation of Zn was also studied for different depths of the soil. The results of these investigations will be presented in the next chapter.

Chapter Seven

FRACTIONATION OF ZINC IN SEWAGE SLUDGE AND ZINC APPLIED SOILS

7.1. INTRODUCTION

In countries where sewage sludge is applied to the land it is important to identify the available and unavailable forms of the heavy metals from the sludge and the anions controlling the availability of heavy metals. This is to ensure that the soil is strategically managed to prevent the unavailable forms from becoming available. During the application of sewage sludge, the trace metals can saturate the specific sites and can be held in relatively unavailable forms. The trace metals not fixed onto specific sites can still be reactive. Therefore, it may not be possible to predict the long-term fate of trace metals from sewage sludge without knowing their principal forms of combination and the likely transformations these metals undergo on application to the land.

Several procedures have been proposed to determine the chemical forms of metals in soils, sequential extraction or fractionation of metals from soils being a useful technique for this purpose. Therefore, a sequential fractionation scheme initially proposed by Shuman (1985) and recently modified by McGrath and Cegarra (1992) was followed. This initial fractionation scheme does not extract the carbonate forms of Zn separately. Therefore, 0.05 M Na_2-EDTA solution was included in the fractionation to dissolve carbonates (Beckett 1989; McGrath & Cegarra, 1992). The fractionation used in this study is to assess (i) the effect of equivalent amounts of Zn applied with sludge and inorganic metal salts and (ii) the effect of phosphate and nitrate on the distribution of chemical forms of Zn in a volcanic Egmont soil.

Statistical analysis of each fraction of Zn in different depths was undertaken separately for sewage sludge and metal salt spiking treatments by the least significance difference (LSD) test. Nearly all of the interactions were statistically significant at $P \leq 0.01$ or $P \leq 0.05$.

7.2. FRACTIONATION OF ZINC IN SLUDGE

7.2.1. Unamended (Original) sludge

The fractionation of Zn of the original activated sewage sludge obtained for this study showed very little Zn (194 mg/kg) compared to the Zn content of other wastewater sludge which could be as high as several thousand mg/kg sludge. Therefore, the Zn level of the original sludge was raised by loading 35,420 mg/kg Zn to study the dynamics of the Zn in the soil. The dewatered sludge was air dried and incubated at 25oC for two weeks before soil application. The total Cd and Cu contents in the sewage sludge were 39 and 148 mg/kg and there was no Ni detected in the original sludge.

7.2.2. Amended sludge

The sludge was amended with inorganic Zn (Zinc nitrate solution) to achieve a very high concentration- 35,420 mg/kg of Zn. Nitrate is not likely to have any interaction with Zn for specific sorption compared to sulphate, chloride and phosphate. In the previous Zn amended sludge studies a concentration of 49,000 mg/kg Zn loaded sludge was used (Sommers et al., 1977). After loading the sludge with Zn, the amended sludge was fractioned into various forms of Zn. The fractionation data showed (Table 7.1) that a 18 % of the Zn was extracted as exchangeable and less than 7 % of the Zn was in water-soluble form. Some previous studies suggest that the water-soluble Zn in fresh sludges exceeded 10 % of the total metal (Campanella et al., 1987; Lake et al., 1984). NaOCl (organically bound) extracted 30.1 % of total Zn. The 0.05 M EDTA (33.2 %) and 0.1 M HCl (44 %) extracted the highest proportions of Zn from the amended sludge. These data suggests that a larger portion of Zn in amended sludge was in a carbonate form than in an organic complex form.

Table 7.1. Some detected concentrations of heavy metal in the original sludge and in zinc amended sludge

Forms of heavy metal	Original sludge (mg/kg)	Zn amended sludge (mg/kg)
Total Zn	194	35420
0.1 M $CaCl_2$ extractable Zn (Water-soluble & Exchangeable)	99	8902.3
Water soluble Zn	22	2534
Organic complexed	40.4	10675
0.05 EDTA extractable	126	11746
0.1 M HCl extractable Zn	n.d•	15601

n.d• denotes not detected

7.3. FRACTIONATION OF ZINC IN SOIL

7.3.1. Control soil column (Volcanic Egmont soil)

Table 7.2. The distribution of different forms of Zn along the control soil column

Depth (cm)	Water soluble & exchangeable (mg)	Organic (mg)	EDTA extractable (mg)	Fe-Mn Oxide (mg)	Residual (mg)	Total acid digestible (mg)
0--5	1.21	6.12	2.15	11.90	2.18	23.56
5-10	0.98	4.03	3.13	10.60	10.86	29.60
10-15	0.92	3.69	2.87	9.13	15.60	32.21
15-20	0.67	2.83	2.30	7.90	21.40	35.10
20-25	0.77	2.90	2.42	6.26	38.95	51.30
25-32	0.48	1.45	3.28	4.76	37.73	47.70

The water soluble and exchangeable fraction of Zn in the top 5 cm of the original soil was 1.21mg (5.14 % of total Zn) (Table 7.2) and decreased with the increasing soil depth and reached 0.48 mg (1% of total Zn) in the lowest depth (25-32 cm) (Figure 7.1). This shows a even distribution of the Zn down the profile of this volcanic soil. The 0.05 M EDTA extractable carbonate fraction of Zn was uniform throughout the profile ranging from 2.15 – 3.28 mg. The organic fraction of Zn in the topsoil (0-5 cm) of the control soil column was 6.12 mg (25.9 % total Zn) and this also decreased with the depth and at the lowest depth (25-32 cm) of the soil showed 1.45 mg (3.04 % total Zn). This could be due to the fact that soil organic matter accumulates on the surface of the volcanic soil leading to a decrease on the amounts in subsurface horizons. Among the non-residual fractions, the Fe-Mn oxide fraction contained the greatest amount of Zn in all depths of the control soil column, decreasing with the depth from 11.9-4.8 mg (50.5-10 % of total Zn). The residual fraction increased with the depth ranging from 2.2mg to 37.7 mg (9.3-79.1 % of total Zn) at the lowest depth (25-32 cm). The highest percentage of Zn in the form of residual fraction probably reflects the tendency for Zn to become unavailable in soil.

The total fractions of Zn in the control soil column (0-32 cm depth) in different forms: water-soluble, carbonate (0.05 M EDTA extractable Zn), organic, Fe-Mn oxide, and residual were 2.3, 7.3, 9.6, 23 and 58 % of total Zn, respectively. The range of total Zn and its various fractions obtained in this control soil are within the levels reported for other soils in New Zealand (Warren, 1994). These are in agreement with the results of Ma and Uren (1995) who noted higher proportions of water-soluble, exchangeable and oxide-bound Zn fractions in the topsoil than in the subsoil.

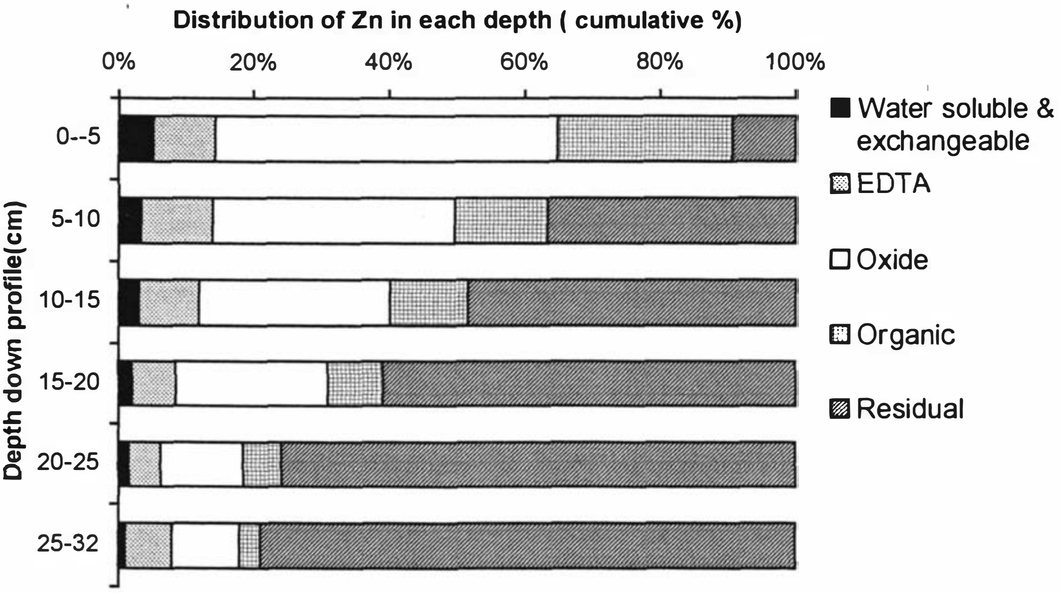


Figure 7.1. **Comparison of Zn fractions extracted from different depths of the control soil column**

The water-soluble and exchangeable form of Zn is held on inorganic and organic sites predominantly by electrovalent forces (Beckett, 1989). However, the $CaCl_2$ solution displaces Zn weakly from minerals. This indicates that the readily available form of Zn may be more than what was observed in the experiment.

7.3.2. Sewage sludge applied soil columns

7.3.2.1. Water-soluble and exchangeable forms of Zn

Sewage sludge application raised the water soluble and exchangeable forms of Zn at a higher level in the first 15 cm depth in all three treatments (T1 - Sewage sludge applied no anion treated soil column, T2- Sewage sludge applied nitrate treated soil column and T3- Sewage sludge applied phosphate treated soil column). Between 437 mg and 534 mg (53 %-57 % of the total water soluble form of Zn) was accumulated in the top 5 cm depth of the T1, T2 and T3 columns respectively (Tables 7.3, 7.4 & 7.5). At the lowest depth (25-32 cm) these amounts were 2.5, 2.3 and 0.55 mg respectively. The fractions of Zn varied with the soil depth between 18.2 and 3.92 %, 18.5 and 4 %, and 20 and 1.1 % of total Zn in T1, T2 and T3 columns (Figures 7.2, 7.3 & 7.4). This water-soluble form of Zn may be free ions or complexed with inorganic anions or organic ligands. On the organic ligands there may be some sites that can hold trace metals. Soluble or colloidal organics emanating from sewage sludge have the ability to mobilise the metals adsorbed on soil or sludge particles (Christensen, 1985; Del-Castilho et al., 1993).

The overall value of the water-soluble and exchangeable fraction of total Zn was found to be 18.8 % (824.6 mg), 19.2 % (846.2 mg) and 20.2 % (931.3 mg) of the total Zn in the T1, T2 and T3 columns respectively (Figure 7.8). These levels of water soluble and exchangeable fraction of Zn in sewage sludge applied soil are similar to the levels reported by McGrath and Cegarra (1992) who studied chemical extractability of heavy metal after long term application of sewage sludge. The sludge loading rate used was 16.4 t / ha. Some previous studies on the extraction of sewage sludge applied soil were done three years after the sludge application. The readily available Zn (water soluble and exchangeable fractions of Zn) was less than 10 % of the total Zn (McBride et al., 1997). He suggested that this very low level of water-soluble and exchangeable fraction of Zn could be due to plant uptake. This study is a comparatively short-term study and the columns did not have plant growth during the experimental period.

Table 7.3. The distribution of different forms of Zn along the sludge applied, no anion treated soil column (T1)

Depth (cm)	Water soluble & exchangeable (mg)	Organic (mg)	EDTA extractable (mg)	Fe-Mn Oxide (mg)	Residual (mg)	Total acid digestible (mg)
0--5	437.00	875.80	690.80	167.70	231.10	2402.40
5-10	266.90	574.80	437.80	36.80	151.80	1468.10
10-15	108.60	18.00	97.30	10.54	81.91	316.35
15-20	5.20	6.60	33.30	9.58	26.57	81.25
20-25	4.60	3.90	10.20	7.60	42.30	68.60
25-32	2.25	1.90	7.00	5.80	40.50	57.45

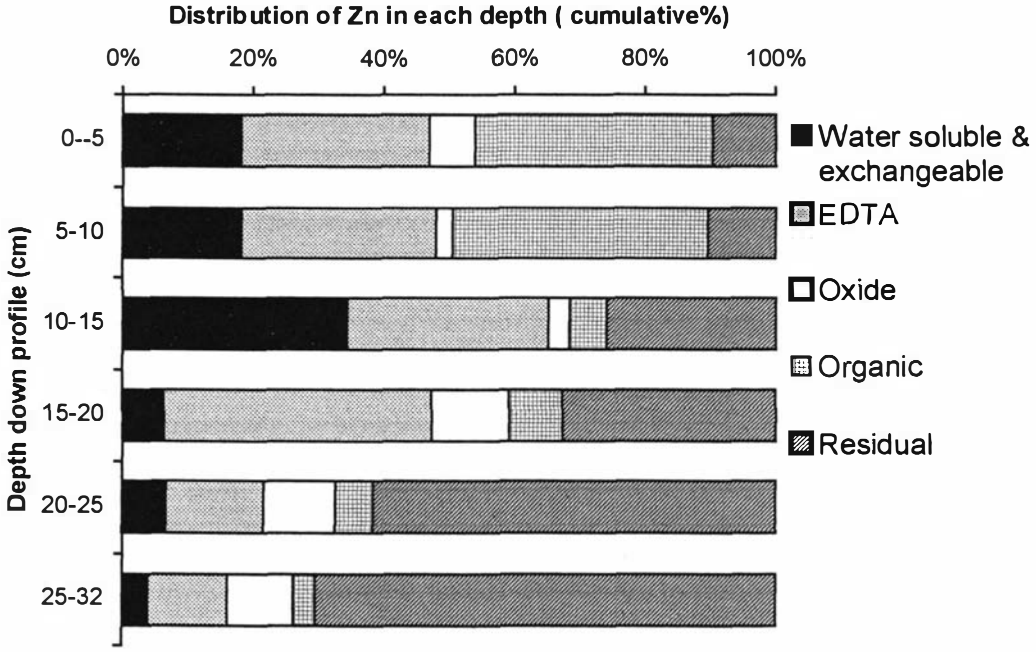


Figure 7.2. Comparison of Zn fractions extracted from different depths of the sludge applied, no anion treated soil column (T1)

The exchangeable form of Zn is held by electrostatic forces on negatively charged sites on clays, other minerals or organic matter or on amorphous materials (Beckett, 1989). Since the activation energy of exchange is low, this exchange is rapid and complete.

7.3.2.2. Carbonate (EDTA extractable) form of Zn

Sewage sludge application considerably raised the carbonate form (0.05 M EDTA extractable Zn) of Zn in T1, T2 and T3 columns compared to the control column (Figures 7.2, 7.3 & 7.4). The carbonate fraction of Zn decreased with the depth, leaving 690.8 mg (54 % of total Zn), 710.4 mg (56 % of total Zn) and 745 mg (59% of total Zn) at 0-5 cm depth in T1, T2 and T3 columns respectively (Tables 7.3, 7.4 & 7.5). This carbonate fraction of Zn in the control soil column varied between 4.7 - 10.6 % in the depths, whereas it varied between 12.2 - 41%, 12.8 - 34.6 % and 5.8 - 33.6 % in columns T1, T2 and T3 respectively. This could be due to the movement of some sludge particles as well as soil particles down the soil column.

The overall EDTA extractable carbonate fraction of Zn in the control column was 7.4 % of its total Zn, which increased to 29, 28.8 and 27 % in no anion, nitrate and phosphate treated columns (Figure 7.8). The data of EDTA extractable Zn obtained from this study in agreement with the results of some other researchers (Taylor et al., 1995; McGrath & Cegarra, 1992). They concluded that a single application of high concentration of Zn in sewage sludge builds up the carbonate fraction of Zn in soil. These results also support the results of fractionation of amended sewage sludge in section 7.2.2 of this chapter and confirm that Zn in the sludge could be precipitated as Zn carbonate rather than in an organically complexed form. They are also in aggrement with the results of some researchers who confirmed that Zn carbonate is a predominant form of Zn at higher rates of sludge application. A large portion of Zn was associated with the carbonate fraction in this sludge treated soil over a short term- which could reflect the fact that carbonates are freshly formed compounds and often form mixed crystals in the presence of cations such as calcium, magnesium, iron or aluminum in soil (Beckett, 1989). This form of Zn is potentially more bioavailable even when it is applied with the sludge. LSD analysis indicated that there was no significant difference between treatments on the amount of overall value of the carbonate fraction of Zn extracted.

Table 7.4. The distribution of different forms of Zn in the sludge applied, nitrate treated soil column (T2)

Depth (cm)	Water soluble & exchangeable (mg)	Organic (mg)	EDTA extractable (mg)	Fe-Mn oxide (mg)	Residual (mg)	Total acid digestible (mg)
0--5	457.95	876.30	710.43	175.50	253.25	2473.43
5-10	281.36	590.80	428.76	37.15	138.80	1476.87
10-15	95.77	10.95	95.10	11.15	61.85	274.82
15-20	4.97	5.25	17.70	9.10	25.70	62.72
20-25	3.86	3.00	8.10	7.35	40.30	62.61
25-32	2.30	1.50	7.45	5.60	41.19	58.04

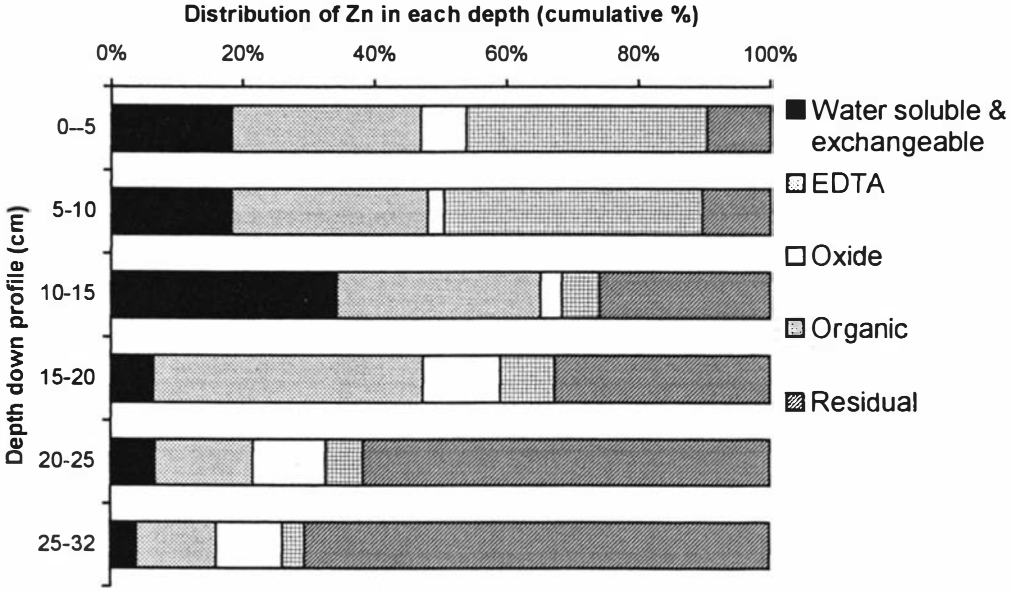


Figure 7.3. **Comparison of Zn fractions extracted from different depths of the sludge applied, nitrated treated soil column (T2)**

7.3.2.3. Organically complexed form of Zn

Application of sewage sludge increased the amount of the organic form of Zn at a higher level in 0-5 cm and 5-10 cm depths of the T1, T2 and T3 columns (Figures 7.2, 7.3 & 7.4). The amounts of the organic form of Zn at 0-10 cm depth were 1450 mg, 1467mg and 1473 mg in T1, T2 and T3 columns respectively (Tables 7.3,7.4 & 7.5). This high accumulation of the organic fraction of Zn in the top layer could be due to the surface incorporation of the sewage sludge in the treatment columns. The presence of hydroxyl and carboxyl functional groups and amide groups of peptide bonds in residual protein is a possible reason for the organometallic complexation of Zn and the sewage sludge solids.

