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ADSORPTION OF ZINC AND CADMIUM  
BY SOILS AND SYNTHETIC  
HYDROUS METAL OXIDES

A thesis presented in partial fulfilment  
of the requirements for the degree of  
DOCTOR OF PHILOSOPHY  
in Soil Science  
at Massey University

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## ABSTRACT

This study involved an investigation into the adsorption of Zn and Cd by soils and synthetic hydrous metal oxides, and the effect of several factors on the adsorption reactions in controlled laboratory experiments.

Initially, in order to determine low concentrations of Zn and Cd in solution, a concentration procedure involving solvent extraction was developed. The procedure utilised a chelating agent, dithizone, and an organic solvent, carbon tetrachloride. Zinc and Cd were back-extracted from the organic solvent into hydrochloric acid to achieve a ten-fold increase in concentration.

For soils and Fe gel, adsorption of both Zn and Cd was characterised by an initial, rapid removal from solution which was followed by a much slower, continuing decrease in solution concentration.

Isotherms (40 hr) for Zn and Cd adsorption from  $3 \times 10^{-2}$  M NaCl by soils, synthetic hydrous ferric oxide (Fe gel) and allophane, were described using two Langmuir equations. Values for the derived free energies of adsorption, for each region of adsorption, were similar for both Zn and Cd on all soils and on Fe gel. Allophane, however, had higher free energies of adsorption than either the soils or Fe gel. For all adsorbents, Langmuir constants derived from adsorption data indicated that the adsorbing surface contained a relatively small number of sites with a high free energy of adsorption and a much larger number of sites with a lower adsorption energy. Iron gel appeared to provide a satisfactory model for describing Zn and Cd adsorption by soils.

Amounts of Zn and Cd adsorbed by Fe gel increased as pH increased. Adsorption of Zn and Cd by Fe gel in each Langmuir region appeared to be

affected similarly by changes in pH, although the  $\text{pH}_{50}$  values (the pH at which 50% of the initial amount added was adsorbed) were higher for Cd than for Zn.

Experimental data obtained in the study are consistent with a two-mechanism model for both Zn and Cd adsorption. It is proposed that the first mechanism involves the formation of a bidentate complex. Adsorption of Zn and Cd into this region involves the release of two protons for each Zn or Cd ion adsorbed, resulting in a bond of higher energy than when Zn or Cd is adsorbed by the second mechanism. In this latter case, it is proposed that a monodentate complex is formed with one proton released for each cation adsorbed.

In addition to proton release, data in support of the two-mechanism system was obtained in isotopic exchangeability and desorption studies. For example, the mole ratios (i.e., number of protons released for every Zn or Cd ion adsorbed) for Zn and Cd were non-integer values. For Zn the mole ratios ranged between 1.31 and 1.67, and for Cd from 0.80 to 1.12, at pH 6.4. There was no obvious trend in mole ratios for Zn either with increasing amounts of Zn adsorbed or increasing pH, but for Cd mole ratios increased with increasing amounts of Cd adsorbed or increasing pH. The isotopic exchangeability of Zn was similar at all levels of Zn adsorbed, but decreased with increasing pH (pH 5.85 - 6.65) from 58% exchangeability to 27%, possibly due to an increased proportion of more-tightly bound Zn. Cadmium, by contrast, had a lower exchangeability at low levels of Cd adsorbed (55 - 76%) than at higher levels (80 - 85%) but was more exchangeable (55 - 85%) than Zn at equivalent pH values and lower surface coverages, indicating that a greater proportion of adsorbed Cd was less tightly bound compared to Zn. Sequential desorption of Zn by calcium ions followed by copper ions showed that a

proportion of Zn (12 - 24%) was retained by the surfaces against desorption, further indicating the presence of two adsorption mechanisms of different binding strength. Only at low levels of adsorbed Zn did the amount of desorbed Zn closely approximate the amounts of Zn calculated (from Langmuir constants) to be in region II. These desorption data, together with the exchangeability data for Zn, point to the possible limitations in the use of Langmuir equations for quantifying the amount of Zn adsorbed by each mechanism.

The Langmuir isotherm studies, together with proton release, exchangeability and desorption data, indicated two mechanisms of adsorption for Zn and for Cd. However, the greater exchangeability and fewer protons released per mole adsorbed suggest that more Cd is held by the mechanism involving monodentate bonding than is the case for Zn.

Zinc or Cd was not observed to be absorbed or "occluded" by synthetic ferric oxide gel or goethite. There was evidence to suggest that Zn and Cd might diffuse into cracks or defects in the crystal structure of natural goethite, developed by grinding. Although some fraction of adsorbed Zn or Cd was non-exchangeable and non-desorbable (by copper) for all three adsorbents, this Zn and Cd was not in the absorbed phase.

Long term (up to thirty year) additions of superphosphate fertiliser to three soils did not produce measurable accumulations of Zn or Cd in the soils. The calculated additions agreed well with actual increases measured in total Zn, but not with actual increases in total Cd.

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## INTRODUCTION

The New Zealand economy is dependent on agricultural and horticultural industries and thus any factor causing either an increase or a decrease in primary production is of great importance to the country.

Obviously, many factors affect the level of production obtained from plants and animals, not all of which are able to be manipulated. Nutrient limitations to production, however, can and should be removed wherever practicable. In addition to the macronutrient elements (N, P, K, S) which form the basis for most of the fertilisers used on New Zealand soils, the importance of some micronutrients in New Zealand agriculture is well recognised. For example, major problems associated with Co, Se, Cu, I and Mo have been identified in the past, and appropriate measures used to alleviate them.

In addition to outright deficiencies, concern is often expressed that certain other elements may be present in sub-optimum amounts in the diet, resulting in impaired health or performance of the animal. One such element is Zn. Grace (1972) reported low plasma Zn levels in sheep in many districts in New Zealand. The significance of these low plasma values is not yet clear, but is at least circumstantial evidence of sub-optimum dietary Zn intakes in many situations. According to During (1972), however, Zn deficiency in pasture plants is virtually unknown in this country.

Possible reasons for the previous low incidence of Zn deficiency are either that few New Zealand soils are naturally low in available Zn

content or that the widespread use of superphosphate, which contains appreciable amounts of Zn, prevents or even cures incipient deficiencies (During, 1972). Neither of these possibilities has been intensively studied to date and it is not possible to determine which is the most likely explanation.

The ever-increasing costs of fertilisers and accompanying changes in strategy of fertiliser use may well result in a decrease in annual inputs of superphosphate fertiliser on many New Zealand soils and a further reduction in the Zn status of soils, plants and animals. Hence, it may be necessary to consider the introduction of Zn fertilisers in the near future.

Whereas the contamination of fertilisers with Zn is regarded as fortuitous, the situation can be quite different for other metals. For example, the Cd content of superphosphate is regarded as a potential hazard when the fertiliser is used on crops grown for human consumption (Schroeder and Balassa, 1963).

Interest in Cd has increased in recent years due to reports of both its toxicity to animals and man at high concentrations, and health problems associated with its progressive accumulation in biological systems at the lower levels at which it occurs as an environmental contaminant. Zinc and Cd have many properties in common and in fact prove difficult to separate (Lagerwerff, 1972). Although native soil levels of Cd are generally low (Swaine, 1955), they can increase as a result of superphosphate fertiliser use (Schroeder and Balassa, 1963; Williams and David, 1973) or from the addition of industrial or municipal wastes to soil (Beavington, 1973; Fleischer et al., 1974; Bradford et al., 1975; Hinesly et al., 1977).

The suggestion has been made that the undesirable accumulation of

Cd in the food chain could in fact be limited by the competitive antagonism that exists between Cd and Zn. Thus it may be possible to control Cd entry into plants and animals by manipulating the Zn status of the soil.

Because of the similar chemistries of Zn and Cd (Cotton and Wilkinson, 1966) it is generally believed that they react similarly in soils and are bound by identical mechanisms to the same components.

There is virtually no information on the reactions and fate of Zn and Cd in New Zealand soils. Such information is needed to provide an adequate understanding of both the agricultural and the environmental requirements concerning these elements. However, as the soil is a very complex mixture of constituents, simpler synthetic hydrous metal oxides are sometimes used as model surfaces (James and Healy, 1972; Bowden et al., 1973; Bar-Yosef et al., 1975; Kalbasi et al., 1978) to provide an understanding of the important soil reactions of these two elements and factors controlling their concentration in the soil solution.

The following study, then, involved an investigation of the adsorption of Zn and Cd by some New Zealand soils and the use of synthetic hydrous metal oxides to help elucidate the reaction mechanisms.

## CHAPTER ONE

## LITERATURE REVIEW

### Importance of Zn and Cd, Origin of Zn and Cd in Soils, and Adsorption of Zn and Cd by Soils and Soil Components

#### 1.1 Zn and Cd in Living Organisms

The essentiality of Zn for plants and animals was first suggested by Raulin (1869), on the basis of studies with the fungus Aspergillus niger. However, it was not until 1940 that a specific biological function was found for Zn. Keilin and Mann (1940) found subcellular fractions of red blood corpuscles which contained high Zn content and high carbonic anhydrase activity. The carbonic anhydrase enzyme is involved in acid-base homeostasis of most living organisms because the enzyme catalyses the reversible dehydration of carbonic acid, which is critical to the transport and removal of carbon dioxide in organisms (Parisi and Vallee, 1969). Carboxy-peptidase A extracted from bovine pancreas was the next Zn-containing enzyme to be found (Vallee and Neurath, 1954). Other Zn metalloenzymes were discovered including carboxy-peptidase B, dehydrogenases, alkaline phosphatases, aldolases, peptidases and phospholipase C (Vallee, 1959; Vallee and Wacker, 1970; Vallee, 1976). The presence of Zn in organisms containing these enzymes is thus essential for nucleic acid metabolism, protein synthesis and carbohydrate metabolism.

Both plants and animals have many enzymes in common, such as carbonic anhydrase, various dehydrogenases and aldolase (Lindsay, 1972)

and thus require Zn as an essential element. In plants, there is some evidence of Zn being required for auxin formation (Thorne, 1957; Price et al., 1972).

Although much has been reported about the biochemistry of Zn and its role with enzymes, it is not known whether Zn has other important functions or what specific enzymatic impairment or biochemical derangement causes the pathological changes exhibited by Zn-deficient organisms (Vallee, 1959).

Although Zn is required for many enzymes, no known enzyme requires Cd (Schroeder and Balassa, 1961) for activity. The effect of Cd on Zn-requiring enzymes is inhibitory, partly explaining the toxicity of Cd (Schroeder et al., 1967). The inhibition of Zn-requiring enzymes by Cd is due to the affinity of Cd for the same sites, on the enzymes, to which Zn is bound. However, Vallee (1971) has shown that Cd can be substituted, in vitro, for the native Zn atoms in several Zn metallo-enzymes, while the enzyme remains active. In some cases, then, Cd may proxy for Zn without deleterious effect. Cd can also act as an anti-metabolite for Zn (Cotzias et al., 1961), however.

#### 1.1.1 Zinc requirements of organisms

Zn deficiency symptoms are usually exhibited in most plant species at Zn levels lower than 300-400  $\mu\text{mol Zn l}^{-1}$  and toxic levels for plants are 6000  $\mu\text{mol Zn l}^{-1}$  and higher (Haan and Zwerman, 1976). Zn toxicity in animals occurs when the Zn content of the diet exceeds approximately 15,300  $\mu\text{mol Zn l}^{-1}$  (Haan and Zwerman, 1976), and although the daily requirement of Zn by humans has not been established, it has been calculated that 1.0 to 2.2 mg Zn/day are needed to maintain Zn balance (Schroeder et al., 1967), and most mixed diets supply 12-15 mg Zn/day to humans (Underwood, 1977).

### 1.1.2 Toxic effects of Cd

Since 1945 "Itai-Itai" disease, or osteomalacia, became prevalent in the Jintsu River Basin in Japan (Malin, 1971). One of the causal factors was shown to be exposure to Cd, arising from smelter wastes, of rice plants which concentrated the metal ions to levels in excess of the ambient environment (Fleischer et al., 1974).

However, of equal concern in recent times has been the recognition that Cd can be accumulated in mammalian organs. Cd in mammals has a long biological half-life and accumulates in tissues throughout the life of that mammal (Webb, 1975). The low tolerance of mammals to Cd may be due to the lack of a homeostatic control mechanism for Cd in the organism (Lagerwerff, 1971). Therefore, Cd is able to be absorbed irrespective of the Cd concentration already present in the organism (Cotzias et al., 1961).

Continued exposure to small amounts of Cd, rather than high, infrequent doses may ultimately present the greater health hazard to animals and humans, since Cd so accumulated is stored in the liver and kidneys as a metalloprotein known as cadmium-thionein, resulting in dysfunction and damage to these vital organs (Webb, 1975).

Chronic, low-level Cd exposure has also been implicated in other human diseases such as emphysema, gastric and intestinal dysfunctions, anaemia and hypertensive heart disease (Lagerwerff, 1972).

### 1.1.3 Plant uptake of Cd applied to soils through Superphosphate Fertiliser

Exposure to small, continuous amounts of Cd may result from the diet of an organism, and there is evidence to suggest that soils and fertilisers such as superphosphate could be potential sources of Cd to human foods (Schroeder and Balassa, 1963; Williams and David, 1973).

Schroeder and Balassa (1963) showed that superphosphate, when applied at heavy rates to leafy and root vegetable crops and cereals, was frequently a source of Cd for plant absorption. Schroeder et al. (1967) found that superphosphate increased Cd content in some species of grain, legumes, leafy and root vegetables, but in others there was no change, or even a decreased Cd content. John (1972) demonstrated that Cd concentrations in radish roots and tops increased progressively as more Cd was added to the soil. Plants grown on Cd-polluted soils have been shown to have higher Cd contents than those grown on uncontaminated soils of the same type (Lagerwerff, 1971). The effect of long-term superphosphate, sewage effluent and industrial pollutant additions to soil, on both the soil Zn and Cd levels and plant Zn and Cd levels will be discussed in a later section (Section 1.3).

#### 1.1.4 Soil-plant-animal relationships

Animals require Zn as an essential element (Lindsay, 1972) as an integral part of many enzymes, and while no known function exists for Cd in animals, long-term exposure to Cd intake can cause toxic levels of Cd to accumulate in body tissues (Webb, 1975).

All plants and all animals, including man, depend ultimately on the soil for their supply of mineral nutrients (Underwood, 1977). It has been shown that the major source of Zn and Cd intake for animals is dietary and in the case of grazing animals will be through consumption of herbage. If grazing animals are free to range over wide areas, then they can derive minerals from a variety of plant species on a number of soil types, thus minimizing any nutrient deficiency associated with any particular soil.

As plant materials provide the bulk of the grazing animal's feed intake the factors influencing trace-element content of plants are,

therefore, major determinants of dietary intakes of these elements. The Zn and Cd concentrations in most plant feedstuffs vary over a wide range, the actual concentration depending largely on; 1) trace-element composition in the soil upon which the herbage was grown (Scott, 1972), 2) the availability of the trace-elements for plant uptake, 3) the genus, species or strain of plant and 4) climatic and soil conditions during growth (Underwood, 1977).

Direct supplementation of the diet of animals and man is used as a convenient and effective method of controlling trace-element deficiencies (Underwood, 1977). However, indirect control methods, i.e., raising trace-element concentrations in plant materials, may also be used. Such methods include trace-element fertilisation of soils, selection of soil type and soil management practices directed towards increasing or decreasing the availability of soil trace-elements to plants (Allaway, 1968).

As soils are the primary source of Zn and Cd to plants and ultimately to animals, discussion of the origin and amounts of Zn and Cd in soils and the rock types from which they are derived is pertinent and this is detailed in Section 1.2.

## 1.2 Zinc and Cd in Rocks and Soils

Zinc is the twenty-fifth most abundant element in the lithosphere and the average Zn content of the lithosphere was earlier reported to be approximately  $0.62 \mu\text{mol Zn g}^{-1}$  (Clarke and Washington, 1924; Goldschmidt, 1958; Vallee, 1959) but this estimate has been amended more recently to a value of around  $0.87 \mu\text{mol Zn g}^{-1}$  (Wedepohl, 1972). The natural abundance of Cd in the upper lithosphere is very much less than that reported for Zn. It has been variously reported as  $0.0045 \mu\text{mol Cd g}^{-1}$

(Goldschmidt, 1958) and  $0.0016 \mu\text{mol Cd g}^{-1}$  (Swaine, 1955).

Such values are based on many assumptions about the types and distribution of rocks in the lithosphere.

### 1.2.1 Geochemistry, occurrence and content of Zn and Cd in rocks

Zinc and Cd are predominantly chalcophilic elements (Goldschmidt, 1958), i.e., they have a high affinity for S. Zn can, however, exhibit lithophilic tendencies (i.e., an affinity for O) by substituting for  $\text{Mg}^{2+}$  in a range of silicates (Goldschmidt, 1958; Krauskopf, 1972). Cadmium does not appear to demonstrate any lithophilic tendencies (Mason, 1966).

The most common Zn mineral occurring naturally is the sulphide, sphalerite. This is a cubic form of  $\text{ZnS}$  which also has a hexagonal polymorph, wurtzite, the stable form at temperatures above  $1000^{\circ}\text{C}$  (Goldschmidt, 1958). Other naturally occurring Zn minerals are listed in Table 1.1. The amounts of Zn contributed to soils by Zn minerals are likely to be minor since most naturally occurring Zn minerals are associated with ore bodies and are rarely found outside these localised natural concentrations.

The commonest Cd mineral is a hexagonal cadmium sulphide (greenockite,  $\text{CdS}$ ). Cadmium carbonate (octavite,  $\text{CdCO}_3$ ) and cadmium oxide (monteponite,  $\text{CdO}$ ) are much less common naturally occurring Cd minerals (Wedepohl, 1970).

Cadmium found naturally in primary sulphide ores usually occurs associated with the sulphides of other elements, e.g., in the Zn sulphides sphalerite and wurtzite the Cd content often reaches five per cent (Fleischer et al., 1974) and occurs as a replacement for Zn, by isomorphous substitution, rather than as a separate sulphide.

Table 1.1 Naturally occurring Zn-containing minerals  
(Wedepohl, 1972)

	Mineral	Formula	% Zn
Sulphides	Sphalerite	ZnS (cubic)	67
	Wurtzite	ZnS (hexag.)	67
Oxides	Zincite	ZnO	80
	Franklinite	(Zn, Mn)Fe <sub>2</sub> O <sub>4</sub>	22
Carbonates	Smithsonite	ZnCO <sub>3</sub>	52
	Hydrozincite	Zn <sub>5</sub> (OH) <sub>6</sub> CO <sub>3</sub> ·2	54
Sulphates	Zincosite	ZnSO <sub>4</sub>	41
	Poitevinite	(Cu, Fe, Zn)SO <sub>4</sub> ·H <sub>2</sub> O	22
Phosphates	Hopeite	Zn <sub>3</sub> PO <sub>4</sub> ·2.4H <sub>2</sub> O	43
	Phosphophyllite	(Zn, Fe) <sub>3</sub> PO <sub>4</sub> ·2.4H <sub>2</sub> O	32
Silicates	Willemite	Zn <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	59
	Troostite	(Zn, Mn) <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	39

However, as for Zn, all the Cd minerals occur very rarely in nature (Vlaslov, 1966) and as a result do not make a very important contribution to natural soil Cd content.