The overall organic fraction of Zn in the control soil column was 9.57 % of total Zn, which increased to 33.7, 33.75 and 32.0 % in the T1, T2 and T3 columns respectively (Figure 7.8). This relatively large proportion of organic fraction extracted in the sludge applied soil column indicates that Zn is potentially readily bioavailable and mobile element. This is strongly supported by Cameron et al., (1994) and McLaren (2002) *in situ* lysimeters studies. They observed that Zn was easily leached from the soil following sludge application.

Table 7.5. The distribution of different forms of Zn in the sludge applied, phosphate treated soil column (T3)

Depth (cm)	Water soluble & exchangeable (mg)	Organic (mg)	EDTA extractable (mg)	Fe-Mn oxide (mg)	Residual (mg)	Total acid digestible (mg)
0--5	534.65	884.76	744.97	233.50	279.22	2677.10
5-10	324.17	587.80	422.27	44.68	195.73	1574.65
10-15	66.87	9.70	73.90	10.25	59.20	219.92
15-20	3.45	3.60	4.00	8.45	24.24	43.74
20-25	1.63	2.95	3.20	7.25	40.17	55.20
25-32	0.55	1.71	3.70	5.50	39.23	50.69

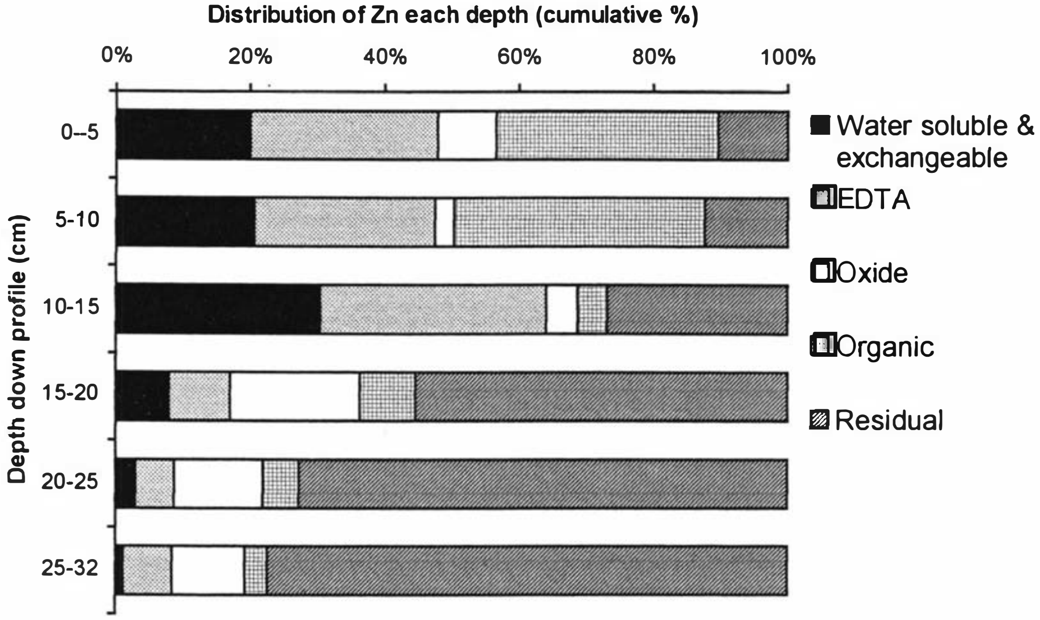


Figure 7.4. **Comparison of Zn fractions extracted from different depths of the sludge applied, phosphate treated soil column (T3)**

7.3.2.4. Fe-Mn Oxide form of Zn

The application of sewage sludge raised the Fe-Mn oxide level of Zn in all three treatment columns compared to the control soil from 50.5 mg (control soil) to 238, 245, and 309 mg in the T1, T2 and T3 columns respectively (Tables 7.3, 7.4 & 7.5). The oxide fraction of total Zn at the top 0-5 cm depth was between only 7 and 8.7 % of the total Zn in the T1, T2 and T3 columns and was very low compared to the control soil (50.5 %). At depths of 5-15 cm, the oxide fractionation was 2.5 - 4.5 % of the total Zn and it was too low compared to control soil (28.3–35.8 %). Between 20-32 cm depth the oxide fraction of Zn was almost the same as in the control soil (10-12 % of total Zn) (Figures 7.2, 7.3 & 7.4).

The percentage of overall Fe-Mn oxide bound Zn in the control soil column was 23 % of the total Zn content. The addition of Zn loaded sewage sludge reduced the proportion of the Fe-Mn oxide bound form of zinc, surprisingly, to a very low level. The percentages of the Fe-Mn oxide bound form of Zn as a percentage of total Zn were 5.4, 5.56 and 6.7 % in the no anion, nitrate and phosphate treated columns respectively (Figure 7.8). Generally the oxide form of Zn is less bioavailable in soil since oxides of Fe, Al and Mn can provide chemisorption sites for Zn. Therefore, the results clearly demonstrate that the application of sewage sludge to this soil did not influence the increment of oxide forms relatively, compared to other forms of Zn such as water soluble and exchangeable (0.1 M CaC12), organically complexed and EDTA extractable forms.

7.3.2.5. ***Residual form of Zn***

Application of Zn loaded sewage sludge significantly increased the amount of residual fraction of soil Zn in the T1, T2 and T3 columns (Tables 7.3, 7.4 & 7.5). Between 39.8-43.8 % (231-279 mg) of the total residual fraction of Zn accumulated in the top 0 - 5 cm in the T1, T2 and T3 columns respectively (Figures 7.2, 7.3 &7.4). The residual fraction increased gradually with the depth from 22 % to 77 % in all three treatments whereas the control column had a gradual increase from 9.2 % to 79.1 %.

The overall percentage of residual fraction in the control column was approximately 57.7 % of the total Zn. This residual form of Zn decreased to 13.0, 12.7 and 13.8 % in no anion, nitrate and phosphate treated columns respectively (Figure 7.8). The percentage of residual fraction (which is the most strongly occluded Zn in the inorganic silicates and noncrystalline) decreased and this reduction been replaced by the 0.05 M EDTA extractable, water soluble and exchangeable (0.1 M $CaCl_2$ extractable) and organic complexed form of Zn. The greater percentage of Zn in the residual fraction probably reflects the greater tendency for Zn to become unavailable in volcanic soil. With the application of sewage sludge this proportion decreased further. This confirms that Zn in these sludge treated columns would be readily available to plants-a finding which was supported by Corey et al. (1987) who found that in high rate applications of sewage sludge, the major factors determining the bioavailability are the form and contents of sludge-borne metals rather than the physiochemical properties of the soil.

However, the level of the residual form of Zn had increased by 447.5 mg, 430.4mg and 511 mg in no anion, nitrate and phosphate treated columns compared to control soil. The hypothesis confirms the fact that a considerable amount of Zn could be in a precipitated form of sulfide or hydroxide of Zn in the sludge and sludge amended soil, which has not been fractioned by the extracting agent used.

The addition of sewage sludge increased the organic, carbonate, residual, Fe-Mn bound and water soluble and exchangeable forms with the order being Carbonate > residual > organic > Fe-Al bound > watersoluble exchangeable. In this study a considerable increase of water soluble and exchangeable forms were found compared to some previous studies on the fractionation of sewage sludge treated soils. This could be due to the higher loading rate of Zn in the sewage sludge and the relatively short period (20 weeks) of time after the sludge application.

7.3.3. Inorganic Zn applied soil columns

Table 7.6. The distribution of different forms of Zn in the inorganic Zn applied, no anion treated soil column (T4)

Depth (cm)	Water soluble & exchangeable (mg)	Organic (mg)	EDTA extractable (mg)	Fe-Mn oxide (mg)	Residual (mg)	Total acid digestible (mg)
0--5	1238.36	30.16	1284.59	535.38	335.28	3423.77
5-10	276.53	16.54	320.12	119.81	98.80	831.80
10-15	127.10	4.50	265.60	71.59	72.46	541.25
15-20	26.32	3.50	37.56	23.28	37.89	128.55
20-25	5.45	3.20	9.80	11.25	45.70	75.40
25-32	2.15	1.95	5.00	6.95	43.98	60.03

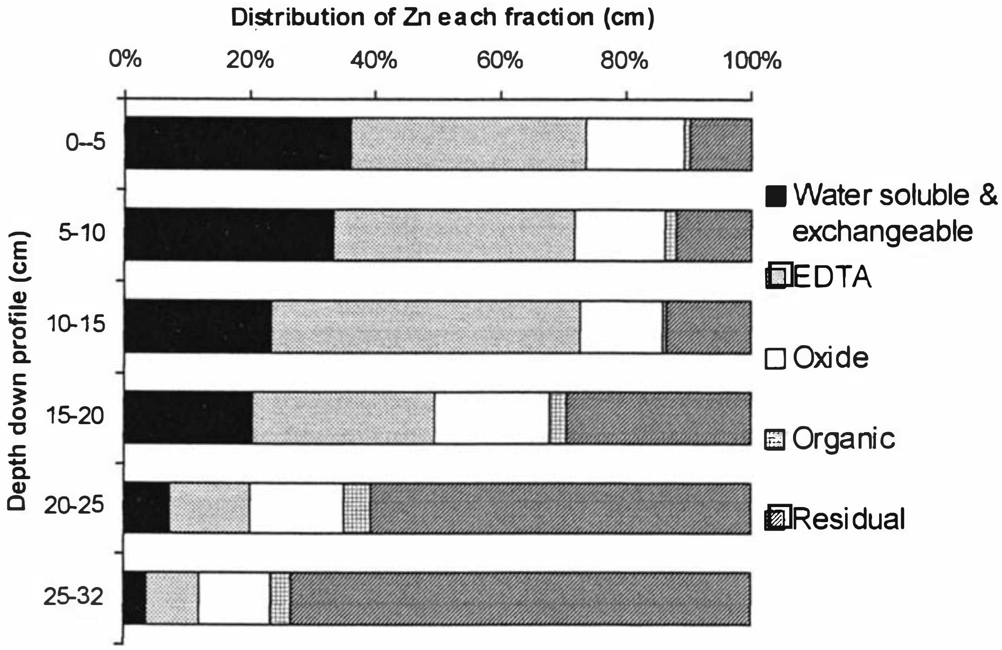


Figure 7.5. **Comparison of Zn fractions extracted from different depths of the inorganic Zn applied, no anion treated soil column (T4)**

7.3.3.1. Water-soluble and exchangeable forms of Zn

Application of inorganic Zn (Zn nitrate) solution increased the water-soluble and exchangeable form of Zn at a higher level (Figures 7.5, 7.6 & 7.7) in all three treatments (T4-no anion, T5-nitrate and T-6 phosphate treated columns). Amounts of the water-soluble and exchangeable form of Zn at 0-5 cm depth were 1238 mg, 1344 mg and 1595 mg in the T4, T5 and T6 columns respectively (Tables 7.6, 7.7 & 7.8). The fraction of the water-soluble and exchangeable form of Zn in the first 20 cm depth gradually decreased with depth from 36.2 -20.5 %, 38.4-25.7 %, and 41.5-12 % of total Zn in the T4, T5 and T6 columns respectively. In the lowest depth the no anion and phosphate treated columns had 3.6 -3.7 5 % total Z and the nitrate treated column had 12.6 5 of total Zn. In control column this fraction gradually decreased with depth (0-32 cm) from 5.1 – 1.0 % of total Zn (Tables 7.6, 7.7 & 7.8).

The overall value of the watersoluble and exchangeable form of Zn in the control soil was 2.29% of total Zn (5.03 mg) whereas in the T4, T5 and T6 columns it was 33.1%

(1676 mg), 35.1% (1770 mg) and 38.4% (1982 mg) of total Zn respectively (Figure 7.8). This higher increase could be due to the highly exchangeable surface in the volcanic soil. The remarkable difference between the no anion and phosphate treated soil could be attributed to the increased negative surface charges and to the creation of the exchangeable sites as a result of phosphate sorption These results are in agreement with the results of Ahumada et al. (1997). They noticed that phosphate influenced the distribution of the extractable Zn fraction in volcanic soil (Andosol) increasing the exchangeable Zn form.

7.3.3.2. Carbonate (0.05 M EDTA extractable) form of Zn

Application of inorganic Zn (Zn nitrate) solution raised the 0.05 M EDTA extractable Zn fraction in the T4, T5 and T6 columns (Figures 7.5, 7.6 & 7.7). There were 66.8 % (1284 mg), 68.2 % (1252 mg) and 71.7 % (1220 mg) of the total 0.05 M EDTA extractable form of Zn found in 0-5 cm depth of the T1, T2 and T3 columns respectively (Tables 7.6, 7.7 & 7.8).

The fractionation of 0.05 M EDTA extractable form of Zn within the first 20cm depth, decreased with the depth, 49-37.5%, 35.7-49.8% and 31.7-45.6% in the T4, T5 and T6 columns respectively. Then it decreased gradually from 29.2-8.3, 27-6.2 and 11.1-7.0 in 20-32cm depth in all three treatments. The overall value of the 0.05 M EDTA extractable Zn was 38, 36.4 and 32.9% of total Zn in the no anion, nitrate and phosphate treated columns-whereas it was 7.4% in control soil (Figure 7.8). Relatively large increases in the proportion of 0.05 M EDTA extractable Zn could maintain the Zn in a labile chemical form that would be more readily available to plants than would be the form found in the unamended soil.

Table 7.7. The distribution of different forms of Zn in the inorganic Zn applied, nitrate treated soil column (T5)

Depth (cm)	Water soluble & exchangeable (mg)	Organic (mg)	EDTA (mg)	Fe-Mn oxide (mg)	Residual (mg)	Total acid digestible (mg)
0--5	1344.27	30.36	1251.72	582.47	292.53	3501.35
5-10	269.23	15.29	284.28	118.58	80.62	768.00
10-15	105.17	4.95	251.94	69.44	73.55	505.05
15-20	31.80	4.20	33.52	15.52	38.96	124.00
20-25	12.15	3.55	8.15	10.42	46.78	81.05
25-32	8.09	2.30	4.00	6.45	43.56	64.40

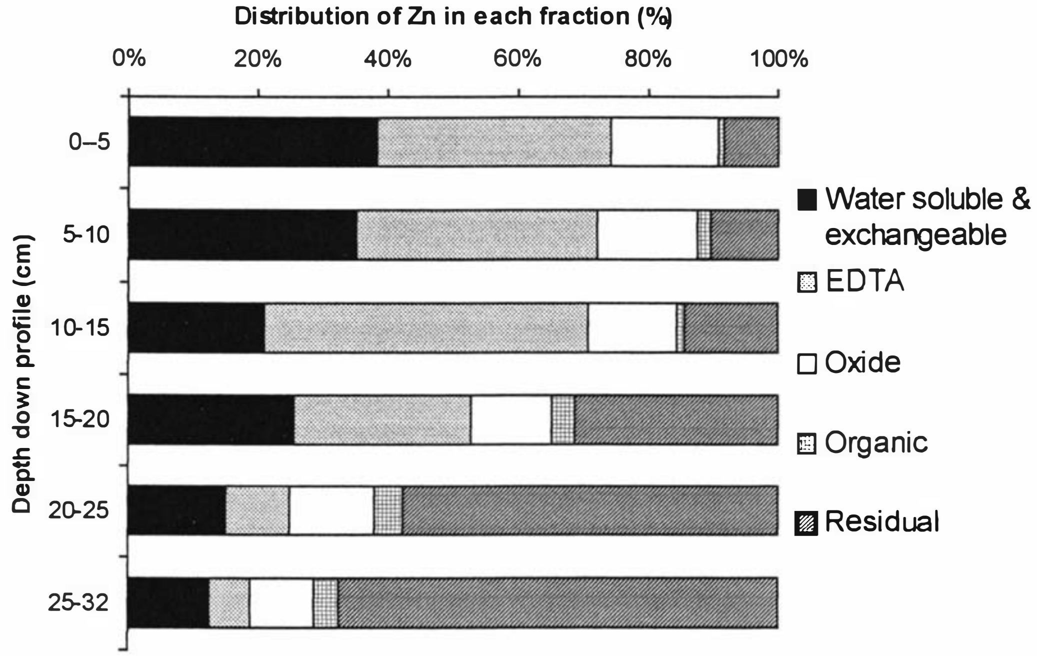


Figure 7.6. **Comparison of Zn fractions extracted from different depths of inorganic Zn applied, nitrate treated soil column (T5).**

7.3.3.3. Organic form of Zn

Application of inorganic Zn (Zn nitrate) solution increased the level of the organically complexed form of Zn in the T4, T5 and T6 columns. However, it was relatively less than the increase in other forms of Zn (Figures 7.5, 7.6 & 7.7). Organic fractions of Zn increased with the depth from 0.9 –3.3 %, 0.9 –3.6 % and 0.8-3.8 % of total Zn in the T4, T5 and T6 columns respectively, whereas this fraction decreased with the depth from 26–3 % in the control column.

At 0-5 cm depth, 50 % (30.1 mg), 50 % (30.4 mg) and 53 % (31.7 mg) of the total organic form of Zn was found in the no anion, nitrate and phosphate treated columns respectively (Tables 7.6, 7.7 and 7.8). At 5-15cm depth it ranged between 15.6-7.1% and at 15-32 cm depth, the range decreased with the depth from 3-0.7% in treatment columns.

The overall organic fraction of Zn in the control soil was 9.6 % of total Zn, which decreased to 1.2, 1.2 and 1.1 % in no anion, nitrate and phosphate treated columns respectively (Figure 7.8). Treatment with Zn nitrate solution increased the organic complexed form of Zn in 0-10 cm in all three treatments. This could be due to the high organic matter content of the volcanic soil on the top (0-10 cm) of the column.

Table 7.8. The distribution of different forms of Zn in inorganic Zn applied, phosphate treated soil column (T6)

Depth (cm)	Water soluble & exchangeable (mg)	Organic (mg)	EDTA extractable (mg)	Fe-Mn oxide (mg)	Residual (mg)	Total acid digestible (mg)
0--5	1595.00	31.72	1219.77	658.68	335.96	3841.13
5-10	282.50	13.83	269.23	104.72	64.75	735.03
10-15	86.74	4.40	170.50	55.50	56.76	373.90
15-20	11.27	3.90	30.58	12.00	36.65	94.40
20-25	4.80	3.10	7.50	7.43	44.32	67.15
25-32	2.05	2.10	3.90	5.50	42.20	55.75

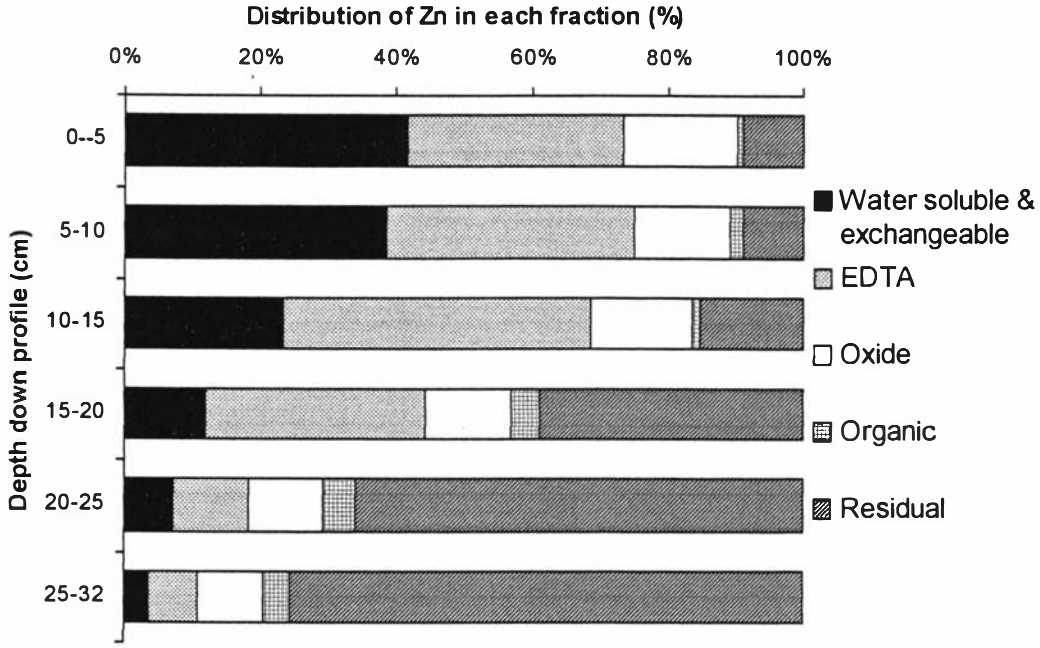


Figure 7.7. **Comparison of Zn fractions extracted from different depths of the inorganic Zn applied, phosphate treated soil column (T6)**

7.3.3.4. Fe-Mn oxide form of Zn

Application of inorganic Zn raised the amount of the oxide form of Zn in every depth of the soil columns with a remarkable increase at 0-15 cm depth (Tables 7.6, 7.7 & 7.8). The oxide form of Zn decreased with the depth leaving 70 % (535 mg), 72 % (582 mg) and 78 % (659 mg) of the total oxide form of Zn at 0-5 cm depth in the T4, T5 and T6 columns respectively. The oxide fraction of Zn gradually decreased with the depth from the top layer to the bottom layer from 15.6 –11.6 %, 16.6-10 % and 17.1-9.9 % of total Zn in the T4, T5 and T6 columns respectively (Figures 7.5, 7.6 & 7.7).

The distribution of oxide fraction was almost even throughout the column. It was interesting to note that the fraction of the oxide form of Zn in the no anion, nitrate and phosphate treated columns was 15.2, 15.9 and 16.4% of total Zn respectively (Figure 7.8). This could be due to an increase in negative charge as a result of more phosphate and less nitrate being retained on Fe, Mn and Al oxide-covered crystalline clay minerals (Ahumada et al., 1997; Xie and Mackenzie, 1989). The increase in Zn retention in the volcanic soil was more substantial, which could be due to an increase in the negative surface charges and to the creation of specific sorption sites as a result of phosphate sorption.

7.3.3.5. Residual form of Zn

The application of inorganic Zn increased the amount of residual fraction of soil Zn in the T4, T5 and T6 columns (Tables 7.6, 7.7 & 7.8). Between 50.8-57.9 % (292.5-336 mg) of the total residual form of Zn accumulated in the top 0- 5 cm in the T4, T5 and T6 columns respectively (Figures 7.5, 7.6 &7.7). Between 15- 32 cm depth there was only a little increase in the amount of the residual form of Zn.The residual fraction of Zn increased gradually with the depth from 9.6- 77.4 % of total Zn in all three treatments whereas the control column had a gradual increase from 9.25 - 79.1 %.

The overall percentage of residual fraction in the control column was 57.7 % of the total Zn. This residual form of Zn decreased to 12.5, 11.4 and 11.2 % in no anion, nitrate and phosphate treated columns respectively (Figure 7.8).

7.3.4. Sludge Zn and inorganic Zn applications

Water-soluble and exchangeable fractions of Zn increased markedly in the inorganic Zn applied columns (anion treated) compared to the columns in which sewage sludge with an equivalent amount of Zn was applied (Figure 7.8). Some previous researchers have observed that EDTA extraction of Zn in inorganic Zn application was significantly (2-3 times) higher than the extraction from equivalent sludge treatment. In this study EDTA fractions of Zn in inorganic Zn applied soil were markedly higher than those from the sewage sludge Zn applied columns (Figure 7.8). In inorganic Zn applied columns, even though it does not have any adsorptive agent, the greater clay

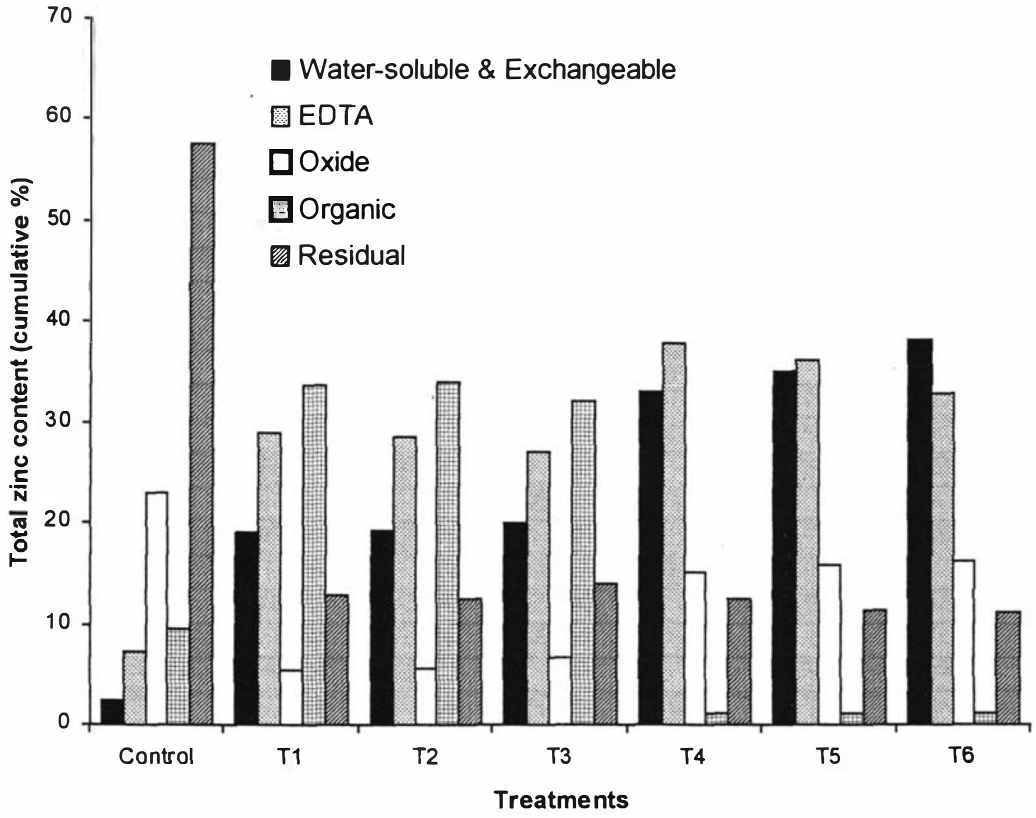


Figure 7.8. **Distribution of Zn in various chemical fractions as a function of total Zn content in soil** **T1- No anion treated sludge applied soil column. T2– Nitrate treated sludge applied soil column. T3 –Phosphate treated sludge applied soil column. . T4 –No anion treated inorganic Zn applied soil column. T5 – Nitrate treated inorganic Zn applied soil column. T6 – Phosphate treated inorganic Zn applied soil column.**

and hydrous Mn and Fe oxide content of allophane rich volcanic soil relatively limited the availability of the Zn in this experiment-which is reflected in the higher portion of the oxide form of Zn in the inorganic Zn applied column (Figure 7.8). The relative proportion of residual fraction of Zn decreased both in sewage sludge and inorganic Zn applied soils. This could be due to the added Zn go as more reactive fractions. The nonresidual-Zn fractions increased in the inorgsnic Zn applied columns, especially the water-soluble and exchangeable, Fe-Mn oxide bound and EDTA extractable fractions compared to the control soil column. In sewage sludge applied soil water-soluble and exchangeable, organic, EDTA extractable and Fe-Mn oxides bound fractions increased compared to the control column.

7.4. CONCLUSIONS

- Activated sewage sludge obtained from the Kapiti Coast wastewater treatment plant contained a comparatively low level of Zn (194 mg/kg), Cu (148 mg/kg) and Cd (39 mg/kg). No nickel was detected.

- Fractionation of freshly Zn loaded activated sewage sludge revealed that 25 % of the Zn was in the water-soluble and exchangeable form. The organically complexed form of Zn amounted to 30 % and the carbonate form of Zn to 33.2%. Thus there are equal amounts of Zn in the carbonate and organically complexed form in freshly loaded activated sewage sludge.

- Fractions of Zn in control volcanic Egmont soil were in the decreasing order of residual (57.7 %)>Fe-Mn oxides (23 %)>organic form (9.6 %)> carbonate form (7.4 %)> water soluble and exchangeable form (2.3 %).

- Fractions of Zn in sewage sludge applied soil columns were in the decreasing order of organic form (32.2-33.7 %)> carbonate form (27-28.8 %)>water soluble and exchangeable form (18.8-20.1 %)>residual form (12.7-13.8 %)>Oxide form (5.4-6.7 %). The residual form of Zn increased and other forms of Zn decreased with soil depth. In soil depths between 25 and 32 cm, 50 – 57 mg of Zn was detected.

- Fractions of Zn in inorganic Zn applied soil columns were in the decreasing order of carbonate form (33-38 %) > water soluble and exchangeable form (33-38 %) > Fe-Mn oxide form (15.2-16.4 %) > residual form (11.2-12.5 %) >organic form (1.1-1.2 %). Between 70 % and 77 % of total Zn accumulated in 0-5 cm soil depth. The residual form of Zn increased and other forms of Zn decreased with soil depth. Amounts of between 50mg and 60 mg of Zn were detected in 25-32 cm soil depth.

- Phosphate treated soil remarkably increased the amount of the exchangeable form and oxide form of Zn compared to no anion and nitrate treated soils. This could be due to an increase in negative surface charge and to the creation of specific sorption sites as a result of phosphate sorption.

Chapter Eight

SUMMARY, CONCLUSION AND FURTHER STUDY

Summary and conclusion

8.1. LITERATURE REVIEW

The review of the literature revealed the current information available on different sources of heavy metals in New Zealand and other countries and the environmental impact of most commonly occurring sludge-borne metals (Chapter Two). Usage of phosphatic fertilizer, pesticides and fungicides and metal working processes, painting, dyeing and dairy farming, and usage of wood preservatives (CCA solution) are the main contributors of heavy metals such as Cd, Cu, Zn, Ni and Cr to the sludge in industrialized areas in New Zealand.

Cadmium and Ni poisoning in humans causes severe disfunction of the entire body system. Cu is very toxic to algae. Also, Zn is more dangerous and biologically toxic when it exceeds the maximum permissible concentration. The potential toxicity basically depends on the availability and mobility of these sludge-borne heavy metals depend entirely on their chemistry and complexing capacity with organic and inorganic ligands which are available in the sludge environment.

The proportion of the different forms of these heavy metals varies considerably depending on the soil and the amount and forms in which the heavy metals are added to the soil (management practices). Sludge application on land is a major environmental issue since land disposal is a more economical way to remove sludge than either incineration or ocean dumping. Sequential extraction is the simplest way of identifying the forms in which heavy metals are found in soils.

Variable charge soils, represented by major volcanic soils, are widely distributed in New Zealand. These soils exhibit a behaviour which is different from that of any other soils in that they show low affinity for heavy metals at low negative surface charge densities. A management practice such as sewage sludge application to this soil may create a soil condition which may lead to a lowering of the negative surface charge of the soil. Also some environmental factors influencing the surface charge of this soil such as pH, ionic strength and anion concentration have to be studied to predict the bioavailability of these heavy metals in this soil since there is a lack of information available in this area - especially in relation to Zn.

This study was conducted with the objective of quantifying the adsorption, desorption and leaching behaviour of these sludge-borne metals in the sludge and soil environment. Laboratory batch studies investigated the (i) biosorption and desorption of Cd, Cu, Zn and Ni in activated sewage sludge, (ii) adsorption-desorption of Zn (most mobile sludge borne metal) in the volcanic Egmont soil. This was followed by in situ studies quantifying the leaching and the downward movement of Zn in both forms of application; sewage sludge and the inorganic form of Zn. The effect of most commonly found anions such as phosphate and nitrate also was studied in relation to the movement of Zn.

8.2. BIOSORPTION AND DESORPTION OF HEAVY METALS ON ACTIVATED SEWAGE SLUDGE

The biosorption of Cd, Cu, Zn and Ni were measured using the biomass of activated sewage sludge in 0.145 N NaCl solution and deionized water as adsorption media. Activated sewage sludge biomass more effectively adsorbed Cd, Zn and Cu than Ni. The extracellular material present in activated sewage sludge could have played a significant role in the removal of these metals. The biosorption process took place in two phases: a very fast step followed by a slower step in all cases.

Equilibrium sorption isotherms were obtained for the first three heavy metals (Cd, Zn and Cu) in varying amounts of sorption sites in selected initial metal concentrations. Cd and Cu showed an “S” shaped isotherm in 5 and 10 mg/L initial metal ion concentrations and “L” shape in 15 mg/L initial metal ion concentrations. It suggested that Cd and Cu have high affinity to activated sewage sludge at lower a metal concentration. Zn showed a linear form of isotherm. The adsorption capacity of the Cd, Cu and Zn ranged from 35.7- 44.8, 14.1-26.4 and 57.5 - 59.5 mg/g biomass respectively.

The percentage of adsorption of Cd and Cu increased with initial metal concentration. However, the adsorption yield decreased with initial metal concentration. This could be because of the lower affinity of the sites for metal cation as the concentration increases. Zn adsorption was increased when the initial Zn concentration was increased to 50 mg/L. But when it was increased to 100 mg/L the adsorption was decreased. Chloride ion concentration at 0.145 N significantly interfered with the adsorption of Cd more than with the adsorption of Zn and Cu. This could be due to the formation of Cd chloro complexation, which is a nonadsorptive and more mobile complex.

The initial adsorption rate increased from 21°C to 30°C and decreased at 40°C. Calculated initial adsorption rates were .07, 0.13, 0.27 and 0.17 mg/g/min at 21, 25, 30 and 40°C respectively. As temperature increases from 21 to 30°C the Cd ions get energized and the adsorption rate increases - but further increment in temperature could reduce the selective adsorption of Cd ions. This could be due to the reduction in magnitude and specificity of van der Waals forces between the solute and solid surface (and between adjacent adsorbed solute molecules) as the temperature increases.

Desorption was carried out on Cu and Zn using mild desorbing agents; deionized water, 0.1 N Na_2SO_4, 0.1 N K_2SO_4, 0.1 N Na citrate, and 0.1 N Na_2CO_3 solutions which are commonly used in activated sewage sludge desorption studies (Butter et al., 1995). The objective of this desorption study was to understand which metal desobes more on activated sewage sludge.In this study Zn desorbed more in every desorbing agent used. The amount of desorption of Zn varied among the desorbing agents used. The higher desorption of Zn may be because of the weak bonding of Zn on the activated sewage sludge biomass surfaces.

The affinity of activated sewage sludge biomass for different heavy metals differs. Activated sludge biomass has greater affinity for Cd, Zn and Cu. It has a little affinity for Ni. Cadmium was more highly mobile in the presence of chloroide ion concentration than in Zn and Cu. This could be because of Cd chloro complexation which is less adsorbable on the biomass surfaces. Biosorption of these heavy metals was affected by pH, temperature, initial metal ion concentration, and chloride ions.

The desorbability of Zn was greater than that of Cu. This could be because of the weak bonding of Zn on the activated sludge biomass surfaces.

8.3. ADSORPTION AND DESORPTION OF ZINC IN VOLCANIC EGMONT SOIL

Volcanic Egmont soil showed a greater retention of Zn in the first few hours of contact with Zn metal solution and took about 10 hours to reach equilibrium. Zinc sorption by volcanic Egmont soil showed a greater retention of Zn in natural soil pH; which was double that of the Zn sorption reported by any other researchers in volcanic soil internationally. Adsorption isotherms were produced with deionised water, 0.1 M KNO_3 and 0.1 M KH_2PO_4 as background electrolytes. The adsorption data explained the Freundlich equation well. The Freundlich adsorption constants of topsoil (0-15 cm depth) samples were 2.23, 1.14, and 1.85 in deionised water, 0.1 M KNO_3 and 0.1 M KH_2PO_4, respectively. In subsoil (15-32 cm depth) samples, the Freundlich adsorption constants were 3.09, 1.57, and 2.54 in deionised water, 0.1M KNO_3 and 0.1 M KH_2PO_4, respectively. The greater sorption of Zn in deionized water could be attributed to the general effect of ionic strength on Zn sorption. The difference between the adsorption constant of Zn in 0.1 M KNO_3 and 0.1 M KH_2PO_4 electrolytes could be because of the difference in Zn sorption in different anion backgrounds which is more pronounced in volcanic Egmont soil. Freundlich constant values increased both in top and subsoils with an increase in pH. The solution Zn concentration in both horizon soils decreased with an increase in soil pH.