#### 1.2.1.1 Occurrence of Zn and Cd in primary rocks

The content of Zn in minerals found in igneous rocks depends, in the main, on the Zn content of the magma and the partitioning of Zn amongst the mineral phases during crystallisation (Wedepohl, 1972).

In general, Zn occurs mostly in ferromagnesium minerals such as pyroxenes, amphiboles, in micas and also in ilmenite and magnetite (Sandell and Goldich, 1943) as Zn substituted for  $Mg^{2+}$  and  $Fe^{2+}$  (Elgabaly, 1950). Zn rarely occurs in siliceous minerals such as quartz or feldspars (Lundegårdh, 1947) because these minerals do not allow ready substitution of Zn in their lattices, because little  $Mg^{2+}$  or  $Fe^{2+}$  occurs in these minerals.

It is not always possible to predict the distribution of many of the minor elements in sedimentary rocks because many factors determine the transportation and deposition of an element in sedimentary processes (Mason, 1966). Such factors include ionic potential, pH and redox potential of the medium, colloidal properties of the sediments and adsorption by components of the sediment. However, the behaviour of Zn during chemical weathering and the low solubility of Zn in natural waters leads to the accumulation of Zn, mainly in detrital matter, in the sedimentary environment. Common detrital minerals such as muscovite, quartz and feldspars are low in structural Zn, while chlorite and magnetite contain higher amounts of Zn in the lattices (Wedepohl, 1972). Appreciable amounts of Zn can become adsorbed onto colloidal Fe oxides and coatings of these on other minerals, in the sedimentary

phase (Wedepohl, 1972). Zinc may also occur in sedimentary rocks as discrete grains of sphalerite or, less commonly, as other Zn minerals. For example, in black shales Wedepohl (1953) showed that a third to a half the Zn is as sphalerite and as this weathers, Zn is released into solution and subsequently adsorbed by clay minerals. In general, clay-rich sedimentary rocks will contain higher Zn levels than clay-poor sedimentary rocks.

It has been postulated that insignificant amounts of Cd will be contained in sediments (Goldschmidt, 1958) and that Cd would probably be less concentrated than Zn in marine muds, clays and shales, because it is readily leached, under saturated conditions, from these materials (Goldschmidt, 1958). However, the adsorption of Cd by clay minerals may account for the presence of Cd in some sedimentary rocks (Goldschmidt, 1958).

Rocks undergo metamorphism as a result of pronounced changes in temperature, pressure and chemical environment (Mason, 1966). These changes induce recrystallisation and the redistribution of elements. During metamorphism and subsequent redistribution of Zn, there may be small losses of Zn. In general, however, metamorphic rocks are found to contain similar amounts of Zn as the rocks from which they are formed. Zn in metamorphic rocks occurs mainly, through isomorphous substitution for  $\text{Fe}^{2+}$  or  $\text{Mg}^{2+}$ , in silicates and oxides such as biotite, phengite, chlorite, amphibole, staurolite, garnet and magnetite. Sphalerite can also occur in minor localised concentrations (Wedepohl, 1972).

The behaviour of Cd in metamorphic processes is not well-understood.

#### 1.2.1.2 Content of Zn and Cd in primary rocks

The Zn and Cd contents of primary rocks are shown in Tables 1.2 and 1.3. The range of Zn contents in primary rocks from New Zealand are significantly lower than the world average values for ultrabasic (dunite, periodotite), and acidic (rhyolite, granite) rocks, greywackes and mica schists (Table 1.2). As the ensuing soils will show the same trends in element distribution evident in the parent rocks (modified by soil-forming processes (Wells, 1960)) many New Zealand soils will have lower natural Zn contents, than soils developed on similar primary rocks in other countries. Some of the more agriculturally important soils developed on primary rocks listed in Tables 1.2 and 1.3 include soils developed from andesitic and rhyolitic ashes in Taranaki and the Central North Island (New Zealand Soil Bureau, 1973), from basalts in North Auckland, Banks and Otago peninsulars (New Zealand Soil Bureau, 1973), from limestones and sandstones in North Auckland, Wanganui and Wairarapa districts (New Zealand Soil Bureau, 1973), from schists in Otago and, to a lesser extent Westland (New Zealand Soil Bureau, 1973) and from greywackes in North Auckland and Wellington districts, as well as large areas of the South Island (New Zealand Soil Bureau, 1973).

There are few reported analyses for the Cd content of primary rocks (Table 1.3). Available evidence suggests that Cd content ranges from  $8.8 \times 10^{-6} \mu\text{mol Cd g}^{-1}$  to  $1.4 \times 10^{-2} \mu\text{mol Cd g}^{-1}$  (Fleischer et al., 1974). Although no information is available on the Cd content of New Zealand primary rocks, it may be reasonable to assume that the Cd contents of New Zealand rocks will be less than, or at most, equal to the world average figures as for Zn.

Table 1.2 Zinc contents of primary rocks

Rock Type	Ave. Zn content ( $\mu\text{mol Zn g}^{-1}$ )		
	U.S.S.R.(1)	N.Z.(2)	World Ave.(3)
Igneous:			
ultrabasic (dunite, peridotite):	0.77	0.11-0.67	0.63-0.92
basic (basalt, gabbro) :	1.99	0.87-1.77	0.92-2.36
intermediate (andesite, diorite):	1.07	0.69-1.04	0.64-1.53
acidic (rhyolite, granite) :	0.92	0.54-0.89	0.35-1.62
Sedimentary:			
limestones :		0.08-0.32	0.09-0.47
sandstones :		0.41-0.78	0.38-0.77
greywackes :		0.51-1.01	1.07-3.00
shales :		1.24-1.97	0.70-3.01
Metamorphic:			
serpentinites :			0.51-1.12
amphibolites :			1.36-3.27
mica schists :		0.58-1.53	0.93-3.06
gneisses :		0.64-1.91	0.20-1.54

## References:

- (1) Vinogradov, 1959
- (2) Whitton and Wells, 1974
- (3) Wedepohl, 1972.

Table 1.3 Cadmium contents of primary rocks

Rock Type	Ave. Cd content ( $\mu\text{mol Cd g}^{-1}$ )		
	Sandell and Goldich (1943)	Fleischer et al. (1974)	World Ave. (Wedepohl, 1970)
Igneous:			
ultrabasic (dunite, peridotite):			$2.7 \times 10^{-5}$
basic (basalt, gabbro) :	$1.7 \times 10^{-3}$	$1.2 \times 10^{-3}$	$1.7 \times 10^{-3}$
intermediate (andesite, diorite):			
acidic (rhyolite, granite) :	$1.1 \times 10^{-3}$	$1.9 \times 10^{-3}$	$1.2 \times 10^{-3}$
Sedimentary:			
limestones :		$8.9 \times 10^{-4}$	$3.1 \times 10^{-4}$
sandstones :		$2.7 \times 10^{-4}$	
shales :		$1.3 \times 10^{-2}$	$7.1 \times 10^{-3}$
Metamorphic:			
garnet schist (Tasmania) :	$8.9 \times 10^{-3}$	(Smythe and Gatehouse, 1955)	
gneiss (Antartica) :	$1.3 \times 10^{-3}$	(Brooks et al., 1960)	

### 1.2.2 Zinc:Cd ratios in rocks

The ratio of Zn to Cd in crustal rocks is generally between 500:1 and 1000:1 (Vinogradov, 1959) with extremes of from 27:1 up to 7000:1 (Fleischer et al., 1974), reflecting the higher abundance of Zn in the lithosphere compared to Cd.

### 1.2.3 Weathering of parent materials

Primary minerals such as olivine, hypersthene, augite, hornblende, glass, mica, feldspar and quartz weather to form secondary minerals such as layer silicates or oxides. These secondary products include micaceous clay minerals, kaolins and amorphous, crystalline and hydrous oxides of Al, Fe and Si. Fieldes and Swindale (1954) postulated the following mechanisms:-

- (1) Primary minerals decompose completely to produce ions which can then reorganise to produce layer silicates, oxides or hydroxides depending on soil conditions.
- (2) Primary micas may, after partial alteration by weathering, form residual crystalline clay minerals.
- (3) Mineral colloids may be formed by hydrothermal synthesis from colloidal hydrous alumina and silica.

During weathering of Zn and Cd bearing primary minerals, Zn is released into solution. Zn concentration and transportation is then controlled by the precipitation of compounds such as Zn carbonates, hydroxides, phosphates and silicates (Day, 1963), and the adsorption of Zn by clay minerals or oxides (Mason, 1966). Oxidation of Zn-bearing sulphides during weathering also leads to relatively high concentrations of Zn in solution as soluble Zn sulphate forms (Wedepohl, 1972).

Cd is released into solution as chloride or sulphate during weathering. Under strongly oxidising conditions Cd forms oxides and carbonates (Goldschmidt, 1958; Wedepohl, 1970).

#### 1.2.4 Origin of Zn and Cd in soils

The content of the parent material is the main factor determining the Zn and Cd contents of soils (Vinogradov, 1959). For example, soils derived from basic rocks such as basalts and gabbros are usually richer in Zn and Cd content than those derived from acidic rocks such as rhyolite and granite.

In a survey of the Zn contents of Californian soils, it was found that soils generally had similar Zn contents to the rocks from which they had formed (Hibbard, 1940). New Zealand soils developed on basalt, andesite and rhyolite reflect the same trends in element distribution as seen in the parent materials, but the actual levels of each element in soils may be altered by soil processes (Wells, 1960). For example, due to the low mobility of Zn and Zn adsorption on clays, clay minerals, Fe, Al and Si oxides, hydrous oxides and organic matter Zn can become residually concentrated in soils and the Zn content then becomes higher than in the parent rocks (Wedepohl, 1972). Cd may also become residually concentrated in soils in the same way.

#### 1.2.5 Total Zn content of soils

The total Zn content of most mineral soils generally lies within the range  $0.153\text{--}4.587 \mu\text{mol Zn g}^{-1}$ , with the majority falling within  $0.153\text{--}1.529 \mu\text{mol Zn g}^{-1}$  (Swaine, 1955a). High Zn contents are generally due to other factors such as proximity to Zn mines, or smelters. The range in total Zn contents of soils from various countries is shown in Table 1.4. Total Zn content in soils is dependent (Table 1.4) on the

Table 1.4 Range in total Zn contents of soils from various countries

Country	Description of Soil	Total Zn Content ( $\mu\text{mol g}^{-1}$ )		Reference
		Range	Average	
Japan	Volcanic ash soils	1.773 - 3.135	1.713	Masui et al., 1972
Russia	Tundra soils, podzols, chernozems, forest soils	0.428 - 1.376	0.856	Vinogradov, 1959
New Zealand	Zonal soils: brown-grey earths; yellow-grey earths; yellow-brown earths	0.245 - 1.086		
	Intrazonal soils: volcanic ash soils; yellow-brown pumice soils; yellow-brown loam; brown gravelly clay	1.214 - 2.706		Whitton and Wells, 1974
	Azonal soils: recent soils from loess; alluvium and volcanic ash	0.688 - 1.086		
Spain		0.107 - 1.911	0.688	Marcias, 1973
U.S.A. (Utah)	Calcareous soils		4.587	Thorne et al., 1942
	Non-calcareous soils		2.294	
U.S.A. (California)		0.841 - 5.122		Hibbard, 1940a

content of organic matter, texture, and pH in addition to the type of the parent rocks (Vinogradov, 1959).

#### 1.2.6 'Available' Zn content of soils

Of more interest, from the point of view of plant requirements, is the content of 'available' Zn in soils. The range of 'available' Zn generally varies from less than 0.015 to 0.153  $\mu\text{mol Zn g}^{-1}$  (Swaine, 1955a). This range of 'available' Zn contents of soils covers the range from deficiency through to adequacy of Zn for plant growth (Thorne et al., 1942). Typical values for 'available' Zn content are shown in Table 1.5.

Table 1.5 'Available' Zn contents of a range of soils

Extractant	Range ( $\mu\text{mol g}^{-1}$ )	Average ( $\mu\text{mol g}^{-1}$ )	Reference
0.2M ammonium oxalate (pH 3.3)	0.015-0.321	0.103	Marcias, 1973
0.02M EDTA	0.015-0.612		Jensen & Lamm, 1959
0.5N KCl + acetic acid (pH 3.2)		0.184 (calcareous)	Thorne et al., 1942
		0.092 (non-calcareous)	
0.05N KCl + acetic acid (pH 3.2)	0.015-0.077		Hibbard, 1940

Various extractants have been used to estimate the availability of soil Zn. Extractants with low pH may, by dissolving the clay minerals release both adsorbed and structural Zn and thereby give an over-estimation of 'available' content. EDTA is commonly used to estimate 'available' Zn. It does so by chelating Zn in solution thereby altering

the equilibrium between solution Zn and adsorbed Zn. Adsorbed Zn then desorbs in an attempt to maintain equilibrium. Plant roots also alter equilibrium between solution Zn and Zn adsorbed on soil surfaces in a similar way to EDTA, hence the use of EDTA to simulate the plant action.

The 'available' Zn data shown in Table 1.5 show the very much lower levels of 'available' Zn compared to total Zn in soils, and soils which have high total Zn contents may still show plant responses if the 'available' Zn contents are not sufficient for plant growth requirements.

#### 1.2.7 Total Cd contents of soils

The average Cd contents in soils range from  $8.9 \times 10^{-4}$  to  $4.5 \times 10^{-3} \mu\text{mol Cd g}^{-1}$  (Wedepohl, 1970). Swaine (1955) stated that it is unlikely that Cd in 'normal' soils would exceed  $8.9 \times 10^{-3} \mu\text{mol Cd g}^{-1}$ . In their review Fleischer et al. (1974) reported average levels of soil Cd less than  $8.9 \times 10^{-3} \mu\text{mol Cd g}^{-1}$ , except in soils which had been contaminated through industrial pollution or in agriculture through application of sewage sludges and phosphate fertilisers.

Thus, under natural conditions the total Cd contents of soils is small enough to pose no problems of toxicity to plants. However, where Cd soil levels do become of concern is when contamination by Cd occurs near highways, metallurgical industries or following the addition of sewage sludge or superphosphate fertiliser to soils. Accumulation of Cd, and of Zn, in soils due to these factors is discussed in the next section.

### 1.3 Possible Sources of Addition of Potentially

#### Available Zn and Cd to Soils

Although total amounts of Zn and Cd, in surface soils, are largely determined by the respective amounts in the parent materials (Section 1.3), soil levels of both Zn and Cd can be increased by direct additions of industrial wastes (particularly from mines and smelters), superphosphate fertilisers, pesticides and sewage effluents (Lagerwerff, 1971). A summary of the contributions of these sources to the Zn and Cd enrichment of soils follows.

#### 1.3.1 Additions from industrial sources

Sources of Zn and Cd include wastes from mines and heavy metal smelters. The soil contents are most likely to be affected around areas of industrial development and as such the effects will involve only restricted areas.

Studies of surface soils around lead smelters have shown that substantial increases in Zn and Cd contents can occur. Increases of soil Zn from  $0.077 \mu\text{mol Zn g}^{-1}$  to  $15.291 \mu\text{mol Zn g}^{-1}$ , and soil Cd from  $0.001 \mu\text{mol Cd g}^{-1}$  to  $0.089 \mu\text{mol Cd g}^{-1}$  (Cartwright et al., 1977) have been found, as have levels of up to  $79.51 \mu\text{mol Zn g}^{-1}$  and  $1.42 \mu\text{mol Cd g}^{-1}$  (Fleischer et al., 1974) in surface soils in areas surrounding lead smelters, while background levels for similar soils were  $0.007 \mu\text{mol Cd g}^{-1}$  and  $0.887 \mu\text{mol Zn g}^{-1}$ . The Zn and Cd was received as aerosols and as fallout of Zn and Cd particulates from the smelters in relation to the prevailing winds. Contributions to plant-available Zn and Cd from smelter emissions has been estimated using acetic-acid extraction for which 50-fold increases in Zn and over 2-fold increases in Cd concentrations were found by comparison with equivalent soils located

in a rural area (Beavington, 1973).

Typically, in situations where aerial deposition of Zn and Cd occurs, soil levels are generally highest in the top 5 to 10cm of soil, decreasing with depth and also with distance from the emission source. The significance of the accumulation of Zn and Cd within the topsoil is that most of the added Zn and Cd is within the rooting zone of most pasture and vegetable plants and therefore positionally available for uptake.

Actual uptake, by plants, of emission-borne Zn and Cd added to soils was shown by results from a comparison of Zn and Cd concentrations in herbage from rural and urban areas. Beavington (1975) found the Zn content of grass and clover plants grown on soils in rural areas to be  $0.44 \mu\text{mol Zn g}^{-1}$  and to increase to  $1.08 \mu\text{mol Zn g}^{-1}$  for plants grown in urban areas. This finding suggests that surface soil enrichment by heavy metals, such as Zn and Cd can result in increased plant contents, which in turn, can lead to increased heavy metal burdens for animals and humans, if they become part of the diet.

### 1.3.2 Motor vehicle emissions

Emissions from motor vehicles can increase Zn and Cd concentrations in soils in close proximity to roadways. Elevated levels of  $\text{NH}_4\text{Cl}$ -extractable Zn and Cd were measured in topsoils adjacent to four heavily travelled roads (Lagerwerff and Specht, 1970). Concentrations of Cd ranged from  $0.008 \mu\text{mol Cd g}^{-1}$  to  $0.016 \mu\text{mol Cd g}^{-1}$ , and Zn from  $0.83$  to  $2.63 \mu\text{mol Zn g}^{-1}$ , at a distance of 8 metres from the roadways. The topsoil content of these metals decreased with increasing depth in the soil and distance from the road. The content of Zn and Cd in motor vehicle oils and tyres is the most likely source of these metals. For example, levels of  $0.002 \mu\text{mol Cd g}^{-1}$  in lubricating oils and from

0.178 to 0.801  $\mu\text{mol g}^{-1}$  in a range of tyres have been reported (Lagerwerff and Specht, 1970). The plant availability of Zn and Cd, added to roadside soils by motor vehicle emissions, was determined (Lagerwerff, 1971) and it was found that 5-fold soil Cd and 7-fold soil Zn increases resulted in only 2-fold increases in both Zn and Cd in roots and tops of radish plants. Hence only a small proportion of the added Zn and Cd was plant-available, the remainder being either lost from the soil by leaching, or adsorbed by soil components.

Thus several studies have shown that heavy-metal pollution of surface soils occurs near metal smelting complexes, mines and near well-used roadways and that these pollutants can be absorbed by plants growing in these localities. However while the pollution problems affect only limited soil areas, the attendant health hazards may extend over a far greater area due to transportation of the plant products grown on such contaminated soil.

### 1.3.3 Municipal wastes

Sewage sludges, effluents and garbage composts are potential sources of additions of heavy metal pollutants to surface soils. At present, the disposal of solid and liquid sewage wastes is a major problem for large cities. Soils are increasingly being used for the disposal of wastes, largely as an alternative to incineration. However, the heavy metal content of these wastes may constitute a potential hazard if large amounts of waste are disposed of in this manner (Berrow and Webber, 1972; Purves, 1972; Bradford et al., 1975). This is especially of concern for the metals Cu, Zn, Cr, Pb, Cd and Sn which are toxic at high concentrations, and which are able to be stored and concentrated in the soil as the result of repeated applications of sludge. The heavy metal contents of sewage sludges in different

countries have been measured. Table 1.6 summarizes the findings of some of these studies. The amounts of Zn and Cd shown are average values. A notable feature of the data in Table 1.6 is that the New Zealand sludges from Levin and Auckland contain less than half the amount of Zn and less than a tenth the amount of Cd, as the sludges from the U.S.A. The lower Zn and Cd concentrations in sludges in New Zealand reflect the low intensity of heavy industry, which can contribute large amounts of these heavy metals to municipal wastes in other countries.