Another batch study on Zn sorption was carried out at different levels of phosphate and nitrate treated soil to test the hypothesis of anion induced Zn retention in the volcanic Egmont soil. After three weeks of incubation, water-soluble Zn in this soil decreased remarkably in both phosphate treatments (500 and 1000 mg/kg soil) compared to nitrate treatements and control. There were no significant differences observed in control and nitrate treated soils on Zn adsorption. This confirmed the fact that phosphate induces Zn retention in volcanic Egmont soil. There are several mechanisms can be proposed for the positive effect of phosphate on Zn sorption. However, the increase in net negative charge on the soil surface resulting from $H_2PO_4^-$

and HPO_4^- adsorption is more conclusive evidence than any other mechanisms given in Chapter Five.

The cumulative amounts of soil Zn desorbed from A and B horizons of volcanic Egmont soil during 24 h desorption periods showed that the differences in the desorbability of Zn were a result of differences in the anionic background. The cumulative amounts of Zn desorbed from A horizon of soils were 22.2, 6.3 and 3.1 % in KNO_3, KH_2PO_4 and deionized water. The cumulative amounts of Zn desorbed from the B horizon of soils were 19.7, 5.1 and 2.6 % in KNO_3, KH_2PO_4 and deionised water respectively.

Desorption of Zn decreased with increasing soil pH. The cumulative amount of Zn desorbed in pH 5.3 from the A horizon of soil was 37 % and from the B horizon of soil, 33 %. The cumulative amount of Zn desorbed in pH 7.5 from the A horizon of soil was 14.3 % and from the B horizon of soil, 12.2 %.

Batch experiments suggest that retention of Zn in volcanic Egmont soil (at native soil pH) is greater than in other volcanic soils reported. This higher retention capacity of Zn could be due to the organic matter, allophonic clays and Fe and Al hydrous oxides in Egmont soils. The adsorption behavoiur of Zn is influenced by pH, background electrolyte and phosphate anion. Desorption is also influenced by pH and background electrolytes.

8.4. MOBILITY AND MOVEMENT OF ZINC IN UNDISTURBED SOIL

An in situ study was carried out with 7 undisturbed volcanic Egmont soil columns (Chapter six). At the beginning of the experiment the treatment columns were saturated with deionised water to ensure the saturated condition. Four of these seven columns were treated with 0.1 M KNO_3 and 0.1 M KH_2PO_4 in duplicates till these columns achieved the breakthrough of nitrate and phosphate. Two columns were treated with deionised water to maintain the equivalent amount of moisture content. The seventh column was kept as a control for the Zn mobility study.

Nitrate appeared in the leachate after passing through the first pore volume of 0.1M KNO_3 solution and reached its peak level of relative solute concentration after passing through the second pore volume. Phosphate appeared much later (after passing through 10 pore volumes of 0.1 M KH_2PO_4 solution) in the leachate and started to increase its relative solute concentration gradually from the 10th pore volume and reached its peak level after passing through 23 pore volumes of 0.1 M KH_2PO_4 solution. The shape of the undisturbed soil breakthrough curves (Figure 6.1) suggests that these undisturbed columns do not appear to have a significant network for preferential flow.

After the anion treatment the columns were kept at 4°C for 4 weeks to avoid any soil microbial growth and to give a time to allow the anion become sorbed in soil. Then the sewage sludge was applied to three of those columns at 180 tons /ha. Three other columns were treated with Zn nitrate solution containing equivalent amount of Zn in sewage sludge. The treatment columns were leached with deionized water until it passed through 15 pore volumes in 16-20 week's times.

Zinc concentrations in the initial leachates were higher than in the final leachate in both sewage sludge and inorganic Zn treated columns. The leachate from the phosphate treated sewage sludge applied soil column was highly coloured and enriched in iron. This could be due to the fact that the phosphate solution had extracted the organically bound iron. The total Zn recovered in leachate from sewage sludge treated columns were 0.11, 0.17 and 0.26 % of the total recovered Zn for no anion, nitrate and phosphate treated columns, respectively. The total Zn recovered in leachate from the inorganic Zn applied columns were 0.12, 0.45 and 0.41 % of the total recovered Zn for no anion, nitrate and phosphate treated columns. The Zn recovered from inorganic Zn applied columns was higher than in the sewage sludge treated columns. The overall amount recovered in the leachate was very low. This reveals that the Zn retention capacity of the volcanic Egmont soil was high. This higher retention capacity could be because of the higher percentage of allophonic constituents and the organic matter content of this soil.

Application of sewage sludge resulted an accumulation of substantial amounts (57-60 %) of Zn in the top layer (0-5 cm depth) of the soil columns. A percentage of 8.5, 7.1

and 4.6 % of the total acid digestible Zn derived from the sludge moved from 0-10 cm depth to the rest of the column of no anion, nitrate and phosphate treated columns respectively. At the lowest soil layer 9.75 mg (0.2 %), 10.34mg (0.2 %) and 2.99 mg (0.07 %) of Zn was determined in no anion, nitrate and phosphate treated columns respectively. In inorganic Zn treated soil columns 70 -77 % of total acid digestible Zn accumulated in 0-5 cm depth of soil. A percentage of 14.2 -16.7 % of Zn was found in 0-10 cm soil depth. Further, 13.3, 11.8 and 8.6 % of the total acid digestible Zn moved below 10cm depth of no anion, nitrate and phosphate treated soil columns, respectively. At 25-32 cm depth 8.05- 12.3 mg of Zn was detected. In both sewage sludge and inorganic Zn treated soil columns phosphate treatements showed a very little percentage of Zn in the lowest soil layers (25-32 cm depth).

Application of sewage sludge reduced the soil pH in treatment columns at 0-20 cm soil depth. The lowered soil pH could be due to the release of organic acids from sewage sludge applied to the surface soil or it could be due to the nitrification of the nitrogenous compounds present in the sewage sludge. In inorganic Zn applied soil columns the soil pH increased throughout the 0-32 cm depth. No anion and nitrate treated soils had a similar trend and pH increased between 0.03 and 0.40 pH units. Phosphate treated soil had an increase varying between 0.25 and 0.58 pH units with the maximum at 5-10 cm depth and having the minimum at 10-15 cm depth (Figure 6.5). The higher increase in phosphate treatment could be due to a phosphate induced increase in negative charge in the volcanic Egmont soil.

Application of sewage sludge increased the extractable soil nitrate levels (2M KCl extractable) in different depths of the sewage sludge applied soil columns compared to the control. This could be due to the increased rate of nitrification in the sewage sludge applied soil. Nitrate treated soil columns showed a greater mobility of Zn compared to no anion and phosphate treated soil columns. This may be because nitrate is more leachable and would carry the Zn on it.

Application of sewage sludge increased the extractable soil phosphorous in different soil depths (Figure 6.7) compared to the control. Moreover, the phosphate level in the phosphate treated column increased throughout the 0-32 cm soil depth. This could be due to the fact that the phosphorus retention capacity (86-100 %) of the volcanic

Egmont soils is high. This adsorbed phosphate in 0-15 cm depth of the soil column had limited the Zn movement significantly compared to other treatments (Tables 6.3a and 6.3b).

Phosphate treatment markedly increased the exchangeable form of Zn and the oxide form of Zn in 0-5 cm depth compared to other treatments. This result strongly supports the results of Ahumada et al. (1997) who reported that phosphate influenced the distribution of the extractable Zn fraction in Andosol (volcanic soil) by increasing the exchangeable Zn. Phosphate adsorption increases the negative surface charge and creates specific sorption sites. This leads to an increase in the exchangeable and Fe-Mn oxide form of Zn.

The recoveries of total Zn extracted from the sewage sludge applied and inorganic Zn applied soil columns were 97.11-99.53 and 83- 87.5% respectively. The low recovery from the sewage sludge treated soil may be due to oils and fats which are present in the sample of sewage sludge and which could limit accessibility to the extractants (Beckett, 1989).

The leachability of both sewage sludge and inorganic Zn applied soils showed a very low level of recovery of Zn in leachate. The recovery of a low level of Zn in the leachate of both inorganic Zn and sewage sludge applied soils may be because of the zero ionic strength of the deionized water which was used as an eluant.

The amount of Zn which moved to the lowest depth in inorganic Zn applied soil isgreater than in sewage sludge applied soil. This could be because of the higher amounts of the water-soluble form of Zn present in inorganic Zn than in sewage sludge. The pretreatment of phosphate limited the Zn movement to the lower depths because of the phosphate induced Zn retention.

8.5. FRACTIONATION OF ZINC IN SEWAGE SLUDGE AND ZINC APPLIED SOILS

8.5.1. Fractionation of Zn in sewage sludge

The original activated sewage sludge obtained for this study had a very low level of total Zn (194 mg/kg) compared to the Zn content of other wastewater sludges. Therefore, Zn loading was done to raise the activated sewage sludge Zn level to 35,420 mg/kg. The total Cd and Cu contents were 39 and 148 mg/kg and no Ni was detected in this sludge. The fractionation data of Zn amended activated sewage sludge revealed that 25 % of Zn was extracted by 0.1 M $CaCl_2$ solution. Less than 7 % of the Zn was watersoluble and 18 % of the Zn was in the exchangeable form. The organically complexed form of Zn with the activated sewage sludge was 30.1 %. Surprisingly, 0.05 M EDTA extractable form of Zn (carbonate form) was 33.2 % of total Zn. Also 0.1 M HCl extractable form of Zn was 44 % of total Zn. This confirmed that a large proportion of Zn in that sludge was in carbonate form.

8.5.2. Fractionation of Zn in sewage sludge and inorganic Zn applied soil columns

Zinc fractionation of soil samples of different depths of three sewage sludge applied soil columns, three inorganic Zn applied soil columns, and the control soil column were carried out with different extracting reagents. The sequential fractionation method used by McGrath and Cegerra (1992) was followed. However, they did not fractionate the carbonate forms of heavy metals separately. Therefore, 0.05 M Na_2-EDTA was additionally used after the extraction of the organically complexed form of Zn in this fractionation scheme.

8.5.2.1. Water-soluble and exchangeable forms of Zn

The water-soluble and exchangeable form of Zn in the control soil column was very low in overall compared to other fractions of Zn. This water soluble and exchangeable form of Zn gradually decreased with soil depths having 1.21 mg at the top 5 cm depth and 0.48 mg at the lowest soil (25-32 cm) depth. The water-soluble and exchangeable fraction of total Zn decreased with the depth from 5.14-1.05 %. The overall organic fraction of Zn in the control column was 2.29 % of the total Zn.

Application of sewage sludge raised the water soluble and exchangeable form of Zn in all three treated columns in the first 15 cm soil depths. The overall value of the water-soluble and exchangeable form of Zn was 18.8% (824.6mg), 19.2% (846.2mg) and 20.2% (931.3 mg) of the total Zn in the no anion, nitrate and phosphate treated columns respectively.

Application of an equivalent amount of inorganic Zn solution increased the water-soluble and exchangeable form of Zn at the higher level at 0-5 cm soil depth compared to the rest of the column. The water-soluble and exchangeable form of Zn at the 0-5 cm depth was 1238, 1344 and 1595 mg in the no anion and nitrate and phosphate treated soil columns respectively. At the lowest depth (25-32 cm) the amounts of Zn were 2.15, 8.09 and 2.05 mg respectively. The fraction of the water soluble and exchangeable form of Zn ranged between 36-41 % of total Zn in the top (0-5 cm) soil depths and decreased to 3.6, 3.7 % in the no anion and phosphate treated and 12.6 % in the nitrate treated column at the lowest depth. A high accumulation of the water-soluble and exchangeable form of Zn at 0-5 cm depth confirms the fact that the inorganic Zn applied soil had a greater portion of readily available Zn than did the sludge applied soil, which had adsorbing material with it.

The total amount of the water-soluble and exchangeable form of Zn was almost doubled in the inorganic Zn applied soil columns compared to the sewage sludge applied soil columns.

8.5.2.2. Carbonate (0.05 EDTA extractable) form of Zn

The carbonate form of Zn in the control soil column was almost evenly distributed in the various soil depths. It ranged from 2.15 mg in the topsoil layer to reach 3.28 mg in the lowest soil layer 25-32 cm). The total amount of the carbonate form of Zn in the control column (0-32 cm depth) was 16.15 mg .The carbonate fraction of the total Zn in each depth ranged between 2.15 % and 3.28 %. The overall organic fraction of Zn in the control column was 7.35 % of the total Zn.

Sewage sludge application considerably raised the carbonate form of Zn in all three treatments. The carbonate form of Zn in the top 0-5 cm of the columns totalled 690.8, 710 and 745 mg. The carbonate fraction of Zn in the control soil column ranged from 4.7 to 10.6 % of total Zn whereas it ranged between 12.2-41, 12.8-34.6 and 5.8-33.6 % in no anion, nitrate and phosphate treated columns respectively. The overall value of the EDTA extractable carbonate fraction of Zn in the control soil column was 7.4 % of its total Zn, which increased to 29, 28.8 and 27 % in the no anion, nitrate and phosphate treated columns respectively. A large proportion of Zn associated with the carbonate fraction in this sludge treated soil confirmed the fact that carbonates are freshly formed compounds. These carbonates are mixed crystals associated with the heavy metal cations or any other cations such ascalcium, magnesium, iron and aluminum.

Application of inorganic Zn also raised the 0.05 M EDTA extractable Zn fraction in all three treatments. The amount of the carbonate form of Zn in the first 0-5 cm soil depths of soil were 1284, 1252 and 1220 mg in the no anion, nitrate and phosphate treated columns respectively. The carbonate form of Zn gradually decreased with the depths up to 15 cm. Then it suddenly declined at 15-20 cm soil depth and reached 4-5mg in the lowest soil depth of the treatments. The carbonate fraction of Zn gradually decreased as the soil depth increased, ranging from 37.5-8.3 %, 35.7-6.2 % and 31.8-7 % in no anion, nitrate and phosphate treated columns respectively. The overall fraction of 0.05 M EDTA extractable Zn was 38, 36.4 and 32.9 % of total Zn in no anion, nitrate and phosphate treated columns respectively.

Inorganic Zn applied columns had approximately 50 % more EDTA extractable carbonate fraction than sewage sludge applied soil columns.

8.5.2.3. Organically complexed form of Zn

The organically complexed form of Zn decreased with the soil depth of the control soil column. The total amount of the organically complexed form of Zn in the control column (0-32 cm depth) was 21.02 mg and it gradually decreased with the depth having 6.12 g at 0-5 cm depth and 1.45 g at the lowest (25-32 cm) depth. The organically complexed fraction of total Zn decreased with the depth from 6.12-1.45%. The overall organic fraction of Zn in the control column was 9.57 % of the total Zn.

The application of sewage sludge increased the amount of the organically complexed form of Zn at a higher level compared to other forms of Zn. The organic form of Zn at 0-5 cm depth was 876, 870 and 885 mg in no anion, nitrate and phosphate treated columns respectively. Surprisingly a large accumulation of the organic form of Zn was found in 5-10 cm depth of columns - 575, 591 and 588 mg. This could be due to the transport of organic colloidal particles from the sewage sludge to the nearest layer. Between 10-32 cm depth the organic form of Zn decreased with the depth ranging from 18-1.9 mg, 11-1.5 mg, 9.7-1.7 mg in no anion, nitrate and phosphate treated columns respectively. The organically complexed fraction of Zn decreased with the increase in depth from 36.5-3.31 %, 35.4-2.6% and 33-3.4 % of total Zn in no anion, nitrate and phosphate treated columns respectively. The overall organic fraction of Zn in the control soil column was 9.57 % of the total Zn which increased to 33.7, 33 and 32.2 % in no anion, nitrate and phosphate treated columns. This large proportion of Zn in organic fraction in the sewage sludge applied soil column indicates that Zn is potentially more bioavailable and mobile.

Application of inorganic Zn increased the organic form of Zn marginally compared to other fractions of Zn. It decreased with soil depths from 30.2-1.9 mg, 30.4-2.3mg and 31.7-2.1mg in no anion, nitrate and phosphate treated soil columns respectively. The organic fraction of Zn decreased with the depth (0-32 cm) from 0.9 –3.3 %, 0.9-3.6 % and 0.8-3.8 % the of total Zn in no anion, nitrate and phosphate treated columns respectively. The overall organic fraction of Zn was 9.6 % of total Zn, which decreased to 1.1, 1.2 and 3.8 % in no anion, nitrate and phosphate treated columns respectively.

Inorganic Zn application had only a small impact on the increase of the organic fraction of Zn, whereas sewage sludge application raised the organic fraction of Zn by a large amount.

8.5.2.4. Fe-Mn oxide form of Zn

The Fe-Mn oxide form of Zn in the control soil column decreased with the soil depth. The total amount of the oxide form of Zn in the control column (0-32 cm depth) was 50.55 mg and it gradually decreased with the depth having 11.9 g at 0-5 cm depth and 4.7 g at the lowest (25-32 cm) depth. The oxide fraction of the total Zn in the column decreased with the depth from 50.5 to 10%. Overall the oxide fraction of Zn in the control column was 23 % of the total Zn.

The application of sewage sludge relatively raised the Fe-Mn oxide level of Zn in all three treatments. At 0-5 cm a high amount of the oxide form of Zn accumulated - 168 mg, 171 mg and 234 mg in no anion, nitrate and phosphate treated columns respectively. The oxide form of Zn decreased with the depth (10-32 cm) from 36.8–5.8 mg, 37.2–5.6 mg and 44.7–5.5 mg in no anion, nitrate and phosphate treated columns respectively. The oxide fraction of total Zn increased with the depth from 7-10.1%, 7.1-9.7 % and 8.7-10.8 % in no anion, nitrate and phosphate treated columns, respectively. The overall oxide fraction of Zn was 23 % in the control column which decreased to 5.4 %, 5.6 % and 6.7 % of the total Zn in no anion, nitrate and phosphate treated columns respectively.

Application of inorganic Zn raised the amount of oxide form of Zn in every depth of all three columns remarkably. A large amount of the oxide fraction of Zn was accumulated in 0-5 cm depth of the columns- 535.4 mg, 582.5 mg and 658.7 mg in no anion, nitrate and phosphate treated columns. It decreased with soil depths (5-32 cm) from 71.6–7 mg, 69.5-6.5 mg and 104.7-5.5 mg respectively. The oxide fraction of total Zn decreased with the depth from 15.6-11.6 %, 16.6-10 % and 17.2-10 % in the no anion, nitrate and phosphate treated columns respectively. The overall oxide fraction of Zn decreased to 15.2, 15.9 and 16.4 % of total Zn in the treatment columns compared to the control column. The oxide form of Zn in inorganic Zn treated soil columns was 2.5-3 times the Zn in sewage sludge treated columns.