Studies have been undertaken, mainly in the United States, to determine whether or not additions of sewage sludge to soils increase the heavy metal contents of the soils to which they are added. Soils amended with sludge have been shown to contain more Zn and Cd than unamended soils (Bradford et al., 1975; Hinesly et al., 1977). For example, additions of sewage sludge, for seven years, at an average concentration of  $65.75 \mu\text{mol Zn g}^{-1}$  and  $1.78 \mu\text{mol Cd g}^{-1}$  increased the Zn and Cd contents of the top 15cm of soil to  $15.29 \mu\text{mol Zn g}^{-1}$  and  $0.36 \mu\text{mol Cd g}^{-1}$  (Hinesly et al., 1977) values which were 50% higher than Zn and Cd levels in corresponding unamended soils. In contrast to these reported findings, Quin and Syers (1978) concluded from a trial on the effect of 16 years irrigation of pastures with treated sewage effluent (containing  $0.23 \mu\text{mol Zn l}^{-1}$  and  $0.001 \mu\text{mol Cd l}^{-1}$ ), that there were no measurable increases in heavy metal content of soils, either as total or 0.1N HCl-extractable Zn or Cd. The study involved the use of effluent in New Zealand and it would appear from these findings that it may be relatively safe to add New Zealand sewage sludges to soils, without undue risk of a build-up of toxic metals.

The importance of Zn and Cd additions to soils from sewage sludges depends on the availability of the added Zn and Cd to plants,

Table 1.6 Total Zn and Cd content of sewage sludges

Source of Sludge	No. Sites	Zn	Cd
		$\mu\text{mol g}^{-1}$ dry wt. basis	$\mu\text{mol g}^{-1}$ dry wt. basis
1. U.S.A. (Furr et al., 1976)	16	32.569	0.581
2. U.S.A. (Clark and Hill, 1958)	15	36.865	-
3. California (Bradford et al., 1975)	6	11.468	0.658
4. U.K. (Berrow and Webber, 1972)	54	62.691	n.d.
5. Singapore (Wells and Teoh, 1975)	2	35.168	0.078
6. Templeton, N.Z. (Quin and Syers, 1978)	1	16.820	0.038
7. Levin, N.Z. (Wells and Whitton, 1976)	1	18.349	n.d.
8. Auckland, N.Z. (Wells and Whitton, 1979)	1	10.703	0.040

n.d. = not detectable

as it is only through edible plant products that toxic metals enter the food chain. It is important to determine whether or not the Zn or Cd, added to soils in sewage sludges and composts is available for plant uptake.

#### 1.3.3.1 Plant availability of Zn and Cd added to soils in sludges and composts

Corn and beans grown on soils treated with sewage sludge were found to contain levels of Zn and Cd exceeding  $4.59 \mu\text{mol Zn g}^{-1}$  and  $0.027 \mu\text{mol Cd g}^{-1}$  (Hinesly et al., 1977) values which have been suggested as being at about the tolerable limits of these elements for plants (Allaway, 1968; Melsted, 1977). However, even at these high tissue levels no yield depressions occurred. Elevated plant tissue concentrations of Zn and Cd in corn grown on sludge amended soils have been demonstrated (Mays et al., 1973; Giordano et al., 1975; Mortvedt and Giordano, 1975) with Cd in sewage sludges appearing to be more plant-available than Zn. For example, crop uptake has been shown to be less than 5% of the extra Zn added, much lower than would occur from  $\text{ZnSO}_4$  solution at similar soil pH (Mortvedt and Giordano, 1975) while Cd added either by way of sewage sludge or solution was readily available for absorption and translocation within the plant (Jones, Hinesly and Ziegler, 1973).

Thus, numerous investigators (Allaway, 1968. Jones et al., 1973; Mays et al., 1973; Giordano et al., 1975; Mortvedt and Giordano, 1975; Hinesly et al., 1977; Melsted, 1977) have highlighted the need for careful application of municipal wastes to soils, if heavy metal accumulations and toxicity problems are to be avoided.

### 1.3.4 Superphosphate fertilisers

Macronutrient fertilisers, such as superphosphate made from phosphate rock of both marine and continental origin are often used in large quantities on agricultural and intensive horticultural systems. Long-term high rates of application of fertilisers can be important contributors of heavy metals, such as Zn and Cd, which can thereby enter the food chain through edible plant products (Schroeder and Balassa, 1963; Williams and David, 1973).

On some soils the addition of Zn via phosphate fertilisers, may be advantageous as the Zn added may contribute substantially to plant requirements (Ozanne et al., 1965), but may also be disadvantageous in some soils as the concentration range between deficiency and toxicity of Zn is very narrow (Barrows, 1966).

The Zn and Cd found in superphosphate fertilisers may derive from several sources. The contribution from sulphuric acid used in the manufacture of superphosphate depends on whether the acid is synthesised from Zn concentrates (sulphides) by the chamber process, from elemental S, or from either sulphide or sulphur by the contact process (Walkley, 1940; Oertel and Stace, 1949). Another source is the rock phosphate from which the fertiliser is manufactured (see Table 1.7 after Swaine (1962)).

As can be seen from Table 1.7 the particular rock phosphate used for superphosphate manufacture is likely to have a major bearing on the Zn and Cd contents of the resultant fertiliser. The rock phosphates used in New Zealand have come mainly from Nauru, Christmas and Ocean Islands.

#### 1.3.4.1 Zinc and Cd contents of superphosphate fertilisers

The ranges of Zn and Cd contents, in superphosphate fertilisers

Table 1.7 Zinc and Cd contents of rock phosphates

Source of Rock Phosphate	Zn content ( $\mu\text{mol g}^{-1}$ )	Cd content ( $\mu\text{mol g}^{-1}$ )	
Nauru Island	13.762	0.667	Walkley, 1940
Nauru Island	-	0.774	Williams and David, 1973
Nauru Island	-	significant amount	Oertel and Stace, 1947
Ocean Island	15.291	1.022	Walkley, 1940
Ocean Island	-	significant amount	Oertel and Stace, 1947
Christmas Island	-	0.356	Williams and David, 1973
Cavacao Island	3.211-4.587	-	Clark and Hill, 1958
Tennessee, U.S.A. (West)	3.211-5.122	-	Clark and Hill, 1958
Montana, U.S.A. (East)	0.275-2.370	-	Clark and Hill, 1958
Florida, U.S.A.	0.367-2.095	0.890	Collins (1950) as quoted in Swaine, 1962

given by various authors are shown in Table 1.8. The values shown for Zn especially highlight the variability due to sources of rock phosphate and sulphuric acid used.

For example, with differing rock phosphate sources, superphosphate fertiliser made from rock phosphate of the Eastern U.S.A. varied by almost one-hundred fold in Zn content compared to superphosphate made from Western U.S.A. rock phosphate (Bingham, 1959). Fertiliser made from the Nauru rock phosphate was 50% less in Zn content solely due to the use of sulphuric acid made from elemental S or the contact process, as opposed to acid made from sulphide ores and the chamber process (Walkley, 1940). The range of Cd reported in superphosphate fertilisers is 0.08 to 1.51  $\mu\text{mol Cd g}^{-1}$  and arises from both sulphuric acid and rock phosphate used in the manufacture of the fertiliser (Walkley, 1940).

An important consideration is whether or not the metals added in fertilisers are plant available once applied to soil.

#### 1.3.4.2 Plant availability of Zn and Cd in superphosphate fertilisers

Soil factors important in determining the overall plant availability of added heavy metals include pH, organic matter content, cation exchange capacity and sesquioxide content (Williams, 1974). Evidence suggests that Zn and Cd applied to soils in superphosphate does become plant available. Zinc has been found to be relatively immobile, persisting in the soil near the point of application and in the top 5 cms of soil, hence remaining within the rooting depth of many plant species (Gilkes et al., 1975).

In Hawaiian soils, significant increases in 0.1N HCl-extractable Zn were found with increasing phosphate fertiliser application (Saeed and Fox, 1978), while some Australian soils, which had received superphosphate

Table 1.8 Zinc and Cd contents of some superphosphate fertilisers

Source of Rock Phosphate	Source of H <sub>2</sub> SO <sub>4</sub>	Zn content (μmol g <sup>-1</sup> )	Cd content (μmol g <sup>-1</sup> )	Reference
Idaho, U.S.A.	Sulphide ores	6.376- 7.309	-	Clark and Hill, 1958
Florida, U.S.A.	S	0.765- 2.523	-	Clark and Hill, 1958
Nauru Island	ZnS concentrates	10.245-16.667	0.445-1.513	Walkley, 1940
Nauru Island	Unspecified	8.257- 9.480	-	Walkley, 1940
Nauru Island	Unspecified	4.128-11.468	0.178-0.463	Williams, 1974
U.S.A. (Western)	Unspecified	20.642 (av.)	-	Bingham, 1959
U.S.A. (Eastern)	Unspecified	2.385 (av.)	-	Bingham, 1959
		0.765-21.865	0.445-1.513	Burrows, 1966
		26.682	-	Broawn, Viets and Crawford, 1954
			0.080-0.320	Schroeder and Balama, 1963
Triple Superphosphates				
Idaho, U.S.A.	Sulphide ores	9.572-19.572	-	Clark and Hill, 1958
Florida, U.S.A.	S	0.765- 1.529	-	Clark and Hill, 1958
		21.407	-	Saeed and Fox, 1978

fertiliser for over thirty years, had significantly higher HCl-, EDTA- (pH 7.0) and  $\text{NH}_4\text{Cl}$ - extractable Zn, than the respective unfertilised soils (Williams and David, 1976). Two-fold increases in the tissue levels of Zn were found in subterranean clover and lucerne grown on the fertilised soils and Zn contamination of the superphosphate was cited as one possible cause of these results. Subterranean clover was able to recover only up to 14% of Zn added by way of superphosphate (Ozanne, Shaw and Kirton, 1965) and the data suggested that the total amount of Zn applied was the important factor governing the amount of Zn absorbed by plants, rather than the rate of superphosphate used.

Cadmium added to soils via superphosphate applications is thought to remain largely plant available. Approximately 85% of the amount added to soils by superphosphate additions was found retained in the cultivated layer of the soil, and hence within the rooting depth of most plant species (Williams and David, 1976). Under field conditions the effect of Cd impurities on soil and plant Cd contents will depend on soil type, amounts of fertiliser used, and the plant species grown (Williams and David, 1973).

Heavy applications of superphosphate fertiliser can cause significant increases in Cd contents of vegetables (Schroeder and Balassa, 1963; Schroeder et al., 1967), pasture plants and grain crops (Williams and David, 1973; Williams and David, 1976). For example, the addition of 1000 kg/ha of superphosphate (with a mean Cd content of  $0.383 \mu\text{mol Cd g}^{-1}$ ) increased the Cd contents of oats, subterranean clover and lucerne approximately ten-fold, i.e., from 0.0002, 0.0009 and  $0.0003 \mu\text{mol Cd g}^{-1}$  to contents of 0.0025, 0.0119 and  $0.0053 \mu\text{mol Cd g}^{-1}$  respectively (Williams and David, 1973).

The important factor, with respect to animal and human health, is

the Cd content of the plant material actually consumed. In this respect leaf and root crops are generally found to accumulate more Cd in the edible portions than do grain crops (Williams and David, 1973).

Accumulation of Cd in soils and the subsequent transfer of increased amounts of Cd to plants, due to the application of phosphate fertilisers (Schroeder and Balassa, 1963; Schroeder et al., 1967; Williams and David, 1973; Williams and David, 1976) gives cause for concern as it affords the opportunity for entry of Cd into the food chain.

#### 1.4 Adsorption of Zn and Cd by hydrous oxides and soils

In this, and subsequent sections, the terms "hydrous oxide" or "hydrous metal oxide" will be used as a general term to include oxides, hydrous oxides and hydroxides unless otherwise specified.

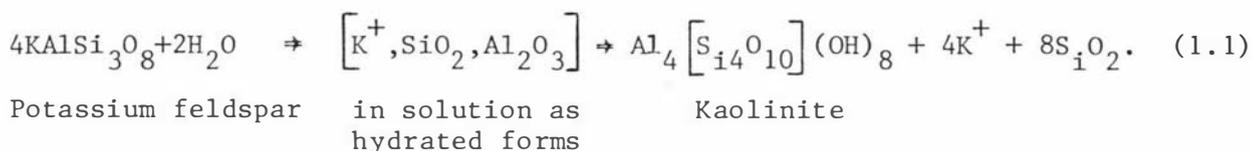
##### 1.4.1 The role of hydrous oxides in the chemistry of soil Zn and Cd

Inorganic components of soils that have been shown to be active in the retention of heavy metal cations, such as Zn and Cd, include short-range order hydrous oxides of Fe, Al and Mn (Jenne, 1968; Gadde and Laitinen, 1974; Kinniburgh et al., 1976; Loganathan et al., 1977); crystalline Fe and Al oxides, e.g., goethite, gibbsite (Parfitt and Russell, 1977; Kalbasi et al., 1978) as well as clay minerals, e.g., montmorillonite (Bingham, Page and Sims, 1964; Reddy and Perkins, 1974).

Hydrous Fe, Al and Mn oxides are formed from the weathering of Fe-, Al-, and Mn- containing primary and secondary minerals. Primary minerals decompose to produce hydrous oxides and less commonly layer silicates, depending on soil conditions (Fieldes and Swindale, 1954).

The weathering of minerals to hydrous oxides involves hydration of the mineral surface and then a decomposition reaction (Barshad, 1955). A generalised weathering reaction has been given by Yaalon (1959) as:

Aluminium silicate + water → amorphous intermediate products + ions →  
clay minerals + soluble salts which more specifically is:



Fe and Mn hydrous oxides are ubiquitous in soils (Jenne, 1968) except possibly in young soils on unweathered volcanic ash and pumice or in the eluvial horizon of podzols where the hydrous oxides have been removed by acidic leaching at low redox potentials.

Amounts of hydrous Fe oxides in soils range from 1-11% of soil (Carroll, 1958), while amounts of hydrous Mn oxides range from 0.02-0.4% of soil (Daniels et al., 1962; Biswas and Gawande, 1964). For New Zealand soils the amounts of hydrous Fe oxides range from 1-16% of soil (Fieldes and Swindale, 1954; New Zealand Soil Bureau, 1968).

These hydrous oxides occur in soils either as partial coatings on silicate minerals (Jenne, 1968) or as discrete minerals (Kinniburgh et al., 1975). The ability of hydrous oxides to specifically adsorb divalent cations (Jenne, 1968; Vésely and Pekárek, 1972; Quirk and Posner, 1975) coupled with the occurrence of hydrous oxides, in soils, as partial coatings on clay minerals, points to the potentially important role of hydrous oxides in the retention of cations by soils. It has been suggested (Jenne, 1968) that organic matter serves to maintain hydrous oxides in their micro-crystalline, short-range order form preventing their regular crystallisation, as would normally occur under oxidising soil conditions.

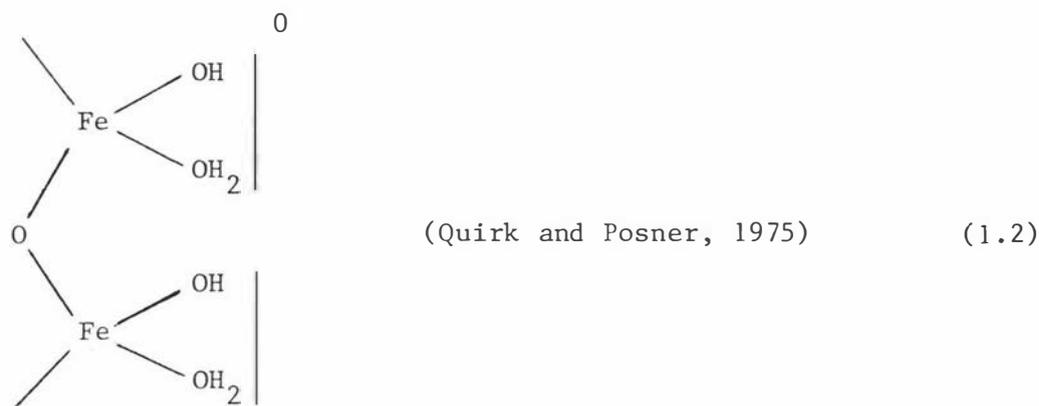
Iron gel has been used as a synthetic model oxide for investigating the mechanisms by which cations, such as Zn and Cd, are adsorbed by soils. Such a simple synthetic hydrous oxide can be used to simulate the effect of the more complex heterogeneous soil hydrous oxide systems. Cations shown to be adsorbed from solution by hydrous Mn and Fe oxide materials include Cd, Co, Cu, Ni, Pb, Tl and Zn (Krauskopf, 1956; Gadde and Laitinen, 1974), and Cd, Co, Mg, Ni, Pb, Sr and Zn adsorption by hydrous Fe and Al oxide gels has been studied (Stanton and Burger, 1970; Kinniburgh et al., 1976).

The adsorption of cations by hydrous oxides and soils depends not only on the chemical and physical properties of the adsorbent but also on the properties of the adsorbing ions. The properties of synthetic hydrous oxides and more particularly those of the surfaces of these hydrous oxides are discussed in the following section, and the ionic properties of interest are discussed in a later section.