8.5.2.5. Residual form of Zn

The residual form of Zn in the control soil column was high in all depths compared to all other fractions of Zn in the control soil column. The total amount of the residual form of Zn in the control column (0-32 cm depth) was 126.72 mg. The residual fraction of Zn increased with the depth from 10- 80 % of total Zn. The overall percentage of residual fraction in the control column was 57.7 % of total Zn.

Application of sewage sludge significantly increased the amount of residual fraction in all three treatment columns only in the first 15 cm. Generally there was little increase of residual fraction throughout in all treatments. The overall percentages of residual fraction were decreased to 13, 12.7 and 13.8 % of total Zn in no anion, nitrate and phosphate treated columns respectively. The 57.7 % of total Zn in the residual fraction reflects the greater tendency for Zn to become unavailable in control volcanic soil. With the application of sewage sludge this proportion decreased to 13, 12.7 and 13.8 % in no anion, nitrate and phosphate treated columns, respectively. This reveals the fact that the Zn in these sewage sludge treated columns would be more bioavailable.

Application of inorganic Zn also increased the amount of residual fraction in the first 15 cm of the treatment columns significantly and there was only a little increase in the rest of the columns. This also showed a similar trend as in the sewage sludge treated columns. The overall percentage of residual fractions decreased to 12.5, 11.4 and 11.2 % of total Zn compared to the control column, in no anion, nitrate and phosphate treated columns respectively. The increase in the residual form of Zn to 634.1, 576 and 580.6 mg in no anion, nitrate and phosphate treated columns could be due to the fact that the available forms of Zn had penetrated into inorganic crystals and noncrystalline minerals and bound in occluded form during the 20-week experimental period.

Sewage sludge application increased the water-soluble form of Zn, EDTA extractable form of Zn and organic form of Zn to 18-20 %, 27-29 % and 32-34% respectively. The Fe-Mn oxide form of Zn and residual form of Zn decreased to 5-6 % and 13-14 %. Inorganic Zn application increased the water soluble and exchangeable form and EDTA extractable form of Zn to 33-35 % and 33-38 % respectively. The Fe-Mn oxide, organic and residual forms of Zn decreased to 15-16 %, 1.1-1.2 % and 11.2-12.5 % respectively. These results reveal that the reactive forms of Zn in soil increased because of the sewage sludge and inorganic Zn application. Levels of nonreactive forms of Zn decreased with both sewage sludge and inorganic Zn application. This change leads to an increase in the bioavailability and potential mobility of Zn in volcanic Egmont soil in the long term.

8.6. SUGGESTIONS FOR FURTHER STUDY

The effect of phosphate was significant in increasing the adsorption and limiting the movement of Zn in volcanic Egmont soil. Nitrate increased the leachability. Further studies should be carried out to see the effect of other forms of anions such as sulphate, carbonate and chlorides so that a better understanding of the environmental impact of anions on the mobility and availability of the Zn could be achieved.

Zinc was found to be more mobile than Cd and Cu in sludge and soil. A considerable amount of Zn moved to 32 cm soil depth over a 20-week period. Leaching was studied only with deionized water in this study. If the leaching had been examined with any other desorbing agents such as 0.1 M KNO_3 or 0.1 M $NaNO_3$ solution there would have been more chances for greater movement of Zn than were observed in this experiment. Therefore, Zn availability might go to a biologically toxic limit in the soil where high Zn loaded sewage sludges are disposed of in the long term. Sewage sludge application caused the soil to decline in pH in the profile of volcanic Egmont soil. A further study should be carried out to measure the change of negative surface charge of the volcanic Egmont soil after a few years of sewage sludge application and its impact on the mobility of Zn and other heavy metals.

The fractionation of sewage sludge and inorganic Zn applied soils revealed that the presence of the exchangeable and Fe-Mn oxide form of Zn was remarkably increased in the phosphate treated volcanic Egmont soil compared to no anion and nitrate treated soil. A further study should address the biological importance of these chemical fractions with cropping or with microorganisms.

REFERENCES

Adriano D.C. (2001) Trace elements in the terrestrial environments: Biogeochemistry, Bioavailability, and Risks of Metals. Springer- Verlag New York.

Adriano D.C. (1986) Trace elements in the terrestrial environment. Springer- Verlag, New York.

Agbenin J.O. (1998) Phosphate- induced zinc retention in tropical semi- arid soils. *European J. Soil Science* **49,** 693-700.

Ahuja P., Gupta R. and Saxena R.K. (1999) Zn^{2+} biosorption by Oscillatoria anguistissima. *Process Biochemistry* **34,** 77-85.

Ahumada I., Mendoza J., Navarrete E. and Ascar L. (1999) Sequential extraction of heavy metals in soils irrigated with wastewater. *Commun.Soil Sci.Plant Anal.* **30**(9&10), 1507-1519.

Ahumada I.T., Bustamante A. and Schalscha E.B. (1997). Zinc Speciation in Phosphate affected soils. *Commun. Soil Sci. Plant Anal.* **28**(11&12), 989-995.

Aksu Z. and Kutsal T. (1990) A Comparative study for biosorption characteristics of heavy metal ions with C.vulgaris. *Env.Tech.* **11**, 979-987.

Aksu Z. and Yener J. (1998) Investigation of the biosorption of phenol and monochlorinated phenols on the dried activated sludge. *Process Biochemistry* **33**(6), 649-655.

Al-Asheh S. and Duvnjak Z. (1995) The effect of phosphate concentration on phytase production and the reduction of phytic acid content in canola meal by Aspergillus Carbonarius during a solid state permentation process. *Applied Microbiology and Biotechnology,* **43,** 25-30

Alesh B.A., Fuller W.H. and Boyle M.V. (1980) Effect of leachate flow rate on metal migration through soil. *J.Environ.Qual.* **9**(1), 119-126.

Alloway B. J. (1995) Heavy metals in soils. Elsevier Sciences publishers, The Netherlands.

Al-Wabel M.I., Al-omran A.M., Shalaby A.A. and Choudhary M.I. (1998) Effect of sewage sludge on some chemical properties of calcareous sandy soils. *Communication in Soil Science & Plant Analysis* **29**(17-18), 2713-2724.

Anderson P. R. and Christensen T. H. (1988) Distribution coefficients of Cd, Co, Ni and Zn in soils. *J. Soil. Sci.* **39**, 15-22.

Andreu V. and Gimeno-Garcia E. (1996). Total Content and Extractable Fraction of Cadmium, Cobalt, Copper, Nickel, Lead. And Zinc in Calcareous Orchard Soils. *Commun. Soil Sci. Plant Anal.* **27**(13&14), 2633-2648.

ANZECC/NHMRC (1992) Australia and New Zealand Environment and Consrvation Council, National Health and Medical Research Council. Australian and New Zealand Guidelines for the Assessment and Management of Contaminated sites 57 p.

Atkinson B.W., Bux F. and Kasan H.C. (1996) Bioremediation of metal contaminated industrial effluents using waste sludges. *Water Science Tehnology* **34**(9), 9-15

Backes C.A., McLaren R. G., Rate A. W. and Swift R. S. (1995). Kinetics of Cadmium and Cobalt Desorption from Iron and Manganese Oxides. *Soil Sci. Soc. Am J.* **59,** 778-785.

Bagby M.M. and Sherrard J.H. (1981) Combined effect of cadmium and nickel on the activated sludge process. *Process Research* (W.P.C.F). **47** (2), 362-376.

Bailey J.E. (1986) Biochemical Engineering Fundamentals. Singapore:McGraw-Hill Book Co.

Baillet F., Magnin J.P., Cheruy A. and Ozil P. (1997) Cadmium tolerance and uptake by a Thiobacillus ferrooxidans Biomass. *Environmental Technology.* **18,** 631-638.

Bakkaloglu I.,. Butter T.J, Evison L.M., Holland F.S. and Hancock I.C. (1998) Screening of various types biomass for removal and recovery of heavy metals (Zn, Cu, Ni) by biosorption sedimentation and desorption. *Water Science Technology* **38**(6), 269-277.

Barak P. and Helmke P.A. (1993) The chemistry of zinc. **In** Zinc in Soils and plants, Proceedings of the International Symposium, University of Western Australia, 27-28 September, ed. A. D. Robson., Developments in Plant and Soil Sciences, Vol. 55. Kluwer Academic Publishers, Dordrecht, pp. 1-13.

Barrow N.J. (1993) Mechanisms of reaction of zinc with soil and soil components. **In** Zinc in Soils and Plants, Proceedings of the International Symposium on 'Zinc in Soils and Plants', University of Western Australia, 27-28 September 1993. ed. A.D. Robson., Kluwer Academic Publishers, Dordrecht, pp. 15-29.

Barrow N.J. (1983) A mechanistic model for describing the sorption and desorption of phosphate by soil. *Journal of Soil Science* **34,** 733-750.

Barrow N.J. and Cox V.C. (1990) A quick and simple method for determining the titration curve and estimating the lime requirement of soil. *Australian Journal of Soil Research* **28,** 685-694

Barrow N.J. and Whelan, B.R. (1998). Comparing the effects of pH on the sorption of metals by soil and by goethite and on uptake by plants. *European Journal of Soil Science* **49,** 683-692.

Barrows Harold L., Neff Marshall S., and Gammon Nathan (1960). Effect of Soil Type on Mobility of Zinc in the Soil and on its availability from Zinc Sulfate to Tung. *Soil Science Society Proceedings.* 367-372.

Basta N.T. and Sloan J.J. (1999). Bioavailability of heavy metals in strongly acidic soils treated with exceptional quality bio solids. J. Environ.Qual. **28,** 633-638.

Basta N.T. and Tabatabai M.A. (1992) Effect of cropping systems on adsorption of metals by soils.II. Effect of soil pH. *Soil Science* **153,** 195-204.

Beate Mattuschka and Gunhild Straube (1993) Biosorption of metals by a waste biomass. *J. Chem.Tech. Biotech.* **58,** 57-63.

Beckett P.H.T. (1989) The use of extractants in studies on trace metals in soils, sewage sludges, and sludge treated soils. *Advances in Soil Science.* **9,** 144-171.

Benefield L.D., Judkins J.F. and Weand B.L. (1982) Process Chemistry for Water and Wastewater Treatment. Prentice-Hall, Inc., New Jersey.

Bevacqua R.F. and Mwllano (1994) Cumulative effect of sludge compost on crop yields and soil properties. *Commun. Soil Sci. Plant. Anal.* **25,** 395-406.

Bingham F.T., Sposito G. and Strong J.E (1984). The effect of chloride on the availability of cadmium. *Journal of Environmental Quality* **13,** 71-74.

Blakemore L.C., Searle P.L. and Daly B.K. (1987) Methods for chemical analysis of soils. New Zealand Soil Bureau Scientific Report 80. (NZ Soil Bureau: Lower Hutt, New Zealand).

Blais J. F., Meunier N. and Tyagi R.D. (1997) Simultaneous sewage sludges digestion and metal leaching at controlled pH. *Environmental Technology.* **18,** 499-508.

Blais J. F., Tyagi R.D., Auclair J.C. and Huang C.P. (1992) Comparison of acid and microbial leaching for metal removal from municipal sludge. *Water Science Technology* **26** (1-2), 197-206.

Blanco A., Sanz B., Liama M.J. and Serra J.L. (1999) Biosorption of heavy metals to immobilised Phormidium laminosum biomass. *Journal of Biotechnology* **69,** 227-240.

Boekhold A.E., Temminghoff E.J.M and Van der Zee S.E.A.T.M (1993) Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil. *Journal of Soil Science* **44,** 85-96.

Bolan N.S., Adriano D.C. and Naidu.R. (2003) Role of Phosphorus in (Im)mobilization and Bioavailability of Heavy Metals in the Soil-Plant

System. Springer-Verlag 2003. *Rev. Environ. Contam. Toxicol.* 177, 1-44. (in press)

Bolan N.S., Naidu R., Syers J.K. and Tillman R.W. (1999a) Surface charge and solute interactions in soils. *Advances in Agronomy* **67,** 87-140.

Bolan.N.S., Naidu R., Khan M.A.R., Tillman R.W. and Syers J.K. (1999 b) The effects of anion sorption on sorption and leaching of cadmium. *Aust J. Soil Res.* **37,** 445-60.

Bolan N.S. and Barrow N.J. (1984) Modelling the effect of adsorption of phosphate and other anions on the surface charge of variable charge oxides. *Journal of Soil Science* **35,** 273-281.

Bolland M.D.A., Posner A.M. and Quirk J.P. (1977) Zinc Adsorption by goethite in the absence and presence of phosphate. *Aust. J. Soil Res.* **15,** 279-286.

Bolt G.H., De-Boodt M F., Hayes M.H.B. and McBride M.B. (1991) Interaction at the Soil Colloid-Soil Solution interface, Kluwer Academic Publishers.

Boswell F.C. (1975) Municipal sewage sludge and selected element application to soil: Effect on soil and fescue. *J. Environ. Qual.* **4,** 267-272.

Bowen H.J.M. (1979 a) Environmental Chemistry of the elements. Academic Press, London.

Boyle C.D. and Reade A.E. (1983) Characterization of Two Extracellular Polysaccharides from Marine Bacteria. *Appl. Environ. Microbiol.* **46**, 392.

Bradley R.F. and Nelson P.O. (1983) Equilibrium chemical modelling of heavy metals in activated sludge. *Water Research.* **17** (7), 771-778.

Brookes P.C. and McGrath S.P. (1984) Effects of metal toxicity on the size of the soil microbial biomass. Journal of Soil Science **35,** 341-346.

Brown M.J. and Lester J.N. (1979) Metal removal in activated sludge: Theory of vacterial extracellular polymers. *Water Research.* **13,** 817-837.

Brown M.J. and Lester J.N. (1982) Role of bacterial extracellular polymers in metal uptake in pure bacterial culture and activated sludge-I : Effects of metal concentration. *Water Res.* **16,** 1539-1548.

Brummer G.W. (1986) The importance of Chemical Speciation in Environmental Process. Springer-Verlag, Berlin, pp. 169-192.

Brummer G.W., Gerth J. and Herms U. (1986) Heavy metal species, mobility and availability in soils. *Zeitschrift fur Pflanzenernahrung und Bodenkunde* **149,** 382-398.

Burgess J.E., Quarmby J. and Stephenson T. (1999) Role of micronutrients in activated sludge based biotreatment of industrial effluents. *Biotechnology Advances* **17,** 49-70.

Butter T.J., Evison L. M., Hancock I.C. and Holland F.S. (1998) The kinetics of metal uptake by microbial biomass: Implications for the design of a biosorption reactor. *Water Science and Technology* **38**(6), 279-286.

Butter T.J., Evison L. M., Hancock I.C. and Holland F.S. (1995) Removal and recovery of cadmium from diluted aqueous streams by biosorption, elution and electrolysis, Proceedings of 9th Forum for applied Biotechnology 2581-2584.

Cameron, K.C., Di H.J. and McLaren R.G. (1997). Is soil an appropriate dumping ground for our waste. *Aust. J. Soil Res.* **35,** 995-1035.

Cameron K.C., McLaren R.G. and Adams J.A. (1994) Application of municipal sewage sludge to low fertility forest soils: The fate of nitrogen and heavy metals. *In* 15th World Congress of Soil Science. Volume 3a. Commission II: Symposia. Acapulco, Mexico. July 10-16, 1994. *International Society of Soil Science* **3**(a), 467-482.

Camobreco V.J., Richards B.K., Steenhuis T.S., Peverly J.H. and McBride M.B. (1996) Movement of Heavy Metals Through Undisturbed and Homogenized Soil Columns. *Soil Sci.* **161**(11), 740-749.

Campanella L., Cardarelli E., Ferri T., Petronio B.M. and Pupella A. (1987) Evaluation of heavy metals speciation in an urban sludge.I. Batch method. *Sci. Total Environ.* **61,** 217-228.

Commission of the European Communities (1986) Council Directive on the protection of the environment and in particular of the soil when sewage sludge is used in agriculture. Official Journal of theEuropean Communities No. L 181/6(86/278/EEC).

Celardin F. (1999) Semi-empirical correlation between so-called mobilizable and mobile concentrations of heavy metals in soils **30**(5-6), 843-854.

Chander K. and Brookes P.C. (1991) Effect of heavy metals from past applications of sewage sludge on microbial biomass and organic matter accumulation in a sandy loam and silty loam UK soil. *Soil Biology and Biochemistry* **23,** 927-932.

Chander K. and Brookes P.C. (1991) Effects of Heavy metals from past applications of sewage sludge on microbial biomass and organic matter accumulation in a sandy loam and silty loam U.K soil. *Soil Biol. Biochem.* **23**(10), 927-932.

Chaney R. L. (1990) Twenty years of land application research. *Bio-cycle* **31,** 54-59.

Chaney R.L. (1993) Trace metal movement:Soil-Plant systems and bioavailability of biosolids-applied metals. P.27-32. *In* C.E. Clapp et al. (ed.) Sewage sludge; Land utilization and the environment. SSSA, Madison, WI.

Chang A.C., Warneke J.E., Page A.L. and Lund L. J. (1984) Accumulation of heavy metals in sewage sludge treated soils. *J. Environ. Qual.* **13,** 87-90.

Chang J.S, Robin L. and Chung- Cheng. (1997) Biosorption of Lead, Copper and Cadmium by Biomass of Pseudomonas aeruginosa PU21. *Water Research.* **31**(7), 1651-1658.

Chang J.S., Robin L. and Chung-Cheng Chang. (1997) Biosorption of lead, copper and cadmium by biomass of Pseudomonas aeruginosa. *Wat. Res.* **31**(7), 1651-1658.

Chareonsudjai P. (1994) Biosorption of copper by activated sludge. M.Sc. Thesis, Massey University, New Zealand.

Chatterjee S., Asthana R.K., Tripathi A.K. and Singh S.P. (1996) Metal removal by selected sorbents. *Process Biochemistry* **31**(5), 457-462.

Cheng M.H., Patterson J.W. and Minear R.A. (1975) (W.P.C.F) *Process Research.* **47**(2), 362-376.

Christensen T.H. (1984) Cadmium soil sorption at low concentration: I. Effect of time, cadmium load, pH and calcium. Water, Air and Soil Pollution **21**,105-114.

Christensen T.H. (1985) Cadmium soil sorption at low concentration: III. Prediction and observation of mobility. Water, Air and Soil Pollution **26,** 255-264.