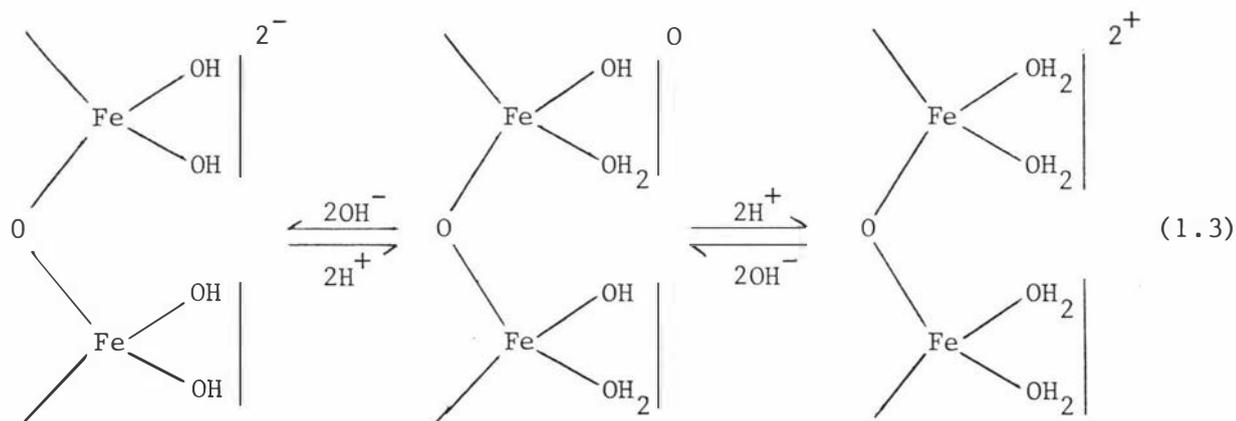
#### 1.4.2 Properties of the hydrous metal oxide/ aqueous interface

##### 1.4.2.1 Development of surface charge

The term "hydrous metal oxide" refers to compounds which have one or more metallic cations combined with the elements water, hydrogen and oxygen and is taken to include metal hydroxides (e.g.,  $\text{Fe}(\text{OH})_3$ -ferric hydroxide); oxyhydroxides (e.g.,  $\text{FeOOH}$ -goethite) and metal oxides (e.g.,  $\text{Fe}_2\text{O}_3$ -hematite), which may have hydrated surfaces (Onoda and de Bruyn, 1966). An example of the surface of one such hydrous metal oxide, goethite, is depicted as follows:



These hydrated surfaces are constant potential surfaces and the adsorption and desorption of protons, as shown in equation (1.3) below, results in a change in surface charge, e.g.,



Ions which adsorb on surfaces of like or zero charge are called "charging" ions (Bowden et al., 1977) and if they are components of the solid phase and are present in the solvent then they are known as 'potential-determining' ions (Parks and de Bruyn, 1962; Bowden et al., 1973). Thus, for hydrous metal oxide systems, protons and hydroxyls as well as the lattice metal ions are the potential-determining ions and the concentration of such ions in solution determines surface charge and potential (Gast, 1977). The potential, however, is only "constant" at a fixed concentration of potential-determining ions. These constant potential systems contrast with the layer silicates, for

which the permanent surface charge arises from an imbalance of charges within the crystal lattices due to interior lattice imperfections and isomorphous substitutions (Toth, 1964). These latter surfaces are classified as constant charge surfaces (van Olphen, 1963).

Differences in electrical potential arise between a constant potential surface and the outer solution when the surface becomes charged as, for example, when a charging ion is adsorbed onto a surface and the ion does not displace an ion of like charge or a counter-ion does not accompany the adsorbed ion (Bowden et al., 1977). Charge separation, or the unequal distribution of charge, also occurs by unequal dissolution, i.e., non-stoichiometric dissolution of the structural ions of the solid (Bowden et al., 1977). The surface charge on hydrous metal oxides arises by charge separation i.e., unequal adsorption described above, and models have been proposed to explain the charge and potential relationships of such interfaces.

#### 1.4.2.2 Models proposed to describe charge and potential relationship of charged interfaces

Various models have been proposed to describe the spatial distribution of charge and potential at an interface. Although these models were originally developed for constant charge surfaces, it appears that the models were first carried over to constant potential surfaces by James and Healy (1972), and have been accepted with no serious objections against the use of such models for constant potential surfaces.

##### 1.4.2.2.1 Helmholtz model.

Helmoltz (1879) first advanced an electrokinetic double layer theory for an electrically-charged planar surface based on the structure of a simple condenser. The "inner" layer in the model is represented by the surface charge of

the particle and the "outer" layer as a plane of ions of opposite charge lined up adjacent to the surface. A schematic representation of charge and potential distribution for this model is shown in Fig. 1.1 from Bear (1964).

1.4.2.2.2 Gouy-Chapman model. Gouy (1910) and Chapman (1913) both developed the model of a diffuse double layer at a charged planar surface. They proposed that the solution surrounding the charged surface contained ions as point charges which were attracted or repelled by the surface depending on the sign of the surface charge and that of the ion. The counter-ion concentration is highest nearest the surface, decreases rapidly at first and then asymptotically with distance, as shown in Fig.1.2 (Bear, 1964). The Gouy-Chapman model contained some unrealistic assumptions, the most important being the neglect of ionic diameters by assuming the ions in solution to be point charges.

1.4.2.2.3 Stern model. Stern(1924) developed the Gouy-Chapman model further by giving fine structure to the outer layer. The model consists of a layer of ions located at a distance equivalent to the radius of the counter-ions, this representing the closest approach of the ions to the surface. Outside this is a diffuse layer of ions as proposed in the Gouy-Chapman model. Thus, the total surface charge is countered by the layer of charged ions close to the surface together with the charge of the ions in the diffuse layer (Fig. 1.3 from Bear, 1964). In the "Stern layer", the zone between the surface and the plane of centres of the counter ions at closest approach to the surface, the electric potential is assumed to decrease linearly with distance, from a value  $\psi_1$  at the surface to a value  $\psi_s$ , called the Stern potential (van Olphen, 1963). Stern proposed that the ions close

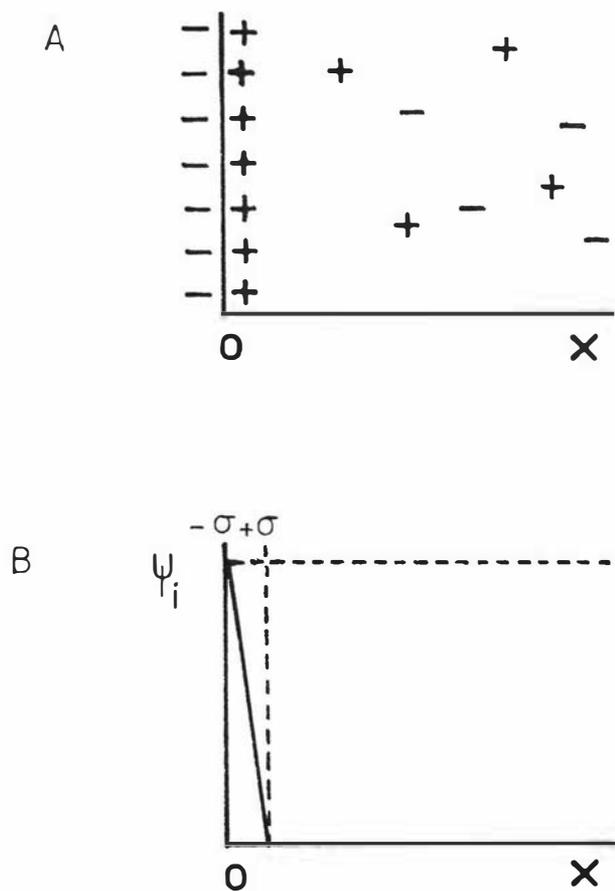


Figure 1.1 Distribution of ions (A) and potential (B) at a negatively charged interface according to Helmholtz, where

$\psi_1$  = total potential

$\sigma$  = surface charge density

$x$  = distance from surface

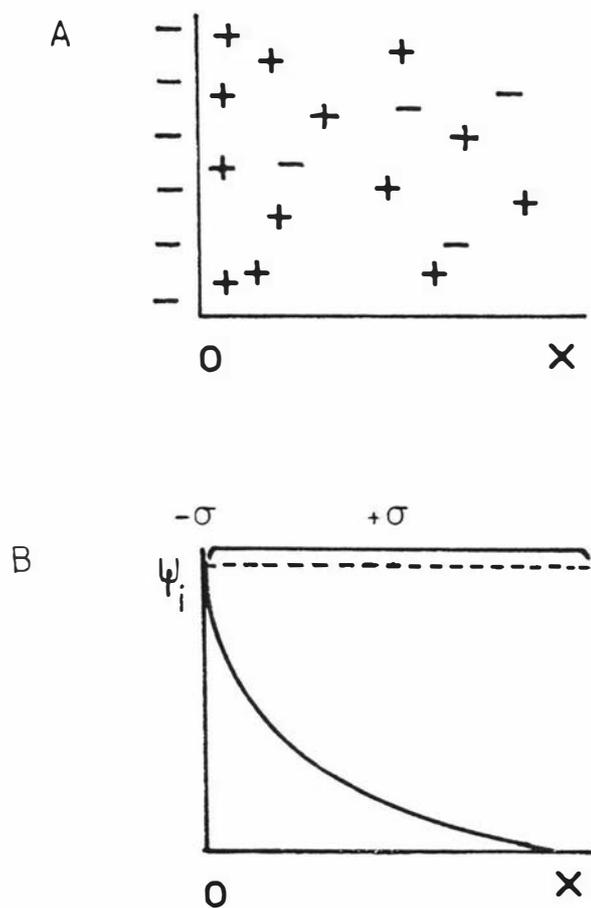


Figure 1.2 Distribution of ions (A) and potential (B) at a negatively-charged interface according to the Gouy-Chapman model.

$\psi_i$  = total potential

$\sigma$  = surface charge density

$x$  = distance from surface

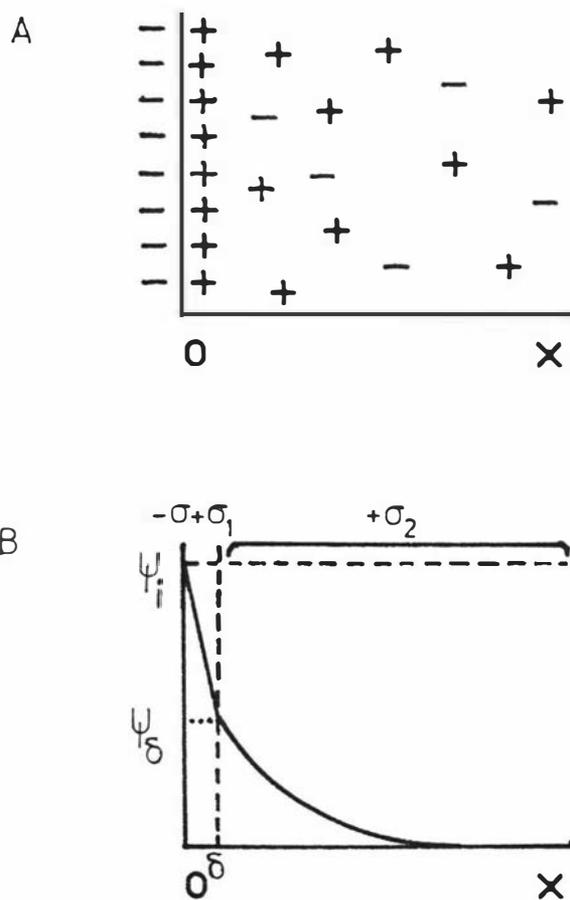


Figure 1.3 Distribution of ions (A) and potential (B) at a negatively-charged interface according to the Gouy-Chapman-Stern model, where:

$\psi_\delta$  = Stern potential

$\delta$  = thickness of Stern layer

to the surface interacted with the surface by both electrostatic (coulombic) attraction and some extra specific "chemical" interaction.

1.4.2.2.4 Grahame model. Grahame (1947) proposed further fine structure of the double layer by suggesting that the cations at the surface lose their respective waters of hydration such that the dehydrated cations can then be adsorbed into a plane in direct contact with the surface. The locus of the centres of such ions becomes the Inner Helmholtz plane (i.H.p.), while the locus of centres of hydrated ions becomes the Outer Helmholtz plane (o.H.p) comparable to the Stern layer. The Grahame double layer model is depicted in Fig. 1.4.

In this model the adsorbed dehydrated ions closest to the surface are said to be specifically adsorbed (Hingston et al., 1967). These specifically adsorbed ions are non-lattice ions that can alter surface charge and determine the potential at and next to the surface (Bowden et al., 1977). Specifically adsorbed ions can adsorb onto neutral or oppositely-charged surfaces irrespective of the solution concentrations of other ions, and can even be adsorbed in excess of amounts required to neutralise the surface charge. Super-equivalent adsorption can result in reversal of the sign of the charge of the diffuse layer, as depicted in Fig. 1.5. Such adsorption occurs against electrical repulsion as a result of extra "specific" chemical attractive forces (proposed by Stern (1924)) which allow adsorption to proceed.

#### 1.4.2.3 Charge distribution at oxide surfaces

For metal oxide systems, surface charge ( $\delta_s$ ) is developed by protonation-deprotonation reactions with oxo-, hydroxo- and aquo-species ligated to surface metal ions (Levine and Smith, 1971; Wright and Hunter, 1973; Bowden et al., 1974). The charge borne by hydrous oxide surfaces is determined by the respective concentrations of

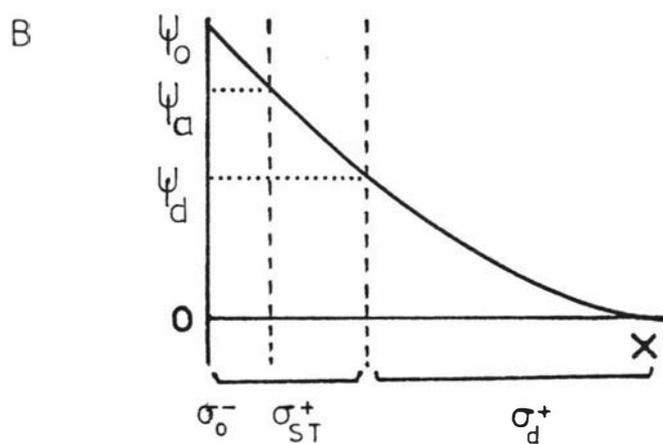
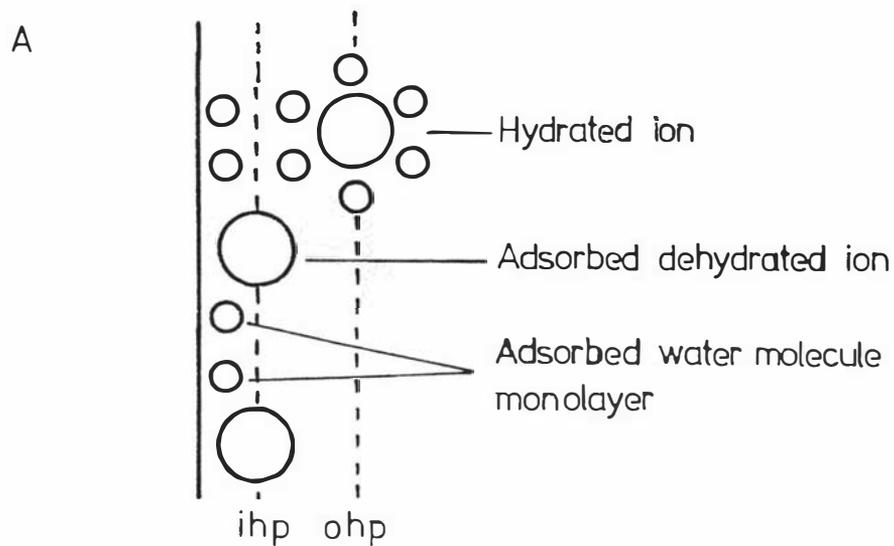


Figure 1.4 Distribution of ions (A) and potential (B) at a negatively-charged interface according to the Grahame model, where:

$\Psi_0$  = surface potential

$\Psi_a$  = potential in plane of specifically adsorbed cation

$\Psi_d$  = potential at diffuse layer

$\sigma_{ST}$  = charge at Stern layer

$\sigma_d$  = charge of diffuse layer.

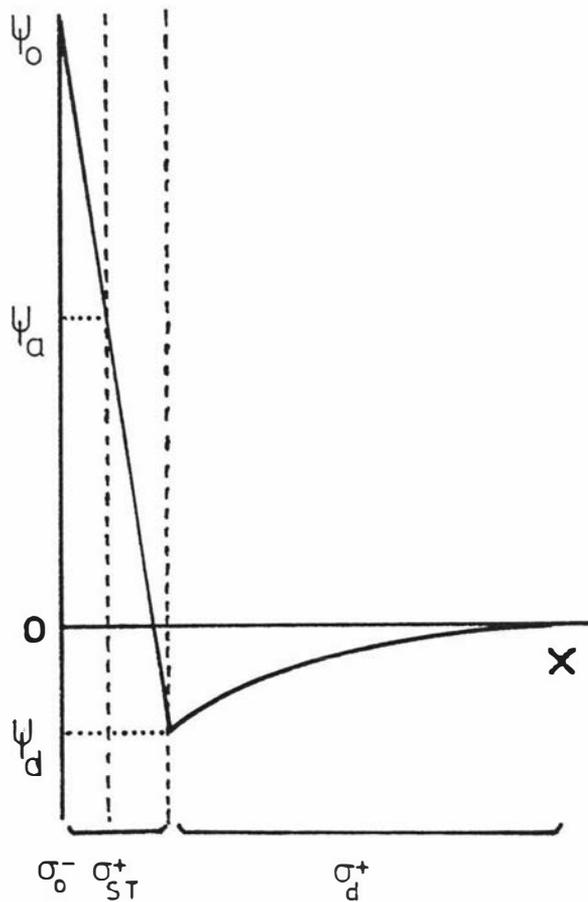


Figure 1.5 Distribution of charge and potential at negatively-charged surface showing charge reversal arising from super equivalent adsorption of cations.

$\psi_0$  = surface potential

$\psi_a$  = potential in plane of specifically adsorbed cation

$\psi_d$  = potential at diffuse layer

$\sigma_{ST}^+$  = charge at Stern layer

$\sigma_d^+$  = charge of diffuse layer.

$H^+$  and  $OH^-$  ions (potential-determining ions). Thus:

$$\delta_s = F(\Gamma H^+ - \Gamma OH^-) \quad (1.4)$$

where  $\Gamma H^+$  and  $\Gamma OH^-$  are the surface excesses of  $H^+$  and  $OH^-$  ions. The net charge, or the amounts of  $H^+$  and  $OH^-$  adsorbed, on surfaces is measured by titrating the hydrous metal oxides in solutions of indifferent electrolyte over a range of concentrations, e.g., 0.01M, 0.1M NaCl (Bar-Yosef et al., 1975; Bowden et al., 1977). An example of such a titration curve for a hydrous metal oxide, goethite, is given in Fig. 1.6. The titration curves cross at a point where the surface charge is independent of ionic strength. For variable charge surfaces this corresponds to the point of zero charge (p.z.c.) and the pH at which the intersection occurs is denoted the pH (pzc) for which the surface excess of  $H^+$  ions is equal to that of  $OH^-$  ions, i.e.,

$$(\Gamma H^+ - \Gamma OH^-) = 0 \quad (1.5)$$

At pH values below the p.z.c., the surface charge,  $\delta_s$ , is positive, whereas at pH values above the p.z.c. the surface charge is negative. For constant potential surfaces, and at a fixed pH, the magnitude of the charge increases with increasing indifferent electrolyte concentration.