Clayton P.M. and Tiller K.G. (1979) A chemical method for determination of the heavy metal content of soils in environmental studies. Division of soils technical paper No 41, CSIRO, Australia.

Corey B.R., King L.D., Lue-Hing C., Fanning D.S., Street J.J. and Walker J.M. (1987) Effects of sludge properties on accumulation of trace elements by crops. *In* Land Application of Sludge—Food Chain Implications, pp. 25-51, eds. A.L. Page., T.J. Logan and J.A. Ryan. Lewis Publishers, Inc., Chelsea, MI.

Dang Y.P., Dalal R.C., Edwards D.G., and Tiller K.G. (1994). Kinetics of Zinc Desorption from Vertisols. Soil Sci. Soc. Am.J. **58,** 1392-1399.

Daniel E. Dodor and Kazuhiro Oya. (2000) Phosphate sorption characteristics of major soils in Okinawa, Japan. *Commun.Soil Sci.Plant Anal.* **31**(3&4), 277-288.

Davis A., Ruby M.V and Bergstrom P.D. (1992). *Environ. Sci. Technol.* **26,** 46-468.

Del-Castilho P., Chardon W.J. and Salomons W. (1993) Influence of cattle-manure slurry application on the solubility of cadmium, copper, and zinc in a manured acidic, loamy sand soil. *J.Environ. Qual.* **22,** 689-697.

De-Vries M.P.C. and Tiller K.G. (1978) Sewage sludge as a soil amendment, with special reference to Cadmium, Cu, Mn, Ni, Pb and Zinc – Comparison of results from experiments conducted inside and outside a glass house. *Environ. Pollut.* **16,** 231-240.

Delgado, A., A.M. Anselmo, and J.M. Novais. (1998) Heavy Metal biosorption by dried powdered mycelium of Fusarium flocciferum. *Water Environment Research.* **70**(3), 370-375.

Dewitt C.W. and Rowe J. A. (1961) Sialic Acids (N,7-o- diacetylneuraminic acid and N-acetylneuraminic acid) *In Escherichia coli . J. Bacterial.* **82,** 838

Dilek, F.B., U.Yetis. (1992) Effects of heavy metals on activated sludge process. *Water Science technology* **26**(3-4), 801-813.

Dowdy A.K., Laterall J.J., Hinesly T.D.,Grossman R.B and Sullivan D.L. (1991) Trace metal movement in an aeric ochraqualf following 14 years of annual sludge application. *J.Env.Qual.* **20,** 119-123

Dowdy R.H. and Volk V.V. (1983) Movement of heavy metals in soils. In Chemical Mobility and Reactivity in soil systems. Special Publication *Soil Science Society of America,* N011, SSSA 229-240.

Duane L. Winegardner. (1996) An introduction to soils for environmental professionals, CRC press, Lewis publishers, Florida.

Dunnivant F.M., Jardine P.M., Taylor D.L., and McCarthy J.F. (1992)Co-transport of Cadmium and hexachlorobiphenyl by dissolved organic carbon through columns containing aquifer material. *Environ. Sci.Technol.* **26,** 360-368.

Eaton A.D., Clesceri L.S., and Greenberg A.E. (1995) "Standard methods for the examination of water and wastewater" 19th Ed., (Publishers: American Public Health Association, American Water Works Association, and Water Environment Federation.

Ekster A. and Jenkin D. (1997) Nickel and copper removal at the San Jose/Santa Clara water pollution control plant. *Water Environment Research* **68**(7), 1172-1178.

Elliott H.A., Liberati M.R. and Huang C.P. (1986) Competitive adsorption of heavy metals by soils. *J.Environ. Qual.* **15**(3), 214-219.

Emmerich W.E., Lund L.J., Page A. L. and Chang A. C. (1982a) Movement of heavy metals in sewage sludge- treated soils. *J. Environ. Qual.* **11**(2), 174-178.

Emmerich W.E., Lund L. J., Page A.L., And Chang A. C. (1982b) Solid phase forms of heavy metals in sewage sludge treated soils. *J.Environ. Qual.* **11**(2), 178-186.

Evans L.J . (1989) Chemistry of metal retention by soils. *Environ. Sci. Technol.* **23**(9).

Evans L.J., Lumsdon D.G. and Bolton K.A. (1991) The influence of pH and chloride on the retention of zinc, lead, cadmium and mercury by soil. In Proc. Technology Transfer Conf. The multimedia approach: Integrated Environmental Protection Vol1, Environment, Canada, Toronto pp.123-130.

Fletcher P. and P.H.T. Beckett. (1987) The chemistry of heavy metals in digested sewage sludge. Copper (ii) complexation with soluble organic matter. *Wat. Res.* **21**(10), 1153-1161.

Florez-Vélez L.M., Ducaroir J., Jaunet A.M. and Robert M. (1996) Study of the distribution of copper in an acid sandy vineyard soil by three different methods. *European Journal of Soil Science.* **47.** 523-532

Forster C.F. (1976) *Water S.A.* **2,** 119.

Fourest E. and Roux J. (1992) Heavy Metal biosorption by fungal mycelial by-products: mechanisms and influence of pH. Appl. Microbil. Biotechnol. **37,** 399-403.

Frank L. Slejko. (1985) Adsorption Technology. Marcel Dekker, Inc., New York.

Fristoe B.R. and Nelson P.O. (1983) Equilibrium chemical modeling of heavy metals in activated sludge. *Wat. Res.*17, 771-778.

Gambrell R.P. and Patrick W.H. (1978) **In** Plant Life in Anaerobic Environments. Ann Arbor Sci. Publ., Ann Arbor, MI.

Garcia –Miragaya J. and Page A.L (1976). Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. *Soil Science Society of America Journal* **40,** 658-663.

Gardea-Torresdey J.L., Tieman k.J., Gonzalez J.H., Henning J.A. and Towsend M.S. (1996) Ability of *Midicago sativa* (alfalfa) to remove copper ions from solution. *Journal of Hazardous Materials* **48,** 181-190.

Gardiner J. (1974) The chemistry of cadmium in natural water: II. The adsorption of cadmium on river muds and naturally occurring solids. *Water Res.* **8,** 157-164.

Geesey G. and Jang L. (1990) Extracellular Polymers for Metal Binding. *In* Microbial Mineral Recovery, eds. H. L. Ehrlich and C. L. Brierley, McGraw-Hill Publishing Company, New York.

Gelmann I. (1955) M.Sc. Thesis, Rutgers University, U.S.A.

Gerriste R.G., Vriesema R., Dalenberg J.W., and De Roos H.P. (1982) Effect of sewage sludge on trace element mobility in soils. *J. Environ. Qual.* **11,** 178-181.

Giller K.E., McGrath S. P. and Hirsch P.R. (1989) Absence of nitrogen fixation in clover grown on soil subject to long term contamination with heavy metals is due to survival of only ineffective rhizobium. *Soil biology & Biochemistry* **21,** 841-848.

Giller K.E., Witter E. and McGrath S.P. (1998) Toxicity of heavymetals to microorganisms and microbial processes in agricultural soils- a review, *Soil biology & Biochemistry* **30**(10-11), 1389-1414.

Giordana P.M. and Mortvedt J.J. (1976). Nitrogen effects on mobility and plant uptake of heavy metals in sewage sludge applied to soil columns. *J. Environ. Qual.* **5**(2), 165-168.

Giusquiani P.L., Gigliotti G., and Businelli D. (1992) Mobility of heavy metals in urban waste amended soils *J. Environ. Qual.* **21,** 330-335.

Giusquiani P.L., Giovanni Gigliotti and Daniela Businelli. (1992) Mobility of heavy metals in urban waste- amended soils. *J. Environ Qual.* **21,** 330-335.

Goldstone A.J. (1983) Report on the effluent from the Kiwi fertilizer Works, Morrinsville, and its receiving waters. Report' No.146, Haurki Catchment Board Regional Water Board, Te Aroha.

Gong C.R. and Donahoe R.J. (1997) An experimental study of heavy metal attenuation and mobility in sandy loam soils, Applied Geochemistry **12** (3), 243-254.

Gould M.S., and Genetelli E.J. (1984) Effects of competition on heavy metal binding by anaerobically digested sludges. *Wat. Res.* **18**(1), 123-126.

Gould M.S., and Genetelli E.J. (1978) Heavy metal complexation behaviour in anaerobically digested sludges. *Water Res.***12,** 505-512.

Gourdon R., Rus, E., Bhende, S. and Sofer, S.S. (1990). Mechanism of cadmium uptake by activated sludge. *Appl.Microbiol.Biotech.* **34,** 274-278.

Gray C.W., R.G. McLaren, a.H.C. Roberts, and L.M. Condron. (1998) Sorption and desorption of cadmium from some New Zealand soils: effcet of pH and contact time. *Aust. J. Soil Res.* **36,** 199-216.

Greenland D.J. and Hayes M.H.B. (1981) The Chemistry of Soil Processes. John Wiley & Sons, New York, 469.

Guggenberger G.B., and Zech W. (1994) Heavy metal binding by Hydrophobic and hydrophilic dissolved organic carbon fractions in a Spodosol A and B horizons. *Water Air Soil Pollut.* **72,** 111-127.

Hahne, H.C.H and W. Kroontje. (1973) Significance of pH and chloride concentration on behavior of heavy metal Pollutants: Mercury, Cadmium, Zinc, and lead. Journal of *Environmental Quality* **2**(4), 444-450.

Harter R.D. and Naidu R. (1995) Role of metal organic complexation in metal sorption by soils. *Adv. Agron.* **55,** 219-263.

Harter R.D. (1983) Effect of soil pH on adsorption of lead, copper, zinc and nickel. *Soi. Sci.Soc. Am. J.* **47,** 679-683.

Hassler J. W. (1974) Purification with activated Carbon. Chemical Publishing Company, New York.

Hayes G. (1981) The chemistry of Soil Processes, John Wiley & Sons, New York.

Haygarth, P.M. and Jones, K.C. (1992). Atmospheric deposition of metals to agricultural surfaces. *In* Biogeochemistry of trace metals. ed. D.C. Adriano, Lewis Publishers, Boca Raton, pp 249-276.

Helmke, P.A., and Naidu R. (1996). *In* R. Naidu et al., eds. Contaminants and the Soil Environment in the Australasia-Pacific Region. Kluwer, Dordrecht, The Netherlands.

Herms E., and Brummer G. (1984) Einflussgrössen der schwermetalloslychkeit und bindung in Boden. *Zeitschrift für Pflanzenernährung und Bodenkunde.* **147** (3), 400-424

Hickey M.G. and Kittrick J.A. (1984) Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.***13,** 372-376.

Hogg D.S., McLaren R.G. and Swift R.S. (1993) Desorption of copper from some New Zealand soils. *Soil. Sci. Soc. Am. J.* **57,** 361-365.

Holan Z.R., Volesky B. and Prasetyo I. (1993) Biosorption of cadmium by biomass of Marine Algae. *Biotechnol. Bioengg.* **41**(12), 819-825.

Homann P.S. and Zasoski R.J (1987) Solution composition effects on cadmium sorption by forest soil profiles. *Journal of Environmental Quality.* **16,** 429-433.

Hooda P.S. and Alloway B.J. (1993) Effects of time and temperature on the bioavailability of Cd and Pb from sludge amended soils. *Journal of Soil Science* **44,** 97-110.

Hooda P.S., McNulty D., Alloway B.J. and Aitken M.N. (1997) Plant availability of heavy metals in Soils previously amended with heavy metals applications of sewage sludge. *Journal of the science of Food & Agriculture.* **73**(4), 446-454.

Homburg V. and Brummer G.W. (1993) Behaviour of heavy metals in soils. I. Heavy metal mobility. *Zeitschrift für Pflanzenernährung und Bodenkunde*. **156,** 467-477.

Huang C.P., Hsieh Y.S., Park S.W., Corapcioglu M.O. (1987) Chemical interactions between heavy metal ions and hydrous solids. *In* metal speciation, separation and recovery [proceedings]. Vol. I., eds. J.W.Patterson and R. Passino, Lewis Publishers, Inc., Chelsea, Mich., 437.

Huangi J.P. (1991) Removal of heavy metals by fungal adsorption. *In* Heavy metals in the environment. ed, J. P. Vernet , Elsevier sciences publishers, Netherlands.

Jenkins C.J. (1989) Anoxic-Aerobic digestion of waste Activated sludge: Part II – Supernatant Characteristics ORP Monitoring results and overall rating system. *Env. Tech.Letters* **10,** 371-384.

Jenne E.A. and Luoma S.N. (1977) Forms of trace elements in solids, sediments, and associated waters. An overview of their determination and biological activity.***In*** Biological Implications of Metals in the Environment. (Eds) Druker H. and Wildung R.E.CONF-750929. Tech. Info. Ctr., ERDA Washington.p.110-143

Jennifer I.H and Quarmby J. (1999) Biopolymers in wastewater treatment. *Environmental Biotechnology* **10,** 259-262.

Jinbai and bohumil V. (1999) Cadmium biosorption rate in Protonated sargassum Biomass. *Env.Sci.Technol.* **33,** 751-757.

Jones L.H.P. and Jarvis S.C. (1981) The fate of heavy metals. ***In*** The Chemistry of Soil Processes (Eds) Greenland D.J and Hayes M.H., Eds. John Wiley & Sons Ltd., New York 87-102.

Kabata-Pendias A. and Pendias H. (1992) Trace Elements in Soils and Plants (2nd Ed.). CRC Press Inc., Florida, USA. p. 40.

Kabata-Pendias A. and Pendias H. (2001) Trace Elements in Soils and Plants (3rd Ed.). CRC Press Inc., Florida, USA.

Kao J.F., Hsieh L.P., Cheng S.S., and Huang C.P. (1982) Effects of EDTA on cadmium in activated sludge systems *J. Water Pollut. Control Fed.* **54,** 1118.

Kasimov N.S., Kosheleva N.Y. and Samonova O.A. (1996) Mobile forms of heavy metals in soils of middle Volga forest –steppe. *Eurasian Soil Science* **28**(9), 47-61.

Kenneth M. Holtzclaw D.A. Keech, A.L. Page, Garrison Sposito, T.J. Ganje, and N.B.Ball. (1978). Trace metal distributions among the humic acid, the fulvic acid and precipitable fractions extracted with NaOH from sewage sludges. *J. Environ. Qual.* 7(1), 124-127.

Khan M.A.R. (2001). Transformation and plantavailability of copper in pasture soils. Ph.D thesis, Massey University, Palmerston North, New Zealand.

Kipling J.J. (1965) Adsorption from solutions of non-electrolytes. Academic press inc. London.

Kohsiek L.H.M., Franken R., et al. (1994) *In* Ecotoxicology of Soil Organisms. eds. Donker M., et al., CRC Pr, Florida, USA.

Kookana R.S. and Naidu R. (1996) Effect of soil solution composition on cadmium transport through variable charge soils.p. 29-30. In Proc. Int. Conf. Contaminants and the Soil Environment, Adelaide, Australia. February 1996. Heise Verlag, Amsterdam.

Korte N.E., Skopp J., Fuller W.H., Niebla E.E., and Alesii B. (1976) Trace element movement in soils: influence on soil physical and chemical properties. *Soil Sci.* **122,** 351-359.

Krishnamurti G.S.R., Huang P.M. and Kozak L.M. (1999a) Desorption kinetics of cadmium from soils using M ammonium nitrate and M ammonium chloride. *Communications in Soil Science & Plant analysis* **30** (19-20), 2785-2800.

Krishnamurti G.S.R., Huang P.M. and Kozak L.M. (1999b) Sorption and desorption kinetics of cadmium from soil: influence of phosphate. *Soil Science* **164** (12), 888-898.

Kuo S. (1986) Concurrent sorption of phosphate and zinc, cadmium or Calcium by a Hydrous Ferric Oxide. *Soil. Sci. Soc. Am.* **50,** 1412-1419.

Kuo S., Jellum E.J., Baker A.S. (1985). Effects of Soil type, liming, and sludge application on Zinc and cadmium availability to Swiss chard. *Soil Science* **139**(2), 122-129.

Kuo S. and Mikkelsen D.S. (1980) Kinetics of zinc desorption from soils. *Plant Soil* **56,** 355-364.

Kuyucak, N., Volesky B. (1988) Biosorbents for recovery of metals from industrial solutions. *Biotech letters* **10**(2), 137-142.

Lagerwerff J.V., Biersdorf G.T., and Brower D.L. (1976) Retention of metals in sewage sludge: I. Constituent heavy metals. *J. Environ. Qual.* **5,** 19-25.

Lake, D.L., Kirk, P.W.W and Lester, J.N. (1984) Fractionation, characterization and speciation of heavy metals in sewage sludge and sludge-amended soils: A Review. *J. Env.Qual.* **13**(2), 175-181.

Lamy I., Bourgeois S. and Bermond (1993) Soil cadmium mobility as a consequence of sewage sludge disposal *J. Environ. Qual.* **22**, 731-737

Lawson P.S, Sterritt R. M. and Lester J.N. (1984) Adsorption and complexation mechanisms of heavy metals uptake in activated sludge. *J. Chem. Tech.Biotech.* **34**B, 253-262.

Lee B.D. CarterBJ.Basta NT. Weaver B. (1997) Factors influencing heavy metal distribution in six Oklahoma benchmark soils. *Soil Science Society of America Journal* **61**(1), 218-223.

Lee Sung H., Jung. C.H., Chung H., Lee M.Y. and Yang Ji-Won. (1998) Removal of heavy metals from aqueous solutions by apple residues. *Process Bichemistry* **33**(2), 205-211.

Leeper G.W. (1978) Managing the heavy metals on the land. Dekker, New York.

Leeper G.W. (1972). Reactions of heavy metals with soils with special regard to their application in sewage wastes. Department of Army, Corps of Engineers, D.C., DACW 73-73-C-0026.

Leschber R., Davis R.D. and Hermite P. (1985) Chemical methods for assessing bio available metals in sludges and soils. Elsevier publishers, New York.

Lester N.J. (1987) Heavy Metals in wastewater and sludge treatment processes. Vol. 1 and 2. CRC Press.

Lester N.J., Harrison R.M and Perry R. (1983) The balance of heavy metals through a sewage treatment works I. Lead, cadmium and copper. *Sci. Total Envir.* **12,** 13-23.

Lie E. and Welander T. (1994) Influence of dissolved oxygen-reduction potential on the denitrification rate of activated sludge. *Water Science and technology* **30** (6), 91-100.

Logan T.J. and Chaney R.L. (1983) Utilization of municipal wastewater and sludge on land-metals. *In* A.L.Page et al. (ed.) Utilization of municipal waste water and sludge on land. Univ. of California, Riverside, CA.

Loebenstein J.R. (1993) Arsanic. ***In*** Minerals Yearbook 1993, U.S. Govt. Printing Office, Wasington, D.C. p.167-170

Lombin G. (1983) Evaluating the micro nutrient fertility of Nigeria,s semi- arid soils.1. *Zinc Soil Science.* **136,** 142-147

Luef E., Teodor P. and Kubicek C.P. (1991) Biosorption of zinc by fungal mycelial wastes. *Applied Microbiology Biotechnology* **34,** 688-692.

Lund L.J., Page A.L. and Nelson C.O. (1976) Movement of heavy Metals below sewage disposal ponds. *J. Env. Qual.* **5**(3), 330-334.

Luo Y.M. and Christie P. (1996) Chemical fractions of Copper and Zinc in Organic-Rich Particles from Aqueous Extracts of a Metal- Contaminated Granite Soil. Commun.Soil Sci. Plant Anal. **27**(18-20), 2973-2986.

Ma L.Q. and. Rao G.N. (1997) Chemical fractionation of cadmium, Copper, Nickel and Zinc in Contaminated soils. *J. Environ. Qual.* **26,** 259-264.

Ma Y.B. and Uren N.C. (1995) Application of a new fractionation scheme for heavy metals in soils. *Communication in Soil Science & Plant Analysis* **26**(19-20), 3291-3303.

Macarie N and Guyot J.P. (1995) Use of ferrous sulphate to reduce the redox potential and allow the start up of UASB reactors treating slowly biodegradable compounds: Application to a wastewater containing 4 methylbenzoic acid. *Env Tech.***16,** 1185-1192.

Magesan G.N. (1992) A study of the leaching of non-reactive solutes. Ph.D thesis. Massey University, Palmerston North.

Malik D.J., Streat M., and Greig J. (1999) Characterization and evaluation of sea weed- based sorbents for treating toxic metal bearing solutions. *Trans-1 Chem.* 77 (B), 227-233.

Maranon E. and Sastre H. (1991). Heavy metal removal in packed bed using apple wastes. *Bioresour. Technol.* **38,** 39-43

Marschner B.U.H. and Wessolek.G. (1995) Effects of melioratives on the adsorption and binding forms of heavy metals in a contaminated top soil from a former sewage farm. *Zeitschrift für Pflanzenernährung und Bodenkunde.* **158,** 9-14

Martinez C.E. and McBride M.B. (1999) *Envron. Sci. Technol.* **33,** 745-750.

Martinez C.E. Motto H.L. (2000). Solubility of lead, zinc and copper added to mineral soil. *Environmental Pollution.* **107** (1), 153-158.

McBride M.B., Richards B.K., Tammo Steenhuis., Russo J.J., and Sebastien. (1997) Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Science.* **162** (7), 487-499.

McBride M.B., Sauve S. and Hendershot W. (1997b) Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *Europian Journal of soil science* **48,** 337-346.

McBride M.B. (1995). Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective? *J.Environ. Qual.* **24,** 5-18.

McBride M.B. (1994). Environmental chemistry of soils. Oxford University press, New York. 96-135.

McBride M.B. (1989). Reactions controlling heavy metal solubility in soils. Advances in Soil Science **10,** 1-47.

McBride M.B. (1984) Sorption of copper (I I) on aluminum hydroxide as affected by phosphate. *Soil Sci. Soc. Am. J.* **49,** 843-846.

McBride M.B. (1982) Cu2+ adsorption characteristics of aluminium hydroxide and oxy hydroxides cited in McBride M.B. 1989. Reactions controlling heavy metal solubility. *In* Advances in soil sciences vol. 10. B.A. Stewart. Springer-Verlaginc. New York p. 1-47.

McGrath S.P. and Cegarra J. (1992) Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil. *J. Soi. Sci.* **43,** 313-321.

McGrath S.P. and Lane P.W. (1989) An explanation for the apparent losses of metals in a Long-term field experiment with Sewage Sludge. *Environmental Pollution* **60,** 235-256.

McGrath S.P., Sanders J.R. and Shalaby M.H. (1988) The effect of soil organic matter levels on soil solution concentrations and extractabilities of manganese, zinc, and copper. *Geoderma* **42**, 177-188

McGrath S.P. (1987) Long-term studies of metal transfer following applications of sewage sludge. Cited in : McGrath S.P. and Cegarra J. 1992. Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil. *J. Soil Sci.* **43,** 313-321.

McGrath S.P. (1984). Metal concentrations in sludges and soil from a long term field trial. *Journal of Agricultural Science* **103**, 25-35.

McKeague, J.A. (1967) An evaluation of 0.1 M pyrophosphate and pyrophosphate-Dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. *Can. J. Soil Sci.* **47,** 95-99.

McLaren R.G. (2002) Leaching of nutrients and metals from soils amended with sewage sludge. *Water and waste in New Zealand.* September 2002, pp. 16-17.

McLaren R.G., Backes C.A., Rate A.W. and Swift R.S. (1998) Kinetics of cadmium and cobalt desorption from soil clay fractions. *Soil Society of America Journal* **62,** 332-337.

McLaren R.G., Carey P.L., Cameron K.C., Adams J.A. and Sedcole J.R. (1994) Effect of soil properties and contact period on the leaching of copper, chromium, and arsenic through undisturbed soils. *In* "15th World Congress Soil Science." Vol.**3a**,156-169. Intenational Society of Soil Science and The Mexican Society of Soil Science, Acapulco, Mexico.

McLaren R.G. and Cameron K.C. (1990) Soil Science: An introduction to the properties and management of New Zealand soils. Oxford University Press, Auckland p.237.

McLaren R.G. and Crawford D.V. (1973) Studies on soil copper: II. The fraction of copper in soils. *J. Soi. Sci.* **24,** 172-181.

McLaughlin M.J. Tiller K.G., Naidu R. and Stevens D.P. (1996) Review: the behaviour and environmental impact of contaminants in fertilizers. *Aust. J. Soil Res.* **34,** 1-54.

McLaughlin M.J., Palmer L.T., Tiller K.G., Beech T.A. and Smart M.K (1994) Increased soil salinity causes elevated cadmium concentrations in field grown potato tubers. *Journal of Environmental Quality* **23,**1013-1018.

McLaughlin M.J., Tiller K.G., Naidu R. (1994b) Chloro complexation of cadmium in soil solutions of saline/sodic soils increases phyto availability of cadmium. Transactions 15th world congress of soil science Vol. 3 b, 195-196.

McLean R.J.C. and Beveridge T.J. (1990) Influence of Metal Ion Charge on Their Binding Capacity to Bacterial Capsules. Abstr. 88th Ann. Meet. *Am. Soc. Microbiol.* Q146.

Melcer H., Monteith H. and Nutt S.G. (1992) Activated sludge process response to variable inputs of heavy metal. *Wat. Sci. Tech.* **25**(11), 387-394.

Mellum H.K., Arnesen A.K.M. and Singh B.R. (1998) Extractability and plant uptake of heavy metals in Alum shale soils. *Communication in Soil Science & Plant Analysis.* **29**(9-10), 1183-1198.

Miller W.P., McFee W.W. and Kelly J.M. (1983) Mobility and retention of heavy metals in sandy soils. *J. Environ. Qual.* **12,** 579-584.

Mislin H. (1986) Cadmium in the environment. Boston, Birkhausen.

Moore J.W. and Ramamoorthy S. (1984) Heavy metals in natural waters: Applied monitoring and impact assessment. Springer- Verlag: New York.

Mott C.J.B. (1981) Anion and ligand exchange. In The chemistry of Soil Processes. pp. 179-219, eds. D.J. Greenland and M.H.B. Hayes. John Wiley: New York.

Mullins G.L and Sommers L.E. (1986). Characterization of Cadmium and Zinc in four soils treated with sewage sludge. *J. Environ. Qual.* **15**(4), 382-387.

Naidu R. and Harter R.D. (1997) Effectiveness of different organic ligands on sorption and extractability of cadmium by soils. *Soil Sc. Soc. Am. J.*

Naidu R., Kookana R.S., Summer M.E., Harter R.D. and Tiller K.G. (1997) Cadmium sorption and transport in variable charge soils: A review. *J. Env. Qual.* **26,** 602-617.

Naidu R., Kookana R.S., Oliver D.P., Rogers S. and McLaughlin M.J. (1996) Contaminants and the soil Environment in the Australasia-Pacific region. Kluwer Academic publishers, London.

Naidu R., Bolan N.S., Kookana R.S and Tiller, K.G (1994). Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science.* **45,** 419-429.

Naidu R., Williamson D., Fitzpatrick R.W and Hollingsworth, I (1993) Chemistry of through flow water above clayey sodic B horizon:Implications to catchment mgt. *Aust. J. Exp.Agric.* **33,** 239-244

Naidu R., Syers, J.K., Tillman, R.W and Kirkman, J.H. (1990a) Effect of liming on phosphate sorption by acid soils. *Journal of Soil Science* **41,** 165-175.

Naidu R., Syers J.K., Tillman, R.W and Kirkman, J.H. (1990b) Effect of liming and added phosphate on charge characteristics of acid soils. *Journal of Soil Science* **41,** 157-164.

NATO Advanced Study Institute on Sludge Characteristics and Behavior. (1983) Sludge characteristics and behavior. eds, Carberry J.B. and Andrew J. Distributors for the U.S. and Canada, Kluwer Boston.

Neal R.H., and Sposito G. (1986). Effects if soluble organic matter and sewage sludge amendments on cadmium sorption by soils at low cadmium concentrations. *Soil Sci.* **142,** 164-170.

Nederlof M.M. and Riemsdijk W.H.V. (1995) Effect of Natural Organic Matter and pH on the Bioavailability of Metal Ions in Soils. *In* Environmental impact of soil component interactions, eds. Huang P.M, Berthelin J.,Bollag J.M., McGill W.B.and Page A.L., Vol. Il, pp. 75-84,Lewis Publishers, Florida.

Nelson P.O., Chung A.K. and Hudson M.C (1981) Factors affecting the fate of heavy metals in the activated sludge process. *Process Research* **53**(8),1323-1333.

Neufeld R.D. and Hermann E.R. (1975) Heavy metal removal by acclimated activated sludge. *J. Wat. Pollut. Con. Fed.* **47**(2), 310.

New Zealand Department of Health (1992) Public health guidelines for the safe use of sewage effluent and sewage sludge on land. Department of Health Wellington.

New Zealand Soil Bureau (1968) Soils of New Zealand, Part 3. *Soil Bureau Bulletin* **26**(3).

New Zealand Year Book. (1984) New Zealand Official Yearbook 1984, 89th Annual Edition. Department of Statistics, Wellington.

NSWEPA (1994) Interim Code of Practice for Use and Disposal of Biosolid Products. Draft-June. New South Wales Environment Protection Authority, Sydney, NSW, Australia.

NZWWAA (2002) New Zealand Water and Wastes Association Auckland: Guidelines for the Safe Application of Biosolids to Land in New Zealand.2002.

Overcash M.R., Gilliam J.W., Humenik F.J., Westerman P.W. (1978) Lagoon pretreament: Heavy metal and cation removals. *Journal of the Water Pollution Control Federation* **50,** 2029-2036.

Page A.L et al. (1982) Methods of soil analysis, Part 2, Chemical and microbiological properties 2nd edition, American society of America, Madison, WI.

Pardo M.T., Guadalix M.E. (1996) Zinc Sorption- desorption by two Andepts: effects of pH and support medium. *European Journal of Soil Science* **47,** 257-263.

Parfitt R.L. (1990) Allophane in New Zealand-a review. *Austr. J.Soil Res.* **28,** 343-360.

Peters J.M. and Basta N.T. (1996). Reduction of excessive bioavailable phosphorus in soils by using municipal and industrial wastes. *J. Environ. Qual.* **25,** 1236-1241.

Pinghe Y., Qiming Y., Bo J. and Zhao L. (1999). Biosorption removal of cadmium from aqueous solution by using pretreated fungal biomass cultures from starch wastewater. *Wat. Res.* **33**(8), 1960-1963.

Pinskii D.L. (1998) The problem of the mechanisms of ion exchange adsorption of heavy metals in soils. *Eurasian Soil science* **31**(11), 1223-1230.

Presant E.W. and Tupper W.M.(1965) Trace Elements in some New Bounswick soils. *Can. J. Soil. Sci.* **45,** 305 - 318

Pulford I.D. (1986) Mechanism controlling zinc solubility in soils. *Journal of Soil Science* **37,** 427-438.

Puranik P. R. and Paknikar K.M. (1999) Biosorption of lead, cadmium and Zinc by Citrobacter strain MCM B-181: Characterization studies. *Biotechnol. Prog.* **15,** 228-237.

Purves D. (1981) National standards for metal additions to soil in sewage sludge, Heavy Metals in the Environment. CEP Consultants, Amsterdam 176-180.

Rao M.R.A. (1935) *J. Indian Chem. Soc.,* **12,** 371.

Ray H.C., Karl O., Dwight S., James M. and Darryl R. (1988) Interactions of metals and Protons with Algae. *Environ. Sci. Technol.* **22,** 755-760.

Reimers R.S. (1983) Interaction with heavy metals. In Sludge characteristics and behaviour. Eds. J.B. Carbery and A.J. Englande.Jr. NATO A.S.I. Series,46.

Robson A.D. (1993) Zinc in Soils and Plants. Kluwer academic publishers, U.S.A.

Ronald J.G. and Angelidis. M. (1988) Metal chemistry differences between digested and undigested sludges. *J.Wat.Pollut.Con.Fed.* **60,** 113-118.

Roscoe Ellis, Davis J.J.F. and Thurlow D.L. (1964). Zinc availability in calcareous soils as influenced by Phosphorus level and temperature. Soil Science Society proceedings pp. 83-86.

Ross A.D., Lawrie R.A., Whatmuff M.S., Keneally J.P. and Awad A. S. (1992) *Guidelines for the Use of Sewage Sludge on Agricultural Lands.* New South Wales Department of Agriculture and Fisheries, Sydney, Australia.

Ross S.M. (1994) Toxic metals in Soil-Plant Systems. John Wiley & Sons, England.

Roy W.R., Krapac T.G. and Steele J.D (1993) Sorption of cadmium and lead by clays from municipal incinerator ash- water suspensions. *J. Environ. Qual.* **22,** 537-543.

Rudd T., Sterritt R.M. and Lester J.N. (1984) Complexation of heavy metals by extracellular polymers in the activated sludge process. *Process Research* **56**(12), 1260-1268.

Rudd T., Sterritt R.M. and Lester J.N. (1984) Formation and conditional stability constants of complexes formed between heavy metals and Bacterial extracellular polymers. *Wat. Res.* **18**(3), 379-384.

Rudd T., Sterritt R.M. and Lester J.N. (1983) Stability constants and complexation capacities of complexes formed between heavy metals and Extracellular polymers from activated sludge. *J. Chem.Tech. Biotech.* **33A,** 374-380.

Sabbah I. and Rebhun M. (1997) Adsorption desorption of trichlorophenol in water soil system. *Water Environment Research* **69**(5), 1032-1037.

SAEPA. (1996) South Australian Biosolids Guidelines for the Safe Handling Reuse and Disposal of Biosolids. South Australian Environmental Protection Agency, Department of Environment and Natural Resources, Adelaide, South Australia.

Samuel J. Traina and Valerie Laperche (1999) Contaminant bioavailability in soils, sediments and aquatic environments. *Proc. Natl. Acad. Sci.* **96,** 3365-3371.

Samuel R.F. and Gabriel B. (1984) enteric Bacteria in Aerobically digested sludge. *Applied and Env. Microbiology* **47**(4), 831-834.

Saunders, W.M.H. (1964). Phosphate retention by New Zealand soils and its relation ship to free sesquioxides, organic matter, and other soil properties. N.Z. J. agric. Res. **8,** 30-57.

Sauve (1997) Mobility and Solubility of Toxic Metals and Nutrients in soil fifteen years after sludge application. *Soil Sci.* **162** (7), 487-499.

Schalscha E.B., Ahumada I. and Pratt P.F. (1981) Effects of time and leaching on phosphate-induced increase in cation exchangeable capacity in volcanic ash soils. *Soil Sci. Soc. Am. J.* **45,** 1237-1238.

Schalscha E.B., Escudero P., Salgado P., and Ahumada I. (1999) Chemical Forms and Sorption of Copper and Zinc in Soils of Central Chile. *Commun. Soil Sci. Plant Anal.* **30**(3&4), 497-507.

Schnitzer M. (1978) Humic substances: Chemistry and reactions. *In* Soil Organic Matter, pp. 1-64. eds. M. Schnitzer and S. U. Khan, Elsevier Publication, New York.

Scott J.A., Sage G.K., Palmer S.J., and Powell D.S. (1986) Cadmium adsorption by bacterial capsular polysaccharides coatings. *Biotech. letters* **8** (10), 711-714.

Sherrard J. H. (1983) The effects of nickel on organic removal and nitrification in the completely mixed activated sludge process In Heavy metals in the environment. Proc. Int. Conf., Heidelberg, Ger., **1,** 385.

Shuman L.M. (1986) Effect of ionic strength an anions on zinc adsorption by two soils. *Soil Sci. Soc. Am. J.* **50,** 1438-1442.

Shuman L.M. (1985) Fractionation method for soil microelements. Soil Science **140,** 11-22.

Shuman L.M. (1983) Sodium hypochlorite methods for extracting micronutrients and their distribution among fractions. *Soil Sci. Soc. Am. J.* **47,** 656-660.

Shuman L.M. (1976) Zinc adsorption isotherms for soil clays with and without iron oxides removed. *Soil Sci. Soc. Am. J.* **40,** 349-352.

Sidle R.C., and Kardos L.T. (1977a) Adsorption of copper, Zinc and Cadmium by a forest soil. J.Environ.Qual. **6**(3), 313-317.

Sidle R.C. and Kardos L.T. (1977b) Transport of Heavy Metals in a Sludge Treated Forested Area. *J. Env. Qual.*, **6**(4), 431-437.

Sidle R.C., Kardos L.T., and Van Genuchten M.Th. (1977) Heavy Metal Transport Model in a Sludge treated Soil. *J. Environ. Qual.* **6**(4), 438-442.

Sidle R.C., Hook J.E., and Kardos L.T. (1976) Heavy Metal Application and Plant Uptake in a Land Disposal System for wastewater. *J. Environ. Qual.* **5**(1), 97-101.

Smiley D.W. and WilkinsonB.J. (1983) Survey of Taurinne Uptake and Metabolism in *Stephylococcus aureus. J. Gen. Microbiol,* pp. 129-2421.

Smith D. G. (1995) Cleaning up industrial sites *Waste Manage. Env.* **6**, 16-24.

Smith D.G. (1986) Heavy Metals in the New Zealand aquatic environment: a review, pp 6-12. Ministry of Works and Development, New Zealand.