#### 1.4.2.4 Charge variation in the presence of specifically-adsorbed cations

If the intersection point for the titration curves of hydrous metal oxides shifts from the point  $pH=pzc$  (Fig. 1.6), particularly at high electrolyte concentrations there is evidence that one of the ions in solution is a specifically adsorbed ion. A shift of the  $pH(pzc)$  to a more alkaline pH can be attributed to an increase in positive charge of the surfaces as a result of specific adsorption of cations, and thus

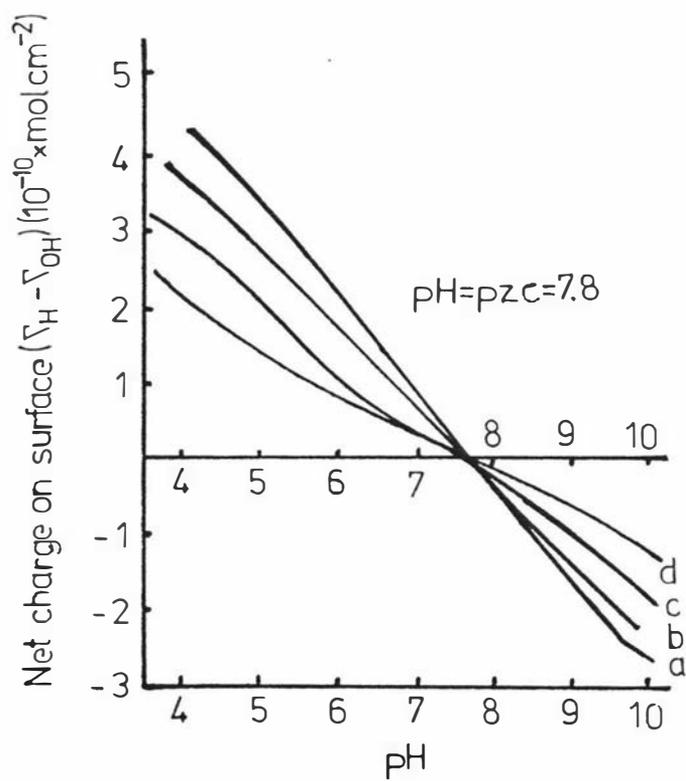


Figure 1.6 pH titration curves for goethite in NaCl solutions of different ionic strengths.

a = 0.01M NaCl;    b = 0.1M NaCl;

c = 1.0M NaCl;    d = 4.2M NaCl.

requiring that more  $\text{OH}^-$  ions must be adsorbed to restore the pzc.

#### 1.4.2.5 Iso-electric point of hydrous oxide surfaces

The pH at which the density of positive sites is equal to the density of negative sites and hence net surface charge is zero, is called the iso-electric point of the surface or pH (iep) (Parks, 1967).

The pH (iep) of a surface arises solely from interaction of  $\text{H}^+$  ions,  $\text{OH}^-$  ions, the solid and water alone (Parks, 1967), and when no other ions are specifically adsorbed the diffuse layer charge depends only on surface charge such that:

$$\text{pH(iep)} = \text{pH(pzc)}$$

Surface charge,  $\delta$ , is negative if pH is greater than pH(iep) and positive if the pH is lower than pH(iep). In general, specific adsorption of cations shifts the point of zero charge, i.e., pH(pzc) to more basic values (Parks, 1967).

#### 1.4.2.6 Points of zero charge in soil components

There is no fixed pH (pzc) for oxides or hydrous oxides (Parks, 1965), the value obtained varying according to the purity, origin, degree of crystallinity and hydration of the sample. From a survey of the literature Ryden (1975) found that pH(pzc) for Fe and Al oxides and hydrous oxides ranged between pH 8.0 and 9.5 with the aluminium-containing oxides tending towards the higher pH values compared to the iron-containing ones.

Thus, at normal soil pH values (acidic to neutral) one would expect hydrous Fe and Al oxides to be positively charged. Silica gels with a pH(pzc) of around 3.0 (Hope, 1977) are expected to be negatively charged at normal soil pH values. However, since hydrous oxides in soils are likely to occur as mixtures of more than one component as opposed to the

simple synthetic laboratory-type hydrous oxides, and because specific adsorption results in a shift of the pzc, it would not be surprising to find major discrepancies between pH(pzc) of natural and synthetic forms.

Fe and Al gel systems admixed with silica and organic matter (Mattson et al., 1950) are probably the rule rather than the exception in soils (Mattingly, 1975). The pH(pzc) of such systems would likely be very different from that of the pure components.

#### 1.4.3 Forms of Zn and Cd ions in solution

To assist with an understanding of the mechanisms of adsorption of Zn and Cd onto mineral or organic surfaces, it is necessary to consider the speciation of soluble forms. In aqueous solutions there are several possible soluble species of Zn and Cd and the predominant ones are discussed below.

##### 1.4.3.1 Evidence for existence of complex ions of Zn and Cd in aqueous solution

The marked similarity between the solution chemistry of Zn and Cd is a further manifestation of their close relationship on the periodic table (Cotton and Wilkinson, 1966) i.e., Zn and Cd are both in Group IIB and are both transition metals, hence Zn and Cd tend to form the same type of complex ions in solution.

Complex ions are defined as "finite groups of atoms, linked by predominantly covalent bonds which remain separate entities in solution, and have properties different from those of their constituents" (Barnard, 1965). Zn and Cd can form important complexes with hydroxyl and chloride ions.

Lindsay (1972) proposed that in the absence of other complexation reactions at pH below 7.7 the predominant soluble species in equilibrium

with soil Zn is  $Zn^{2+}$  (Fig. 1.7), while at higher pHs the neutral species,  $Zn(OH)_2^0$  (aq.) predominates (Lindsay, 1972). The zincate ion,  $Zn(OH)_4^{2-}$  forms only at higher pHs ( $pH > 9$ ) and is not included in Fig. 1.7 (Lindsay, 1972).

Complex ions are formed by both Zn and Cd, but the equilibrium constants, reported in the literature, vary widely (Cotton and Wilkinson, 1966). All four chloride complexes (i.e.,  $ZnCl^+$ ,  $ZnCl_2^0$ ,  $ZnCl_3^-$ ,  $ZnCl_4^{2-}$ ) of Zn and Cd are possible, with the Cd complexes being more stable than the respective Zn complexes (Cotton and Wilkinson, 1966). In an aqueous solution of  $ZnCl_2$ , the complex ion species present are  $Zn(H_2O)_6^{2+}$ ,  $ZnCl^+(aq.)$ ,  $ZnCl_2^0(aq.)$  and  $ZnCl_4(H_2O)_2^{2-}$  (Cotton and Wilkinson, 1966). The relative importance of the different chloro-complexes are shown in Fig. 1.8 (Horne et al., 1957) which shows that at the  $Cl^-$  concentrations commonly used in adsorption experiments (i.e., 0.01-0.1M NaCl matrix solutions) the divalent cation predominates in solution.

Formation constants for the species present in solution indicate that for Zn, neither chloro-complexes (Horne et al., 1957) nor hydroxy complexes (Lindsay, 1972) are likely to predominate in solution. The major form of Zn being the hydrated divalent  $Zn^{2+}$  cation (Irish et al., 1963). Formation constants for both chloro- and hydroxy species of Cd are greater than those for Zn (Cotton and Wilkinson, 1966) and these complex ions would therefore be expected to be more abundant.

Total Zn adsorption by goethite (positively charged at pH 5.0 - 7.5) was found to be greater in an NaCl matrix ( $10^{-1}M$ ) than in an  $NaClO_4$  matrix ( $1.5 \times 10^{-1}M$ ) (Bar-Yosef et al., 1975). This finding was attributed to an adsorption of the complex  $ZnCl^+$  ion in the NaCl matrix. The ratio  $\frac{ZnCl^+}{Zn_{TOTAL}}$  was approximately 0.3 to 0.05 for the NaCl and  $NaClO_4$

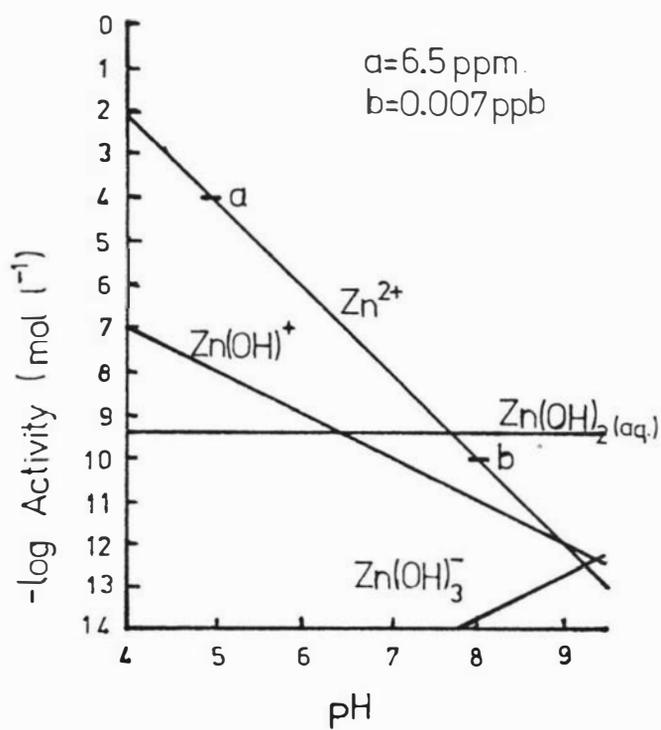


Figure 1.7 Soluble Zn species in solution in equilibrium with adsorbed Zn.

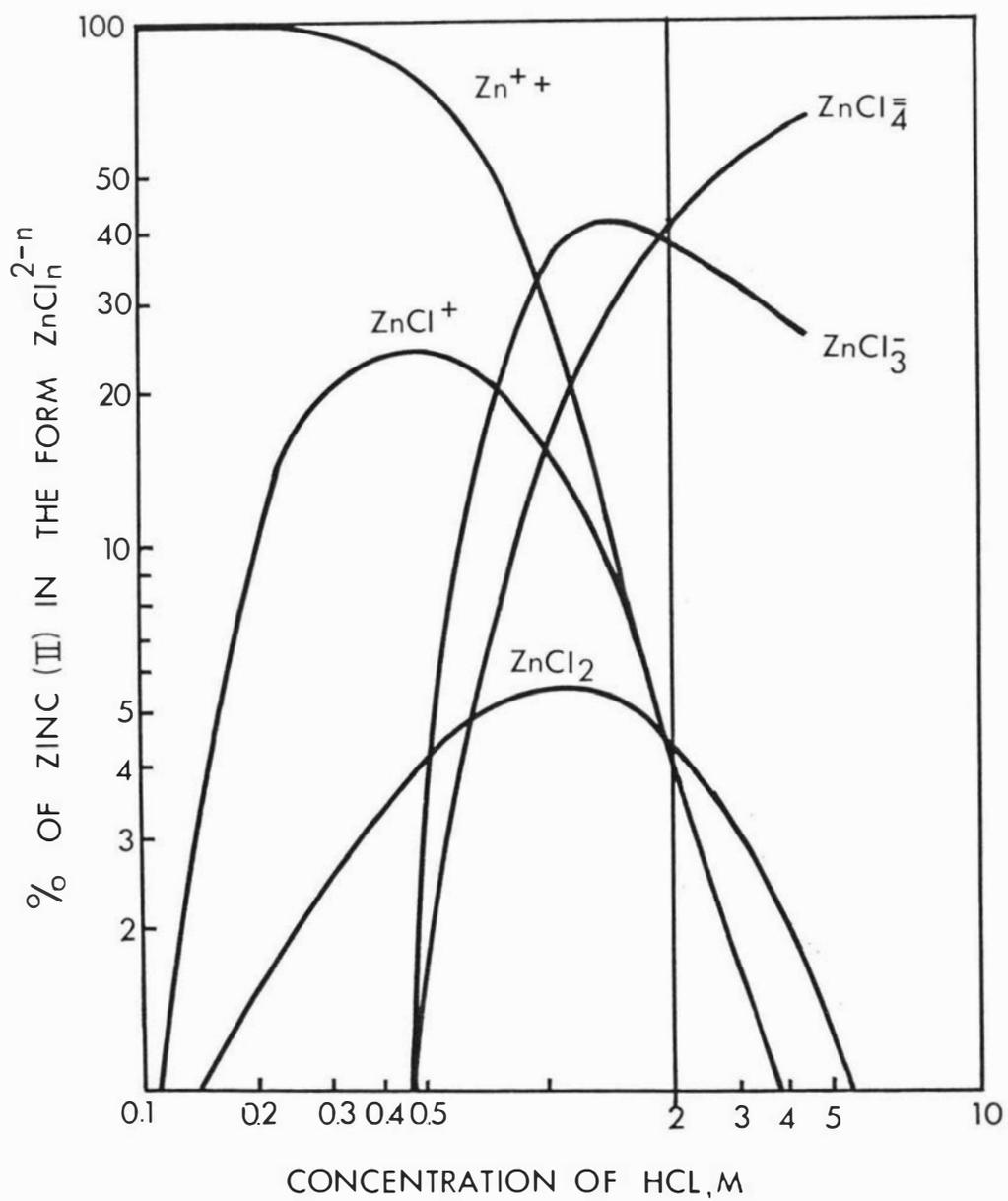
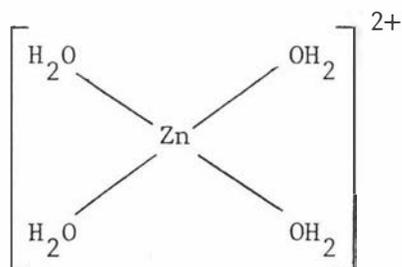


Figure 1.8 Zinc speciation in chloride media.

matrices, respectively, but in both systems the divalent  $\text{Zn}^{2+}$  ion was the major Zn species present. The greater adsorption of  $\text{ZnCl}^+$  in the NaCl matrix was attributed to a higher adsorption energy for the  $\text{ZnCl}^+$  ion (Bowden, 1974) arising, at least partly, from the smaller electrostatic repulsion between the positively-charged goethite surface and the adsorbing ions. Adsorption of Zn, as the monovalent  $\text{ZnCl}^+$  ion, by Al and Fe hydrous oxides has also been proposed by Kalbasi et al., (1978) who found that the mole ratios of protons released to Zn ions adsorbed ranged between 1 and 2, with actual values observed being non-integer numbers. A small uniform uptake of  $\text{Cl}^-$  which was not pH dependent, unlike Zn uptake, was also detected. To explain this data two adsorption mechanisms were proposed, one involving the strong affinity of the surface for monovalent  $\text{ZnCl}^+$ , with one  $\text{H}^+$  ion released per Zn adsorbed, the second mechanism involving uptake of divalent  $\text{Zn}^{2+}$  with concomitant release of two protons per Zn adsorbed.

The complex ion  $\text{Zn(OH)}^+$  can also be specifically adsorbed by hydrous oxides (James and Healy, 1972; Bowden et al., 1973; Bar-Yosef et al., 1975). However, between pH 4.0 and 7.0 this hydroxy ion constitutes a minor fraction of the total soluble Zn (Lindsay, 1972). Also at the concentrations of the  $\text{Cl}^-$  ion in the matrix solutions most commonly used for adsorption studies, the monovalent  $\text{ZnCl}^+$  ion will also be a minor species (Bar-Yosef et al., 1975; Kalbasi et al., 1978). Thus the divalent species,  $\text{Zn}^{2+}$  (aq.) and  $\text{Cd}^{2+}$  (aq.) are thought to be the major species involved in adsorption reactions with hydrous oxides under conditions most commonly encountered in soils (Stanton and Burger, 1969; Hahne and Krootjne, 1973; Gadde and Laitinen, 1974; Forbes et al., 1976; Kinniburgh et al., 1976). Since Zn has a co-ordination number of four (Barnard, 1965), the hydrated  $\text{Zn}^{2+}$  ion in aqueous solution can be depicted as follows:



Data obtained for the adsorption of Zn and Cd by hydrous oxide and soil surfaces can be mathematically treated to obtain descriptive parameters, such as binding energies of the cations to the surface, and adsorption maxima. One such method of treating data is by using adsorption isotherms.

#### 1.4.4 Adsorption isotherms

An adsorption isotherm is constructed by plotting the amount of Zn (or Cd) adsorbed onto a surface against the equilibrium solution concentration of Zn (or Cd) under conditions of constant temperature.

Adsorption isotherms can be broadly classified into four main types (Giles et al., 1960) determined by their initial slopes. The types are S, L (Langmuir), H (high affinity) and C (constant partition) (Fig. 1.9). The L-type isotherm appears to most often describe Zn and Cd adsorption by hydrous oxides and soils. This isotherm type is the one used by Langmuir to model gaseous adsorption, and allows for monolayer coverage of the surface at the limit of adsorption.

Some experimental features of the adsorption of Zn and Cd cations on hydrous oxide, clay and soil surfaces are summarised below. Commonly:

- a) Adsorption isotherms are generally of the L-(Langmuir) type, as defined by Giles et al. (1960) (Bowden et al., 1973; Bar-Yosef et al., 1975; Shuman, 1976), e.g., Fig. 1.9.
- b) Adsorption generally increases as pH increases, thus the amounts

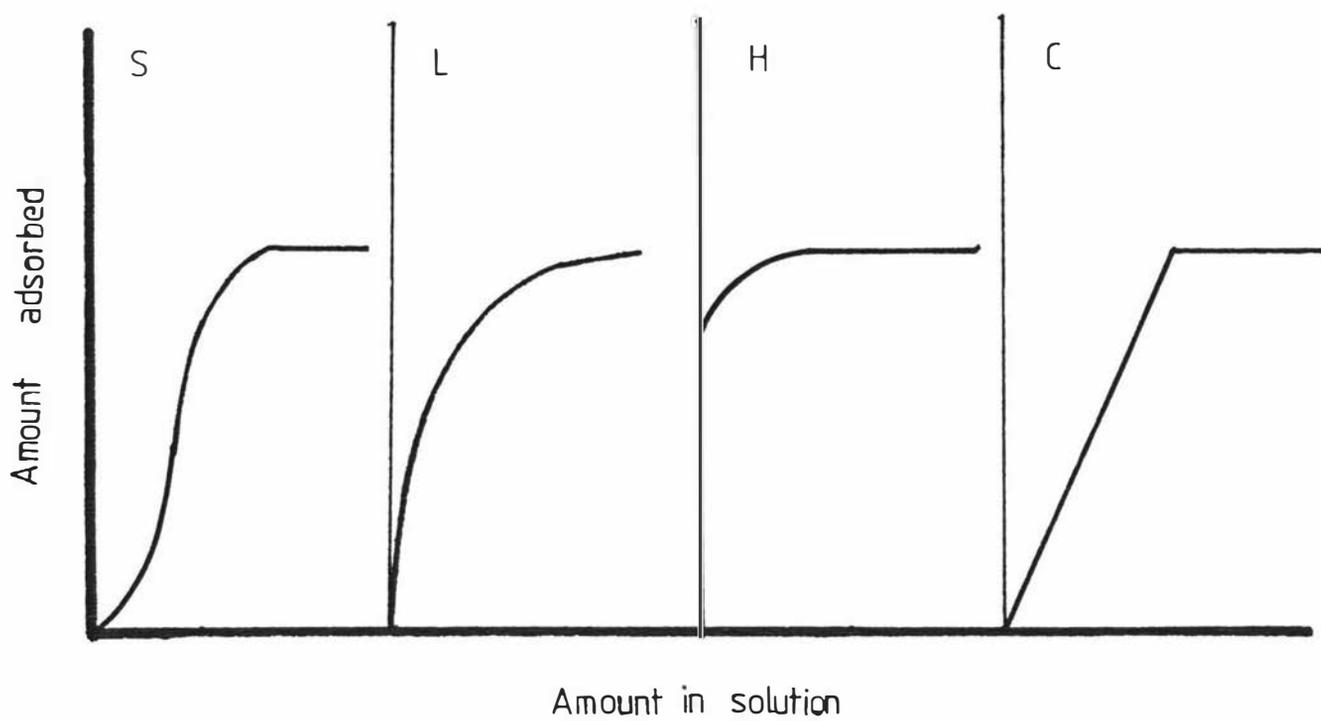


Figure 1.9 Classification of isotherms for solute adsorption  
(Giles et al., 1960).

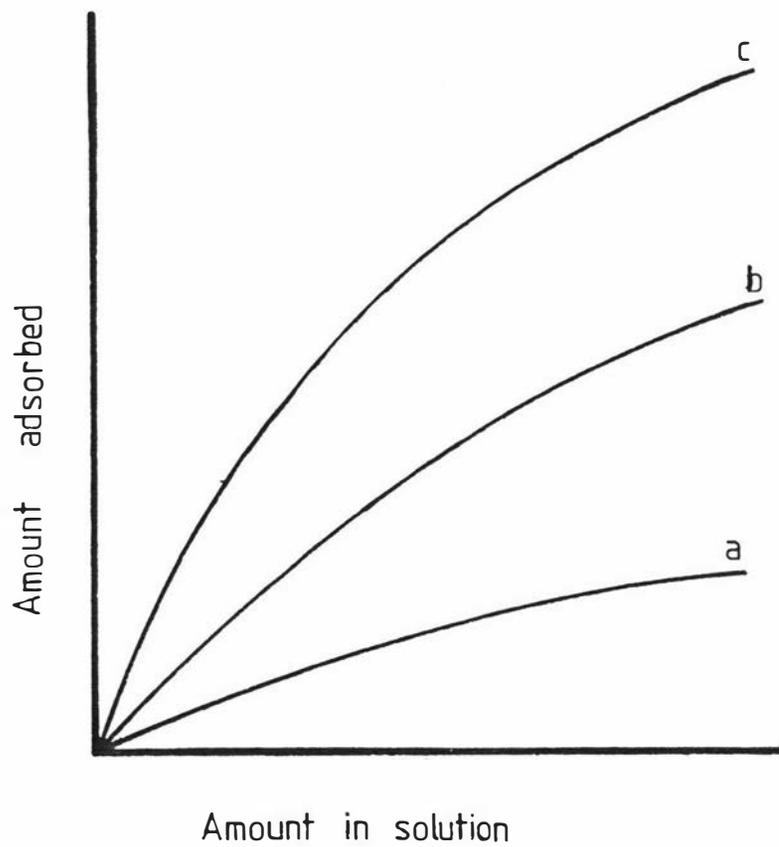


Figure 1.10 Effect of pH on amount of metal ion adsorbed by surfaces of hydrous metal oxides  
a = pH 5.0; b = pH 6.0; c = pH 6.50.

of Zn and Cd adsorbed, at fixed equilibrium concentrations, increase with increasing pH as shown below (Bowden et al., 1973; Bar-Yosef et al., 1975; Bolland et al., 1977; Kalbasi et al., 1978) e.g., Fig. 1.10.

- c) In many cases, adsorption is not completely described by a single Langmuir model. A multiple Langmuir model is sometimes used i.e., the experimental data are only described using two or more Langmuir equations (Levine and Smith, 1971; Bowden et al., 1973; Bar-Yosef et al., 1975).
- d) Specific adsorption of Zn and Cd divalent cations generally leads to an increase in positive surface charge on the adsorbent (Bowden et al., 1973).

A number of models have been formulated to mathematically characterise experimental findings for the adsorption of Zn and Cd. The two most commonly used in soil studies are the Freundlich and Langmuir models.

#### 1.4.4.1 The Freundlich model

This model (Freundlich, 1926) was proposed to describe the adsorption of ions or molecules from a liquid onto a solid surface.

The general mathematical form for the relationship is:

$$\frac{x}{m} = Kc^{\frac{1}{n}} \quad (1.7)$$

Where, x and m are the masses of adsorbate and adsorbent respectively, c is the equilibrium concentration of the adsorbing ion in solution and K and n are empirical constants. The equation is most commonly used in its logarithmic form, i.e.,

$$\log \frac{x}{m} = \frac{1}{n} \log C + \log K. \quad (1.8)$$

For data conforming to the Freundlich model a plot of  $\log \frac{x}{m}$  against  $\log C$  gives a straight line whose slope is numerically equal to  $\frac{1}{n}$  and intercept to  $\log K$ . However, a plot of  $\log \frac{x}{m}$  against  $\log C$  often gives a curve rather than a straight line (Barrow, 1978) possibly due to the transformation of data for the logarithmic plot weighting the values of low concentration more highly than the precision of these values justifies and also to the difficulty in adequately determining the amount of adsorbate already present on the surface (Barrow, 1978). Major limitations of this model are that no adsorption maximum can be found, i.e., adsorption increases continuously as equilibrium concentration increases, and that the model was developed empirically. However, the model has been derived for dilute solutions by combining an expression for the free energy of adsorption on the surface with the Gibbs adsorption isotherm (Kipling, 1965).

#### 1.4.4.2 The Langmuir model

The Langmuir equation was derived theoretically by Langmuir (1918) for adsorption of gases by solids. Originally, an assumption was made that the adsorbent possessed a number of uniform adsorption sites for which the heat of adsorption of the adsorbed species does not vary from site to site i.e., each site has an equal probability of participating in the adsorption. Maximum adsorption occurs when the surface is covered with a monolayer of the adsorbate. Langmuir developed the model from a consideration of the behaviour of gases on solid surfaces. Of the gas molecules colliding with the surface, a proportion adhere and the remainder rebound into the gas phase. Intermolecular forces are assumed to be negligible, and the heats of adsorption are the same for all sites being unaffected by site filling and adsorption is monolayer (thus gas molecules striking gas molecules

adsorbed on the surface rebound). If  $\theta$  is the fraction of the surface area covered by adsorbed molecules at any time, the rate of desorption from the surface is proportional to  $\theta$  or equal to  $k_d\theta$ , i.e.,

$$R_d = k_d\theta \quad (\text{Moore, 1962}) \quad (1.9)$$

where  $k_d$  is a constant at constant T.

The rate of adsorption  $R_a$ , at the surface is proportional to the fraction of surface that is unoccupied,  $1-\theta$ , and to the rate at which molecules strike the surface, which varies directly with the gas pressure at a given temperature. Thus, the rate of adsorption is given as:

$$R_a = k_a P(1-\theta) \quad (\text{Moore, 1962}) \quad (1.10)$$

At equilibrium, when the rate of desorption is equal to the rate of adsorption:

$$k_d\theta = k_a P(1-\theta) \quad (1.11)$$

and solving equation (1.11) for  $\theta$  gives the Langmuir equation:

$$\theta = \frac{k_a P}{k_d + k_a P} = \frac{bP}{1+bP} \quad (1.12)$$

where  $b$  is the ratio of rate constants  $k_a/k_d$ , sometimes called the adsorption coefficient.

To extend this model to the adsorption of ions from solution,  $P$  can be replaced by  $C$  (the equilibrium solution concentration of the adsorbate) and  $\theta$ , the fractional surface coverage by  $x/b$  (where  $x$  is the amount of solute adsorbed and  $b$  the amount adsorbed at full monolayer coverage, i.e., the adsorption maximum) giving:

$$\frac{x}{b} = \frac{kc}{1+kc} \quad (1.13)$$

The conditions of uniform surface for adsorption and a constant free energy of adsorption (i.e., implying no interaction between adsorbed species) are implicit. For this to be true, the heat of adsorption, which is the most important factor in  $k$  must also be constant. Whilst it may not be easy to assume a constant heat of adsorption for a soil or hydrous oxide system, Brunauer et al. (1967) have shown that this can hold true without having an energetically uniform surface on which adsorbed molecules do not interact with each other. At low surface coverages (i.e., low  $\theta$ ) adsorption occurs on sites possessing the highest energies. Thus, as surfaces are generally energetically heterogeneous, a plot of heat of adsorption against  $\theta$  is usually a decreasing function. Lateral interaction energies between adsorbed molecules increase the heat of adsorption, and as the number of molecules adsorbed increases, the lateral interactions increase, and contribute to the heat of adsorption. Thus, a plot of heat of adsorption due to lateral interactions against  $\theta$  is an increasing function. These two opposing effects, in certain cases, compensate each other, making the overall heat of adsorption approximately constant.

Equation (1.13) given above can be written in the following linear forms:

$$\frac{c}{x} = \frac{1}{kb} + \frac{c}{b} \quad (1.14)$$

$$\frac{1}{x} = \frac{1}{kbc} + \frac{1}{b} \quad (1.15)$$

$$x = b - \frac{x}{kc} \quad (1.16)$$

Values of  $b$  (adsorption maximum) and  $k$  (related to binding energy) can be obtained from the intercepts and slopes of the appropriate graphs of the experimental data using one of these relationships. The equations (1.14) and (1.16) are more suited to higher equilibrium

concentrations of ions in solution and for data extending over a wide range of concentrations. Equation (1.15) is particularly suitable for very low equilibrium concentrations and for data covering a narrow range of concentration, owing to the reciprocal nature of the equation.

The standard free energy of adsorption can be obtained from the relationship:

$$\Delta G = -2.303 RT \log k \quad (1.17)$$

Calculation of free energies of adsorption for soils and oxides provides a means of comparing bonding strengths between different soils and soil components within the confines of the assumptions used in the derivation of the theory.

Where it is necessary to invoke the existence of more than one type of binding site in the adsorption process (e.g., as proposed by Bowden et al., 1973) the different sites can be treated as separate components in equilibrium with a common solution phase. Each group of sites is then assumed to have a particular adsorption maximum (b) and a particular binding energy. This method has been used (Shuman, 1975) for studying Zn adsorption by soils.

The use of the Langmuir approach for characterising Zn or Cd adsorption on adsorbents such as Fe gel and soils allows calculation of binding energies and adsorption maxima, unlike the situation with the Freundlich model. The Langmuir model, unlike the Freundlich equation, is not empirically based, but to apply the Langmuir model to describe the adsorption of ions from solution a number of assumptions must be kept in mind. These may be difficult to justify in soil systems. Particular assumptions include (Stumm and Morgan, 1970):

- a) monolayer coverage
- b) adsorption of cations at fixed sites

- c) immobility of adsorbate and
- d) adsorption energy independent of surface coverage.

Nevertheless, the Langmuir model has been used for Zn and Cd adsorption by soils and soil components (Udo et al., 1970; John, 1972; Page et al., 1972; Shuman, 1975; Levi-Minzi et al., 1976; Singh and Sekhon, 1977). It is arguable however, whether the assumptions (a) to (d) above are acceptable, over the whole range of adsorption from trace concentrations to saturation of soil adsorption sites (Navrot et al., 1978).

The conformity of adsorption data to a single Langmuir equation (Udo et al., 1970; John, 1972; Levi-Minzi et al., 1976; Singh and Sekhon, 1977) has been interpreted as evidence that a single adsorption reaction operates for Zn and Cd in soils. However, these studies often cover a wide concentration range. For example, Singh and Sekhon (1977) used a single Langmuir equation to describe Zn adsorption by soils over the concentration range 76-1529  $\mu\text{mol Zn l}^{-1}$ . John (1972) did likewise for the adsorption of Cd over the concentration range 8.9-890  $\mu\text{mol Cd l}^{-1}$ .

The applicability of the Langmuir approach to adsorption data has been criticized by Veith and Sposito (1977) and Barrow (1978) especially when the adsorption data cannot be fitted to a single Langmuir equation. Often, at low concentrations, e.g., 0-0.33  $\mu\text{mol Zn l}^{-1}$ , the use of more than one Langmuir equation is required to adequately describe adsorption data (Shuman, 1975; Shukla and Mittal, 1979). Shuman (1975) used regression analysis to split the isotherms for adsorption of Zn by soils into two regions, each region being described by a separate Langmuir equation. Shukla and Mittal (1979) resolved Langmuir isotherm data into two linear components after excluding data points

representing concentrations in solution below  $10.0 \mu\text{mol Zn l}^{-1}$ .

It is noteworthy that the range of  $k$  values for the adsorption of Zn (Shuman, 1975; Singh and Sekhon, 1977) and Cd (John, 1972; Levi-Minzi et al., 1976; Singh and Sekhon, 1977a; Navrot et al., 1978) are similar, for each metal, considering that the isotherms were determined on soils from widely differing geographical areas.

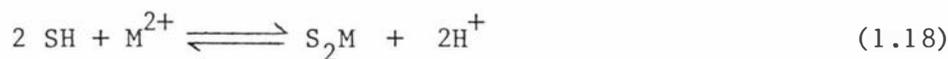
#### 1.4.5 Proposed models and mechanisms of Zn and Cd

##### adsorption by hydrous oxides

Several models and mechanisms have been proposed to describe Zn and Cd adsorption by hydrous oxides. The use of the simple Langmuir model, to describe Zn and Cd adsorption does not allow for changes in surface charge accompanying the adsorption of cations on surfaces such as Fe gels and soils (Bowden et al., 1973). Adsorption of cations, at constant pH, increases surface charge thus rendering subsequent adsorption more difficult, due to electrostatic repulsion. In this way, it is postulated that the affinity of the surface decreases as adsorption increases. The models of Bowden et al. (1973) and Bar-Yosef et al. (1975) incorporate this decrease in the affinity of the surface and aim to describe not only the effects on adsorption of changes in cation concentration, but also effects of a change in pH and concentration of supporting electrolyte (Barrow, 1978). The models are complex; requiring seven parameters to describe Zn adsorption. Three of these parameters relate to the charge characteristics of the surface and may be determined from titration curves, one is an electrical capacitance term, and the remaining three are the adsorption maximum and two affinity constants for the two ionic species assumed to be present between pH 5.0 and 7.0, i.e.,  $\text{Zn}^{2+}$  and

$\text{Zn}(\text{OH})^+$  (Bowden et al., 1973) and  $\text{Zn}^{2+}$  and  $\text{ZnCl}^+$  (Bar-Yosef et al., 1975). Methods for generating adsorption curves to describe adsorption data, using the model of Bowden et al. (1973), involve complex manipulations to enable the model to describe experimental data and the seven required parameters have not yet been determined for soils. Using this model Bowden et al. (1973) did not need to postulate two or more different surfaces or surface sites with differing affinities (Shuman, 1975; Ryden et al., 1977) to describe the adsorption data, and were able to propose a common adsorption maximum at all pHs and ionic strengths. The model has not, however, been applied to soils and additionally the cation adsorption model is in marked contrast to other models (Kalbasi et al., 1978) which require the existence of two populations of sites to explain the experimental data.

Using a much more generalised approach, Forbes et al. (1976) envisaged the surface reaction for divalent cation adsorption on goethite as:



where M is the free metal cation, SH the uncharged adsorption sites, greatly in excess of heavy metal cations adsorbed, and  $\text{S}_2\text{M}$  the adsorbed metal cations. The equilibrium constant for reaction (1.18) is given by

$$K = \frac{(\text{S}_2\text{M})(\text{H}^+)^2}{(\text{M}^{2+})(\text{SH})^2} \quad (1.19)$$

Equation (1.19) can be rearranged to the form:

$$[\text{S}_2\text{M}]^{1/2} = \frac{K \cdot [\text{M}^{2+}]^{1/2}}{[\text{H}^+]} \quad (1.20)$$

with square brackets indicating concentrations ( $\text{mole l}^{-1}$  for  $\text{M}^{2+}$  and  $\text{H}^+$ , and  $\mu\text{mol g}^{-1}$  for  $\text{S}_2\text{M}$ ) and

$$K' = \frac{\gamma_M (\text{SH})^2 K}{\gamma_H \gamma_{S_2M}}$$

where  $\gamma$  = activity coefficient and at constant ionic strength  $\gamma_M$  and  $\gamma_H$  are constant.

Equation (1.20) can then be written in the logarithmic form:

$$-\log K' = \text{pH} - \frac{1}{2}\text{pM} - \frac{1}{2}\log [S_2M] \quad (1.21)$$

with the quantity  $(\text{pH} - \frac{1}{2}\text{pM} - \frac{1}{2}\log [S_2M])$  being related to the relative affinity of the goethite surface for any given metal cation and for  $H^+$  ions. It was found that goethite had a lower relative affinity for Cd than for Zn, but higher affinity for Pb and Cu, with the general order of preference being:



In the description of adsorption in terms of the affinity of the oxide for  $H^+$  and metal cations (Forbes et al., 1976) the adsorbed metal ions were considered to form bonds with hydroxyl groups which caused deprotonation of the hydroxyl group and release of  $H^+$  ions on adsorption of metal ions.

#### 1.4.5.1 Proton release in relation to cation adsorption

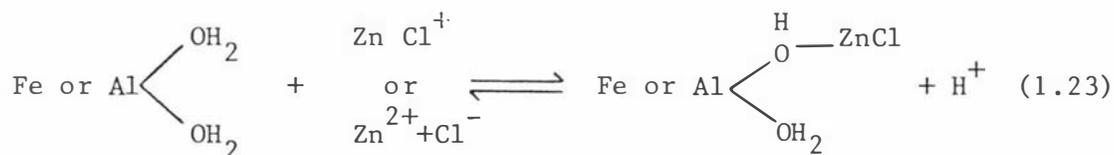
When cations are adsorbed onto hydrous metal oxides, the surface groups, M-OH, may be treated as complex-forming species (Stumm and Morgan, 1970). This complex formation involves both the coordination of surface groups with solute cations and the release of protons from hydroxyl groups. The tendency for complex formation of cations increases with increasing pH and increasing negativity of the surface groups.

The adsorption of ions such as Zn and Cd onto hydrous oxide surfaces is usually accompanied by proton release (Quirk and Posner, 1975; Forbes et al., 1976; Kalbasi et al., 1978). The mole ratios of  $H^+$

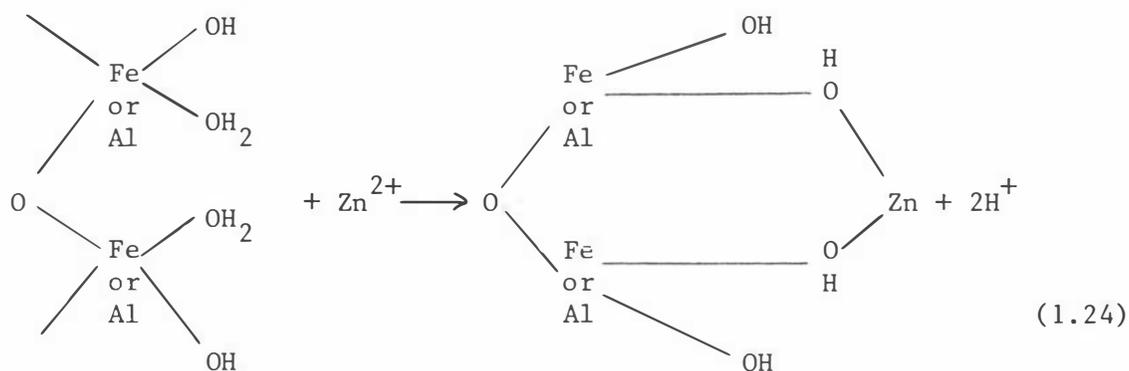
released/ $M^{2+}$  adsorbed on hydrous oxide surfaces was 2.2 for Zn and Cd (Forbes et al., 1976). The adsorption reaction proposed by Forbes et al. (1976) for cations on neutral surfaces was given in equation (1.18) and shows release of two protons for every Zn or Cd ion adsorbed.

Kalbasi et al. (1978) concluded that because  $H^+$  ions were released from Al and Fe oxides, and because Zn retention was pH dependent, surface aquo- and/or hydroxo- groups were involved in the adsorption reaction as proposed by Forbes et al. (1976).