Smith D.G. (1985) Sources of heavy metal input to the New Zealand aquatic environment. *J. Royal Society of New Zealand* **15**(4), 371-384.

Sommers L.E., Nelson D.W., and Silviera D.J. (1979) Transformations of Carbon, Nitrogen, and Metals in Soils Treated with Waste Materials. *J.Environ.Qual.* **8**(3), 287-293.

Sommers L.E. (1977) Chemical Composition of Sewage Sludges and Analysis of Their Potential Use as Fertilizers *J. Environ . Qual.* **6**(2), 225-231.

Sommers L.E., Tabatabai M.A. and Nelson D.W. (1977) Forms of sulphur in sewage sludge. *J. Environ. Qual.* **6,** 42-46.

Sommers L.E., Nelson D.W. and Yost K.J. (1976) Variable Nature of Chemical Composition of Sewage Sludges. *J. Environ. Qual.* **5,** 303-306.

Sparks D.L. (1995) Environmental Soil Chemistry, Academic Press, London.

Sparrow L.A., Salardini A.A., and Johnsone J. (1994) Field studies of cadmium in potatoes III Response of cv. Russet Burbank to sources of banded potassium. *Aust. J. Agric. Res.* **45,** 243-249.

Sparrow L.A., Salardini A.A., Bishop A.C. (1993) Field studies of cadmium in potatoes I. Effects of Lime and phosphorus on cv. Russet Burbank. *Aust. J. Agric Res.* **44**, 243-249.

Sposito G. (1989) The chemistry of Soils. Oxford University Press, New York. pp. 154-169.

Sposito G. (1984) The surface Chemistry of Soils. Oxford University Press, New York. pp. 125-130.

Sposito G., Lund E.L and. Chang A.C. (1982). Trace Metal Chemistry in Arid-zone Field Soils Amended with Sewage Sludge: l. Fractionation of Ni, Cu, Zn, Cd and Pb in Solid Phases. *Soil Sci. Soc. Am. J.* **46,** 260-264.

Sreekrishnan T.R. and Tyagi R.D. (1996) A comparative study of the cost of leaching out heavy metals from sewage sludges. *Process Biochem.* **31.** 31-41

Steenhuis T.S., Parlange J.-Y. and Aburime S.A.(1995) Preferential flow in structured and sandy soils: Consequences for modeling and monitoring. In Handbook of vadose zone characterization and monitoring. pp. 61-77. eds. L. Everett., S. Cullen and L. Wilson. Lewis Publishers, Chelsea, MI.

Stephenson T. and Lester J.N (1987) Heavymetal removal during the activated sludge process- I : Extent of soluble and insoluble metal removal mechanisms. *Sci.Total Envir.* **63,** 199-214.

Sterritt R.M. and Lester J.N. (1981) The influence of sludge age on heavy metal removal in the activated sludge process. *Wat. Res.* **15,** 59-65.

Stevenson F.J. and Ardakani M. S. (1972) Organic matter reactions involving micronutrients in soils. *In* Micronutrients in agriculture, eds. J. J. Mortvedt, P.

M. Giordano, and W. L. Lindsay. Soil Sci. Soc. Am., Madison, Wis., pp. 79-114.

Stover R.C., Sommers L.E. and Silviera D.J. (1976) Evaluation of metal in wastewater sludge. *J. Water Pollut. Control Fed.* **48,** 2165-2175.

Streck I.J., Utermann J. and Richter J. (2000) Ground water preservation by soil protection: Determination of tolerable total cadmium content and Cd breakthrough times. *Journal of Plant Nutrition & Soil Science.* **163** (1), 31-40.

Suryaningtyas D.T. (1998) Characteristics of Volcanic ash soils of southern area of mount Ruapehu, North Island, New Zealand. Ph D. thesis, Massey University, Palmerston North. New Zealand.

Sutherland I.W. (1997) Bacterial Exopolysaccharides-Their Nature and Production. *In* Surface Carbohydrates of the Procaryotic Cell, eds. I. W. Sutherland, Academic Press, London.

Sutherland I.W. (1980) Polysaccharides in the Adhesion of Marine and Fresh Water Bacteria. *In* Microbial Adhesion to Surfaces, eds. R. C. W. Berkeley et al., Ellis Horwood, Chichester.

Suzuki, and Hiroo Otsuka (1999) Properties of soil humic substances in fractions obtained by sequential extraction with Pyrophosphate solutions at different pHs. *Soil Sci. Plant Nutr.* **45**(2), 349-358.

Swift R.S., McLaren R.G. (1991) Micronutrient adsorption by soil and soil colloids. *In* Interactions at the soil colloid-soil solution interface. eds. G. H. Bolt et al., Kluwer Academic Publishers, Netherlands, pp. 257- 292.

Talkett S.L., Winters E.R., and Puz M. (1986) Leaching of metals from sewage sludge: pH effects. *Can. J. Soil. Sci.* **66**, 763-765.

Tam N.F.Y. and Wong Y.S. (1996). Retention and Distribution of Heavy Metals in Mangrove Soils Receiving Wastewater. *Environ. Pollution,* **94**(3), 283-291.

Tan K.H. (2000) Environmental Soil Science, Marcel Dekker, Inc. New York.

Taylor R.W., Xiu H., Mehadi A.A., Shuford J.W. and Tadesse W. (1995) Fractionation of residual cadmium, copper, nickel, lead, and zinc in previously sludge-amended soil. *Commun. Soil Sci. Plant Anal.* **26**(13&14), 2193-2204.

Tester C.F. (1990) Organic amendment effects on physical and chemical properties of a sandy soil. *Soil Sci. Soc. Am. J.* **54,** 827-831.

Tiller, K.G., McLaughlin, M.J., and Roberts, A.H.C. (1997). Environmental impacts of heavy metals in Agro ecosystems and amelioration strategies in Oceania. *In* Soil and Ground water pollution and remediation, pp 1-35.

Tiller, K.G. (1991) Determining Background Levels, in The Health Risk Assessment and Management of Contaminated Sites, Saadi, O.E and Langley A., Eds., South Australian Health Commission, Adelaide, South Australia.

Tiller, K.G. (1989). Heavy metals in soils and their environmental significance. *In* Advances in Soil Science .eds. B. A. Stewart, Vol. 9, Springer-Verlag, New York, pp. 113-141.

Tiller K.G. (1988) Heavy metals in soils and their environmental significance. *Advances in Soil Science* **9,** 113-142.

Tien C.T. and Huang C.P. (1987) Adsorption of Cu (II) onto sludge particulate surfaces. *J. Environ. Eng.*, **113,** 285.

Tiller K.G., Gerth, J. and Brummer G.(1984) The relative affinities of Cd, Ni and Zn for interactions at the soil colloid-soil solution surface different soil clay fractions and goethite. Geoderma **34**, 17-35.

Tsadilas C.D., Matsi Theodora., Barbayiannis N., and Dimoyiannis. (1995) Influence of sewage sludge application on soil properties and on the distribution and availability of heavy metal fraction. *Commun. Soil Sci. Plant Anal.* **26**(15&16), 2603-2619.

Tyler L.D. and McBride M.B. (1982) Mobility and extractability of cadmium, copper, nickel and zinc in organic and mineral soil columns. *Soil sci.* **134,** 198-205.

USEPA (1979) Process designing manual for sludge treatment and disposal. Municipal Environmental Research Laboratory.

USEPA (1983) Process design Manual for Land Application of Municipal Sludge. Centre Environmental Research Information. Cincinnati, OH.

USEPA (1993) Part 503-Standards for the use and disposal of sewage sludge. *Federal Register* **58,** 9387-9404.

Van der Watt H., Sumner M.E. and Carbera M.L. (1994) Bioavailability of copper, manganese and zinc in poultry litter. *J.Environ.Qual.* **23,** 43-49.

Veglio F., Beolchini F. and Gasbarro A. (1997) Biosorption of toxic metals: An equilibrium study using free cells of Arthrobacter sp. *Process Biochem.* **32**(2), 99-105.

Verloo M. (1974) Cited in L. Kiekens (1983) Behaviour of heavy metals in soils. *In* Commission of the European Communities: Utilization of Sewage Sludge on Land: Rates of application a long term effects of metals. Oroc. of Seminar held at Uppsala, June 7-9. 1983. D. Reidal Publishing Co., Boston.

Vernet J.P. (1991) Heavy metals in the environment: Trace metals in the environment 1. Elsevier science publishing company, New York.

Volesky B. and Holan Z.R. (1995) Biosorption of Heavy Metals. *Biotechnol prog.***11**, 235-250.

Volesky B. (1990) Biosorption of Heavy Metals. CRC Press.

Wada K. (1989) Allophane and imogolite, *In* Minerals in soil environments, p. 1051-1088. eds. J.B. Dixson and S.B. Weed, SSSA, Madison,WI.

Wang J., Huang C. P., Allen H. E., Poesponegoro I., Poessponegoro H., and Takiyama L.R (1996) Effects of dissolved organic matter and pH on heavy metal uptake by sludge particles: Three variable model Proc. Water Environ. Fed. 69th Annu. Conf. Expo. Dallas, Tex.,1, 271.

Warren J. (1994) Heavy metal dynamics in soils. Ph.D thesis Lincoln University, Christchurch, New Zealand.

Webber J. (1985) Effects of toxic metals in sewage on crops. Wat. Pollut. Control. 404.

Wesley E., and Santhanam C. (1981) Sludge Treatment. M. Dekker, New York.

Williams C.H and David D.J. (1973) The effect of superphosphate on the cadmium content of soils and plants. *Aust.J.soil Res.***11,** 43-56.

Williams D. E., Vlamis, J., Pukite, A. H., and Corey J. E. (1987) Metal movement in sludge amended soils: A nine year study. *Soil Sci.* **143,** 124-131.

Williams D. E., Vlamis, J., Pukite, A.H., and Corey J. E. (1980) Trace element accumulation, movement and distribution in the soil profile from massive applications of sewage sludge. *Soil Sci.* **129,** 119-131.

Wolt J. (1994) Soil Solution chemistry: application to environmental science and agriculture, John Wiley & sons, New York.

Wong P.K., Lam K.C. and So C. (1993) Removal and recovery of Cu (11) from industrial effluent by immobilized cells of Pseudoomonas putida II-11. *Appl. Microbiol. Biotechnol.* **39,**127-131.

Wong L. and Henry T.G. (1988) Bacterial laeching of heavy metals from anaerobically digested sludge. In Biotreatment Systems.eds. Wise D.L, CRC Press, pp.125-169.

Zachara J.M., Smith S.C., Resch C.T. and Cowan C.E. (1992) Cadmium sorption to soil separates containing layer silicates and iron and aluminium oxides. *Soil Science Society of America Journal* **56,** 1074-84

Zalidis G. Barbayiarinis N. Matsi T. (1999) Forms and distribution of heavy metals in soils of the axios delta of northern Greece. *Communications in Soil Science & Plant Analysis* **30** (5-6), 817-827.

Zanders J. (1998) Studies on the origin, distribution and mobility of cadmium in pastoral soils. Ph.D thesis, Massey University, Palmerston North, New Zealand.

Zhang M., Alva A.K., Li C., and Calvert, D.V. (1997) Chemical Association of Cu, Zn, Mn, and Pb in selected sandy citrus soils. *Soil Science* **162**(3), 181-188.

Zirino A. and Yamamoto S. (1972) A pH dependent model for the chemical speciation of copper, Zinc, Cadmium and Lead in seawater. *Limnology and Oceanography* **17** (5), 661-671.

Zouboulis A., Elen G Rousou, Kostas A Matis and Ian Hancock. (1999) Removal of toxic metals from aqueous mixtures Part1: Biosorption. *Journal of Chem. Technol. Biotechnol.* **74,** 429-436.

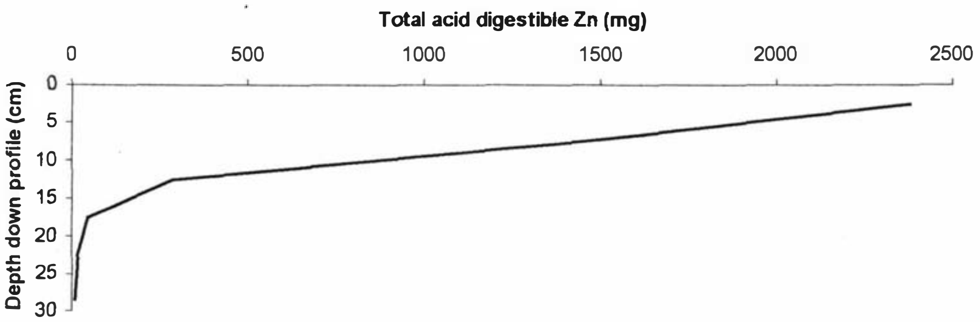
APPENDICES

Appendix-1. Soil weights (oven dry basis) of each desected section of soil column depths

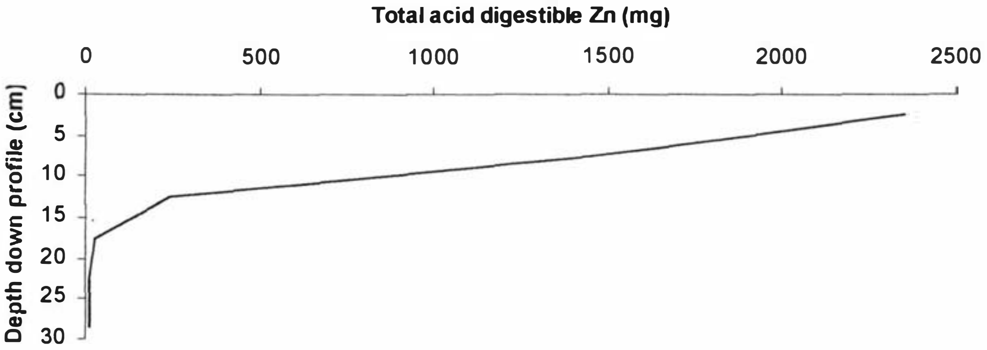
Sewage sludge applied columns			
Soil Depth	No ion treated column	Nitrate treated column	Phosphate treatedcolumn
cm	mg	mg	mg
0—5	285.2	267.6	271.4
5-10	397.6	412.4	408.2
10-15	396.0	402.0	394.5
15-20	425.9	425.7	416.8
20-25	381.3	393.2	347.4
25-32	542.9	560.2	553.9

Inorganic zinc applied columns			
Soil Depth	No ion treated column	Nitrate treated column	Phosphate treatedcolumn
cm	mg	mg	mg
0—5	161.3	153.4	150.7
5-10	369.0	372.3	353.6
10-15	353.0	361.4	352.3
15-20	404.0	387.5	379.5
20-25	370.4	364.5	352.8
25-32	560.0	557.4	544.3

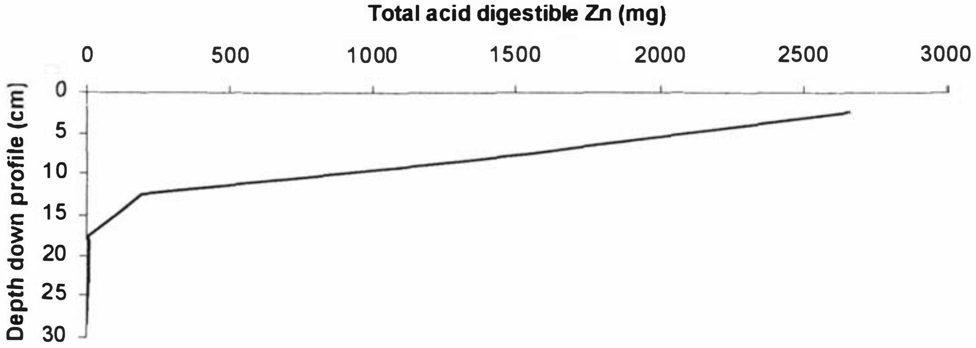
Appendix-2. Distribution of total acid digestible Zn in no anion treated sewage sludge applied soil column



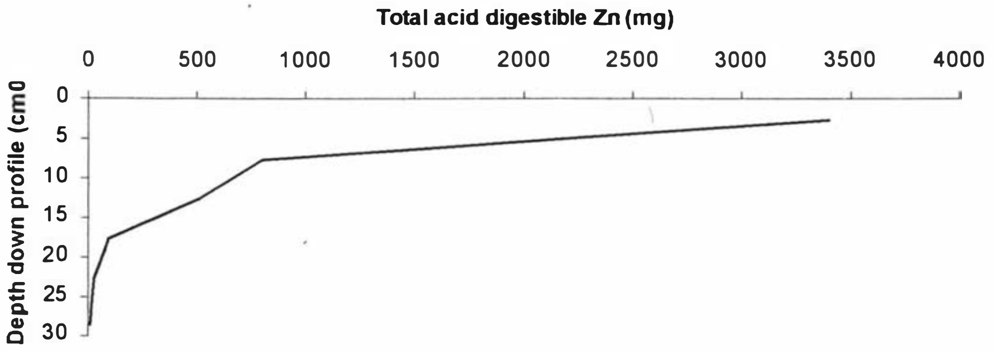
Appendix-3. Distribution of total acid digestible Zn in nitrate treated sewage sludge applied soil column



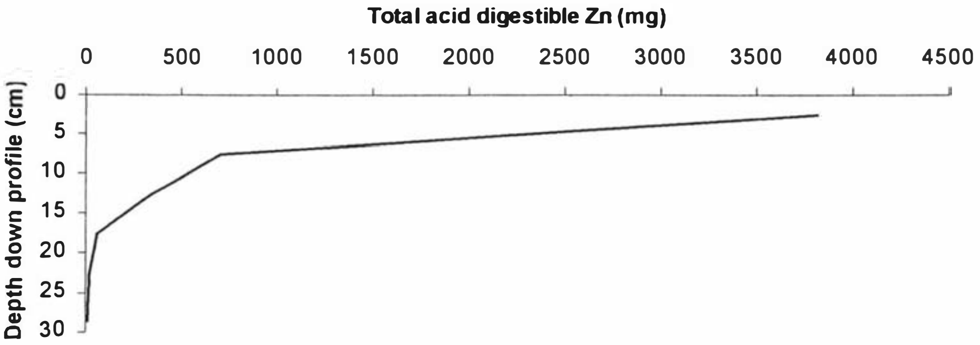
Appendix-4. Distribution of total acid digestible Zn in phosphate treated sewage sludge applied soil column



Appendix-5. Distribution of total acid digestible Zn in no anion treated inorganic zinc applied soil column



Appendix-6. Distribution of total acid digestible Zn in nitrate treated inorganic zinc applied soil column



Appendix-7. Distribution of total acid digestible Zn in phosphate treated inorganic zinc applied soil column