However, Kalbasi et al. (1978) found that the mole ratios of  $H^+$  desorbed to Zn ions adsorbed was less than 2.0, actual values ranging from 1.53 to 1.94 depending on pH and amount of cation adsorbed. They suggested that either the adsorption mechanism was more than a simple stoichiometric replacement of  $H^+$  by the  $Zn^{2+}$  at surface aquo- or hydroxo- groups which would release two protons for each Zn ion adsorbed, or that  $Zn^{2+}$  was not the adsorbing species. As  $Cl^-$  ions were the only major anions present in the system, the adsorption of  $Cl^-$  ions was measured, and a small uniform adsorption of  $Cl^-$  ions, unaffected by pH, was found. The mole ratio of  $Cl^-$  to  $Zn^{2+}$  adsorbed decreased as pH increased, while the mole ratio of  $H^+$  released to  $Zn^{2+}$  adsorbed increased with increasing pH. This evidence, together with desorption data concerning the exchangeability of adsorbed Zn with  $Ba^{2+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  led them to conclude that two adsorption mechanisms appeared to be operating. One mechanism whereby  $Zn^{2+}$  and  $Cl^-$  ions, operating at low pHs, probably bind to surface aquo- groups. Zn and Cl ions may be adsorbed as the monovalent  $ZnCl^+$  or as separate ions. Kalbasi et al. (1978) found that Zn adsorbed in this way, i.e., as  $ZnCl^+$ , could be displaced (or desorbed) by Ba, Ca and Mg ions. The following mechanism was postulated:



The other mechanism involves the release of two protons for every  $\text{Zn}^{2+}$  adsorbed. The amount of this  $\text{Zn}^{2+}$  adsorbed increased with pH. The Zn adsorbed by this mechanism could not be displaced by Ba, Mg or Ca ions. The mechanism given was the same as that proposed by Quirk and Posner (1975) with an oxygen bridge and ring structure viz.,



The adsorption of Zn was represented as a bridging ion between the two "neutral" sites (equation (1.24)), i.e.,  $\text{Fe} \begin{cases} \text{OH} \\ \text{OH}_2 \end{cases} \Big| \text{O}$ . However, Zn could be adsorbed by two positive sites, two negative sites or by one positive and one neutral site. As pH increases, the number of positive sites decrease, and the number of neutral sites (as depicted in equation (1.24)) increase. The mechanism proposed agrees with the experimental finding that the amount of Zn adsorbed increases with increasing pH. The adsorption mechanism is likened to a growth or extension of the surface, which is consistent with the lack of reversibility of this adsorption. The protons released are thought (Quirk and Posner, 1975) to arise from the aquo- surface groups rather than hydroxo- groups because aquo- groups are more abundant at pH values below the IEP of the oxide.

Kinniburgh et al. (1976) suggested that specific adsorption of  $Zn^{2+}$  and  $Cd^{2+}$  involved a hydroxyl ion/metal ion interaction, the hydroxyl ion being derived either from the surface or from hydrolysis of water. Whereas the initial adsorption probably involved coordination of the divalent cation to two or even three surface -OH groups, it was suggested that on aging and consequent structural rearrangement of the gels, incorporation of certain ions, e.g., Zn and Cd into the aged gel may occur.

Stanton and Burger (1970) also suggest that Zn adsorption involved surface -OH groups. They found that when Al and Fe hydrous oxides were ignited at  $600^{\circ}C$  for eight hours, the Fe gel lost its ability to adsorb Zn, while Al gel did not. It has been shown that hydrous Fe oxide can lose water and -OH groups when heated, whereas hydrous Al oxide does not (Kelly and Miggely, 1943; Wild, 1950).

The pH dependence of Zn and Cd adsorption by hydrous Fe and Al oxides, as demonstrated by Kalbasi et al. (1978), has also been demonstrated in many other studies (Stanton and Burger, 1970; Bar-Yosef et al., 1975; Quirk and Posner, 1975; Kinniburgh et al., 1976). At pH values below 4.5 virtually no Zn or Cd adsorption occurs, and for pH values greater than 7.0 almost total adsorption of added Zn and Cd is found. The adsorption of Zn and Cd increases rapidly with increasing pH over the range of pH 5.0 to 7.0.

Similarly, investigations by Loganathan et al. (1977) and Gadde and Laitinen (1974) into the adsorption of Zn and Cd have been carried out on short-range order hydrous oxides of Fe, Mn and Al. Studies on hydrous Mn oxide (Loganathan et al., 1977) and hydrous oxides of Mn and Fe (Gadde and Laitinen, 1974) have shown the pH-dependent adsorption of Zn and Cd, together with hydrogen ion release as adsorption proceeds.

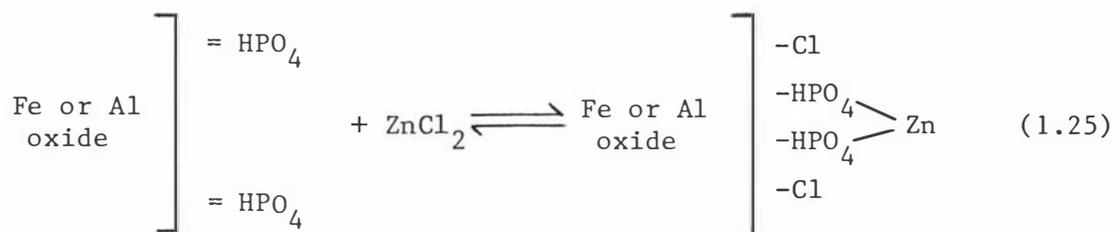
Gadde and Laitinen (1974) observed a linear increase in Zn and Cd adsorption by hydrous Fe (III) or Mn (IV) oxide with increasing pH over the range pH 2 to 6. A concomitant proton release occurred which for hydrous Mn oxide at an initial pH of 6 was found to be 1.1 H<sup>+</sup> ions per Cd ion, and 1.3 per Zn ion, adsorbed. No explanation of the proton release data or proposed mechanisms for Zn and Cd adsorption were given.

Loganathan et al. (1977) using hydrous Mn oxide, found a sharp increase in the amount of Zn adsorbed as pH increased from 6.5 to 7.0. Below pH 5.0 two protons were released for every Zn adsorbed. Two possible mechanisms were suggested for the sharp increase observed in Zn adsorption between pH 6.5 and 7.0:

- (a) either, the formation of a significant amount of the monovalent Zn(OH)<sup>+</sup> species, which may exhibit a strong affinity for the surface,
- (b) or, "precipitation" of Zn(OH)<sub>2</sub> at the hydrous oxide/aqueous interface. At this surface they found a relatively large concentration of Zn, indicative of the formation of a surface hydroxide precipitate.

Zinc adsorption increases with increasing pH and increasing phosphate saturation of Fe oxide gel (Stanton and Burger, 1970).

The effect of phosphate was explained as follows:



Thus, in this postulated mechanism, Zn is adsorbed onto HPO<sub>4</sub><sup>2-</sup> ions which are bonded to the hydrous oxide.

Zinc adsorption at pH values greater than pH 5.00, but still well below the pH p.z.c. of goethite, can occur even when the surface is positively charged and in the presence of  $\text{Na}^+$  ions (Bolland et al., 1977). Addition of P to goethite suspensions increased Zn adsorption, and the addition of Zn, in turn, increased P sorption. These effects were explained as:

- (a) An increase in positivity of the surface accompanying Zn adsorption resulting in increased attraction for the charged P ions, leading to increased P sorption (Bolland et al., 1977) and/or
- (b) formation of a surface complex between Zn and P similar to that proposed by Stanton and Burger (1970) with Al and Fe gels (Bolland et al., 1977).

#### 1.4.6 Adsorption of Zn and Cd by clay minerals

Maes and Cremers (1975) noted that Zn adsorption, by montmorillonite, at high saturations, was neither stoichiometric nor reversible and so could not be considered as simple ion-exchange and a more specific mechanism was indicated. De Mumbrum and Jackson (1956) proposed Zn binding to structural hydroxyl groups of clay minerals.

The adsorption of Cd by montmorillonite, at concentrations of from  $0.13\text{--}1.07 \mu\text{mol Cd l}^{-1}$ , was investigated by Garcia-Miragaya and Page (1976). Adsorption was attributed to the existence of a number of high affinity sites which selectively adsorb low amounts of Cd ions. It has also been proposed that the hydroxy species of heavy metal cations, such as Zn and Cd, adsorb at edge sites, on montmorillonite and other clay minerals, adjacent to the octahedral layer cations (Tiller, 1968) and further that adsorption (and even precipitation) of Zn on kaolinite and montmorillonite can be caused, in part, by any silica naturally

associated with these clays and providing additional adsorption sites (Tiller, 1967; Tiller, 1968).

Adsorption reactions for both Co and Zn can occur with other expanding or non-expanding 2:1 and 1:1 layer silicates (Tiller and Hodgeson, 1962).

Elgabaly and Jenny (1963) suggested that Zn occupied exchange sites on clay minerals such as montmorillonite, but from more recent work (Nelson and Melsted, 1955; Chatterjee, 1974) it was concluded that a proportion of cations, such as Zn, adsorbed onto clay surfaces was non-exchangeable and that such Zn reacted with structural groups in expanding lattice clay minerals (Chatterjee, 1974). Infra-red adsorption studies (De Mumbrum and Jackson, 1956) showed decreased hydroxyl absorption peaks after reaction with Zn, indicative of replacement of the hydrogen of the hydroxyl group by Zn, adding further support to the mechanism proposed by Chatterjee (1974).

It has also been suggested that some Zn may be 'fixed' by clay minerals which enter through breaks or faults in the lattices. Lattice penetration could lead to ionic substitution within the minerals (Elgabaly, 1959).

It has also been shown that Zn enters hydrated 2:1 clay lattices and on drying becomes physically entrapped in inter-lattice wedge zones (Reddy and Perkins, 1974).

The selectivity of the clay minerals kaolinite, vermiculite and montmorillonite for four heavy metals was found to be in the order  $Zn > Mn > Cd > Hg$  (Stuanes, 1976) with Zn more selectively adsorbed than Cd, as was also the case with goethite (Forbes et al., 1976).

The predominant forms of Zn and Cd ion present within the pH range 4.5-7.5 and normal matrix chloride concentrations of from 0.01M to 0.1M,

are divalent ions viz.  $Zn^{2+}$  and  $Cd^{2+}$  (Stuanes, 1976). The adsorption of Cd by montmorillonite was shown to be greatly reduced in the presence of 0.03M to 0.05M chloride matrix indicating a lower affinity of the adsorbing surfaces for Cd chloride complex ions as compared to divalent Cd ions (Garcia-Miragaya and Page, 1976).

The role of the monovalent Zn complex ion,  $Zn(OH)^+$  (Bower and Truog, 1941) thought to be important in adsorption by clay minerals has since been claimed to be of minor significance in the adsorption of Zn by montmorillonite (Maes and Cremers, 1975). In addition, the contributions of  $Zn(OH)^+$  and  $Zn(OH_2)^0$  under the experimental conditions of acid pHs (2.2 to 2.5) and in a chloride matrix (Bingham et al., 1964) are thought to be of minor importance because of the small amounts of such complexes, compared to the divalent cations, under these experimental conditions.

According to Jenne (1968), the importance of lattice clay minerals for the adsorption of Zn and Cd by soils is small by comparison with the major controlling soil components which are the hydrous oxides of Al, Mn and Fe. Additionally, although a range of different pure layer silicate minerals can be shown to adsorb widely different amounts of cations, the amounts of cations adsorbed by a number of different soils were not very different (Tiller et al., 1963). Hence, although Zn and Cd may be adsorbed onto lattice mineral surfaces and through defects in the lattices, lattice clay minerals do not appear to be a major soil component involved in adsorption of Zn or Cd.

## 1.5 Concluding Remarks

The importance of hydrous Fe and Al oxides in cation adsorption has received considerable attention but there have been few detailed investigations involving comparisons between adsorption by these oxides and by soils. This is so for Zn and Cd where there have been few detailed studies of Zn and Cd adsorption by soils and soil components at the low solution concentrations likely to be encountered in soils.

Although adsorption isotherms may give valuable information on the nature of adsorption reactions, many previous studies obtaining adsorption isotherms for Zn and Cd use unrealistically high final solution concentrations. When the experimental data for these studies is evaluated, adsorption of Zn and Cd appears to occur on a single population of sites suggesting only one adsorption mechanism. Very few studies have obtained Zn and Cd adsorption data at low final solution concentrations and evaluation of this experimental data suggests that two populations of adsorption sites may exist. Clearly, detailed investigation of Zn and Cd adsorption at low final solution concentration must be made.

Hydrous oxide surfaces have been shown to be well characterized and this is useful when investigating mechanisms of Zn and Cd adsorption. However, studies investigating mechanisms of Zn and Cd adsorption by hydrous oxides do not always agree on the nature of the reaction between the hydrous oxide surface and Zn or Cd. For example, studies differ in the number of protons released concomitant with the adsorption of Zn or Cd, leading to different mechanisms being suggested to explain Zn and Cd adsorption.

Little, if any, work investigating adsorption reactions of Zn and Cd in New Zealand soils has been carried out and these reactions, as well

as some of the research areas outlined above are investigated in subsequent Chapters. Four soils, both topsoils and subsoils, were chosen to obtain detailed information of Zn and Cd adsorption and to compare the importance of soil components in Zn and Cd adsorption. The effect of time on Zn and Cd adsorption are investigated to establish reliable experimental conditions for subsequent studies. The Langmuir adsorption equation is used to interpret the experimental adsorption data. Zn and Cd adsorption data for soils and synthetic soil components are compared and similarities and differences are discussed.

The mechanisms of Zn and Cd adsorption on hydrous oxides are investigated based on the implications of the use of Langmuir adsorption equations to describe Zn and Cd adsorption, the effect of pH on Zn and Cd adsorption, and proton release concomitant with Zn and Cd adsorption, the isotopic exchangeability of adsorbed Zn and Cd and the desorbability of Zn.

Synthetic hydrous oxides were used to determine whether or not an absorption reaction occurred along with the adsorption mechanisms proposed previously in the study.

This review showed that Zn and Cd soil levels have been shown to increase due to additions of Zn and Cd from other sources, e.g., superphosphate fertiliser. Although several studies have investigated the addition of Zn and Cd to soils through superphosphate fertiliser addition few, if any, similar studies have been undertaken in New Zealand. The effect of long-term superphosphate fertiliser addition on the Zn and Cd content of soils was investigated using a method for the extraction of low amounts of Zn and Cd from soils developed previously in the study.

## CHAPTER TWO

SOIL DESCRIPTIONS, SOIL PROPERTIES  
AND GENERAL METHODS

2.1 Introduction

Several studies have pointed to the importance of soil composition and properties in determining Zn and Cd adsorption by soils. Relationships between soil composition and properties and Zn and Cd adsorption have been established either by the use of correlation analysis (John, 1971; Shuman, 1975; Levi-Minzi et al., 1976; Shuman, 1976; Udo et al., 1976; Singh and Sekhon, 1977; 1977a; Shah Singh, 1979) or by single component studies using synthetic (model) adsorbents, e.g., Fe gel (Bowden et al., 1973; Bar-Yosef et al., 1975; Quirk and Posner, 1975; Kalbasi et al., 1978). For this study a range of New Zealand soils was chosen to provide a diverse range of potential adsorbents, including many of the major soil constituents known, or suspected, to be important for cation adsorption (e.g., iron oxides - Okaihau soil; allophane - Egmont soil; organic matter - Makerua soil, and crystalline layer lattice silicates - Tokomaru soil). A particular question to be investigated was whether or not a common adsorption mechanism operates for all the soils chosen, regardless of chemical and mineralogical composition.

2.2 Soil Descriptions

Samples of Okaihau gravelly clay, Tokomaru silt loam, Egmont brown loam and Makerua peaty silt loam were collected from areas that had not received a regular history of superphosphate fertiliser

additions. With the exception of Makerua peaty silt loam, samples were taken from the Ah and B horizons. For Makerua peaty silt loam, samples were taken from only the Oh horizon. Samples from the Ah horizons are hereafter referred to as topsoils and the B horizon samples as subsoils. The Oh horizon for Makerua peaty silt loam, as well as being a topsoil was used in this study to represent a material of high organic matter content to contrast with the low organic content of subsoils of the other soils. In many of the comparisons made, the Makerua Oh horizon data is considered along with the results for B horizons, in this study. Subsoils were included, wherever possible, to provide materials with low organic matter (c.f. with topsoils) content so as to minimise any masking effect of organic matter on the adsorption of Zn and Cd by the inorganic components. This approach was considered preferable to the alternative of ignition of soils to remove organic matter, which could have been an alternative strategy. Selected site data and information pertaining to the soils used in this study are shown in Table 2.1 and discussed below.

#### 2.2.1 Soil and site information

*Okaihau gravelly clay* was sampled at 0-10 cm (Ah horizon) and 20-40 cm (Bcs horizon) from a site near Okaihau, Northland at an altitude of 268m a.s.l. on a flat plateau which receives an average annual rainfall of 1650mm (New Zealand Soil Bureau, 1968). The vegetation at the site is Manuka (*Leptospermum scoparium*), Hakea species (mainly *Hakea sericea*), gorse (*Ulex europaeus*) and bracken fern (*Pteridium aquilinum* var. *esculentum*), which superceded the original native podocarp - broadleaf forest. The principal clay minerals are kaolinite, gibbsite and free crystalline Fe oxides. Selected soil properties are shown in Table 2.4.

Table 2.1

Site data for soils used in the study

Soil Type	New Zealand Soil Classification	Parent Material	U.S. Taxonomy	Horizons Sampled	Grid Reference
Okaihau gravelly clay	Very strongly leached brown loam with iron-stone nodules	Basaltic tephra over olivine basalt	Gibbsiorthox	Ah Bcs	N15/310456
Egmont brown loam	Moderately leached central yellow-brown loam	Andesitic tephra and tephric loess	Typic Hapludand	Ah Bw1	N129/852328
Tokomaru silt loam	Moderately gleyed central yellow-grey earth	Quartzo-feldspathic loess, derived mainly from greywacke	Typic Fragiaqualf	Ah Btg	N149/076264
Makerua peaty silt loam	Organic soil	Basin peat (with stumps from former swamp forests)	Cumulic Haplaquoll	Oh	N152/825145

*Egmont brown loam* was sampled from under a stand of native forest located close to Normanby, Taranaki. The soil was sampled to a depth of 0-20 cm (Ah horizon) and 20-40 cm (Bwl horizon). The site was situated on easy, rolling land at an altitude of 91m a.s.l. with an average rainfall of 1016 mm (New Zealand Soil Bureau, 1968). The vegetation at the site is native podocarp - broadleaf forest. The principal clay minerals are allophane and hydrous feldspar.

*Tokomaru silt loam* samples were taken, at depths of 0-15 cm (Ah horizon) and 35-50 cm (Btg horizon), from a small stand of native forest situated near Linton in the Manawatu. The stand of forest is located on an elevated and dissected terrace at an altitude of 61m a.s.l. where the average rainfall is 1050 mm. The vegetation at the sampling site is a mixed native broadleaf-podocarp forest. The clay mineralogy is dominated by mica, hydrous mica and mixed layer/chlorite/vermiculite, and some crystalline iron oxides (Pollok, 1975).

*Makerua peaty silt loam* was sampled from a depth of 0-45 cm (Oh horizon). In view of the high water table at this site, a B horizon sample was not obtained. The sample site was located within a flax plantation on the Moutoa estate near Shannon, at an altitude of 6m a.s.l. with an average rainfall of 1000 mm. The present vegetation consists of flax (*Phormium tenax*), but the area was originally covered with swamp forest. The Makerua peaty silt loam, is close to the Manawatu River and because of this the intrusion of young river silts into the peat means that the dominant clay minerals are micaceous.

*New Plymouth black loam*, which is used for one study in Chapter 3, was taken at a depth of 0-15 cm (Ah horizon), from a site approximately 4 km west of New Plymouth. The site is located on flat to rolling country at an altitude of 34m a.s.l. with an average rainfall of

approximately 1461mm (New Zealand Soil Bureau, 1954). The vegetation at the site is scrub, flax (*Phormium tenax*) and tutu (*Coriaria arborea*).

### 2.2.2 Preparation of soils

All soil samples were air-dried and lightly ground to pass a 2mm nylon sieve, using a porcelain mortar and pestle. Nylon was used to minimise contamination of samples. The soils were stored in the air-dried state, in glass jars, until required.

## 2.3 General Methods

### 2.3.1 Adsorption studies

The general method used for studying the adsorption of Zn or Cd was to equilibrate by shaking soil or synthetic gel, with known amounts of Zn or Cd, for 40 hr. The supernatant solutions were then analysed for Zn or Cd, and the amounts adsorbed calculated as the difference between the initial amounts added and the final amounts remaining in solution.

The detailed procedure involved shaking 5-g soil samples with 40 ml of  $3 \times 10^{-2}$  M NaCl containing known concentrations of Zn or Cd, in 50-ml polycarbonate centrifuge tubes. The tubes were shaken on an end-over-end shaker (40 r.p.m.) with the temperature controlled at  $23 \pm 2^{\circ}\text{C}$ . To restrict microbial activity during equilibration, sodium azide ( $154 \mu\text{mol NaN}_3 \text{ l}^{-1}$ ) was used (Mann and Quastel, 1946; Tremaine and Willison, 1962). Sodium azide ( $\text{NaN}_3$ ) was used only after it had been ascertained in a preliminary experiment that adsorption of Zn and Cd by both soils and synthetic Fe gel was unaffected by the addition. Mercuric chloride,  $\text{HgCl}_2$ , was not considered because of the possible competition at adsorption sites between Hg and Zn or Cd cations.

After equilibration, the tubes were centrifuged at 15,000 r.p.m. at  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for five minutes in a Sorvall RC-5 refrigerated centrifuge. The supernatant solutions were then filtered through Millipore ( $< 0.45 \mu\text{m}$ ) filters, and analysed for Zn and Cd.

In all cases Zn and Cd were added as solutions of  $\text{ZnCl}_2$  and  $\text{CdCl}_2$ . Unless otherwise stated the procedure described above was used throughout the study.

### 2.3.2 Preparation of synthetic hydrous metal oxide gels

The gels, prepared as outlined below, were used in studies described in Chapters 4, 5 and 6 of this study.

Prior to the preparation of Zn-free Fe gel, Analar  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was recrystallised. This was achieved by making a saturated solution of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in hot ( $70^{\circ}\text{C}$ )  $1\text{M HNO}_3$ . The hot, saturated  $\text{Fe}(\text{NO}_3)_3$  solution was then cooled in a crushed ice water bath. When cold, the solution was seeded with one or two crystals of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and left to crystallise out slowly. Synthetic Fe gel was prepared by neutralising 2-l of 0.4M solutions of recrystallised  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with approximately 500 ml of 1.0M NaOH in a 4-l plastic container. The base was added slowly as the mixture was continuously stirred with an electrically-driven paddle. Base was added until the pH of the gel suspension reached 7.0. The suspension was then stirred for a further half-hour during which time the pH was maintained at 7.0 by drop-wise addition of 0.1M NaOH solution as required. The gel suspension was stored overnight to allow flocculation. The clear supernatant solution was decanted and discarded, and the remaining Fe gel slurry was centrifuged at 2000 r.p.m. for 10 minutes. The gel was washed four times by suspending in deionised water. Each time the suspension was centrifuged at 2000 r.p.m. and the clear supernatant washings discarded. After the

final washing, the Fe gel was suspended in one litre of deionised water. The concentration of the Fe gel suspension so prepared was approximately 10 mg Fe gel/ml.

The Zn and Cd content of Fe gel prepared by this procedure was assayed following the dissolution of a 5-ml aliquot of the suspension in a minimum amount of 1M HCl. The gel was found to contain less than  $0.15 \mu\text{mol Zn g}^{-1}$  gel. Fe gel prepared with ferric nitrate which had not been recrystallised contained  $0.66 \mu\text{mol Zn g}^{-1}$  gel. No detectable Cd was found in the Fe gel either before or after recrystallisation of the ferric nitrate.

Synthetic allophane was prepared according to the method of van Reeuwijk and de Villiers (1968). Briefly, 1.5 l of  $0.094\text{M AlCl}_3 \cdot 6\text{H}_2\text{O}$  was slowly added (over 10 minutes) with continuous stirring, to 1.5 l of  $0.053\text{M Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  and the suspension adjusted to, and maintained at, pH 6.0 for 2 hr. The suspension was left overnight to allow the gel to flocculate. Most of the clear supernatant was separated from the gel by decanting; the remainder removed by centrifugation at 2000 r.p.m. for 10 minutes. The gel was washed four times, to remove excess chloride ions (as determined using the  $\text{AgNO}_3$  test), by suspending in deionised water and centrifuging at 2000 r.p.m., for 10 minutes, and discarding the washings.

### 2.3.3 Analysis for Zn and Cd.

The centrifuged and filtered supernatants obtained from the adsorption studies described were assayed for Zn and Cd contents by atomic absorption spectrophotometry (AAS).

Using standard operating procedures to obtain maximum sensitivity and detection limits, the operating conditions used are given in Table 2.2.

Table 2.2 Instrument parameters for Zn and Cd analysis  
by atomic absorption spectrophotometry

Operating Conditions	Units	Zn	Cd
Wavelength	$\mu\text{m}$	213.9	228.8
Lamp Current	mA	5	3
Optimum working concentration range	$\mu\text{mol l}^{-1}$	0-30	0-20
Slit Width		4(0.7nm)	4(0.7nm)
Gas Mixture		Air/Acetylene	Air/Acetylene
Flame Conditions		Lean, blue oxidising	Lean, blue oxidising
Light Sources		Hollow cathode lamp	Hollow cathode lamp

For most purposes, the standard curves for Zn and Cd were prepared in a matrix of  $3 \times 10^{-2}$  M NaCl. Where other matrices were used, appropriate standards were prepared.

#### 2.3.4 Soil properties

Soil pH was determined at a soil:solution ratio of 1:2.5 using distilled water (New Zealand Soil Bureau, 1968). Soil organic carbon was determined after digestion with sulphuric acid/potassium dichromate solution (Broadbent, 1965). Cation-exchange capacity (C.E.C.) was determined by leaching soils with ammonium acetate (pH 7.0), elution with sodium chloride and determination of the  $\text{NH}_4^+$  ions by steam distillation (Metson, 1956). The individual exchangeable bases (K, Na, Mg and Ca) leached by ammonium acetate were determined by AAS or flame emission and total exchangeable bases (T.E.B.) were calculated by summation. Particle-size analysis was carried out by the pipette method (Day, 1965).

## 2.4 Results and Discussion

### 2.4.1 Comparison of Zn and Cd adsorption by soils

Results for the 40 hr adsorption of Zn and Cd by Okaihau, Egmont, Tokomaru and Makerua soils are shown in Figs. 2.1 to 2.6. Although the isotherms were all of a similar shape and type (See Chapter 4) the relative extents of adsorption varied considerably for the two cations and also between soils.

Although different absolute amounts of Zn and Cd were adsorbed by these soils (Table 2.3), the relative rankings remained essentially the same at both final solution concentrations ( $2.5 \mu\text{mol l}^{-1}$  and  $40 \mu\text{mol l}^{-1}$ ) of Zn and Cd. The rankings for the topsoils increased in the order Okaihau < Tokomaru < Egmont for Zn and Cd and for the

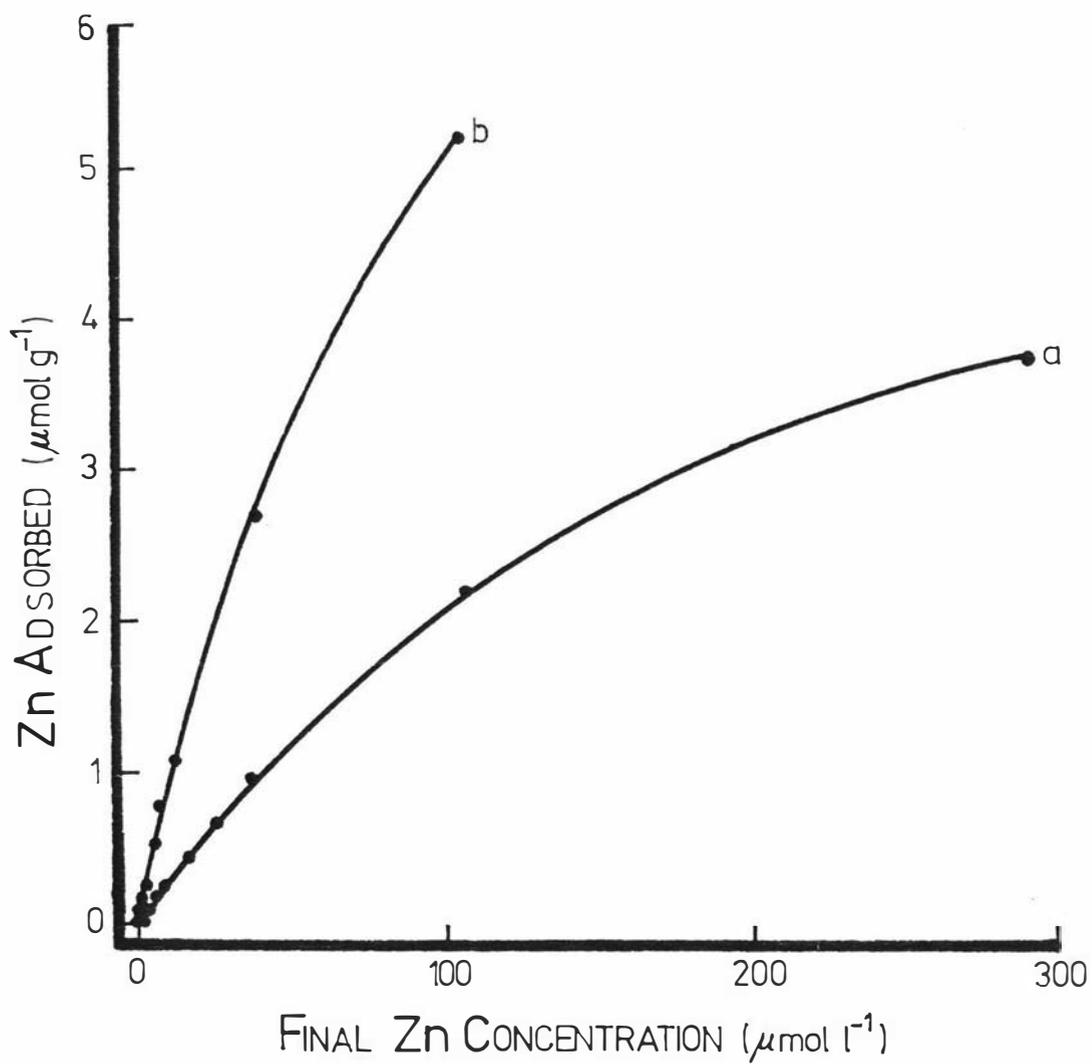


Figure 2.1 Isotherms (40 hr) for the adsorption of Zn by Okaihau (a) and Tokomaru (b) topsoils from  $3 \times 10^{-2}$  M NaCl.

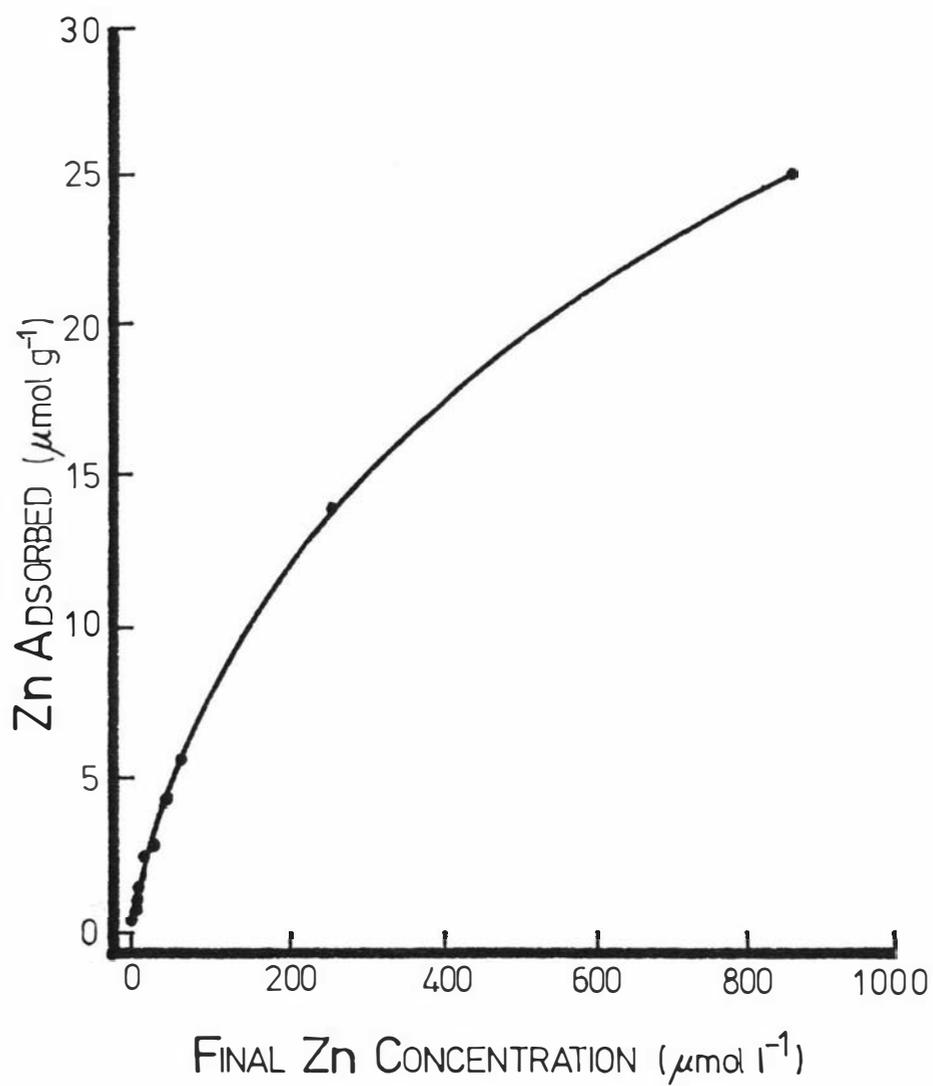


Figure 2.2 Isotherm (40 hr) for the adsorption of Zn by Egmont brown loam topsoil from  $3 \times 10^{-2}$  M NaCl

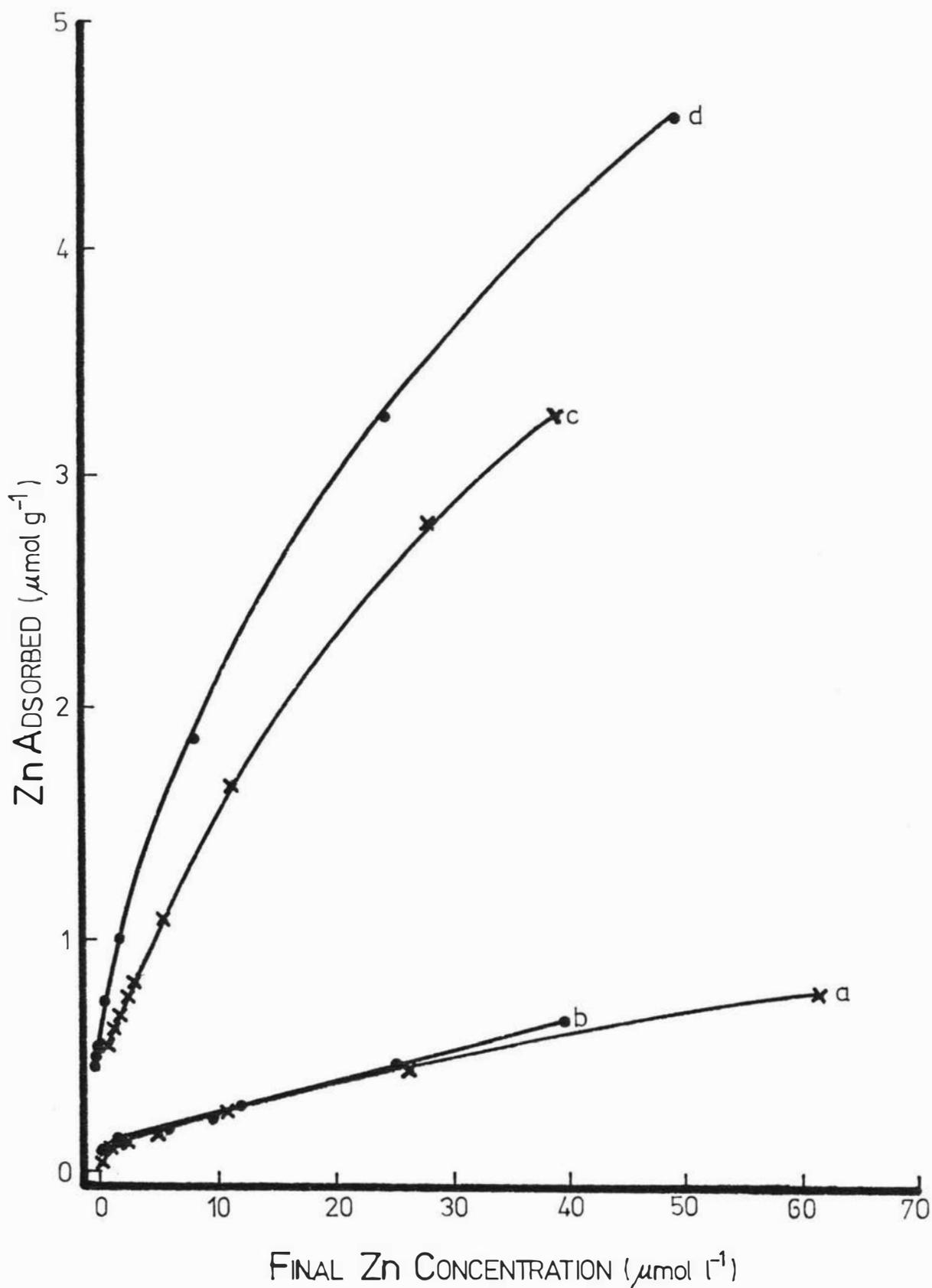


Figure 2.3 Isotherms (40 hr) for the adsorption of Zn from  $3 \times 10^{-2}$  M NaCl by Okaihau (a), Tokomaru (b), Makerua (c) and Egmont (d) subsoils.

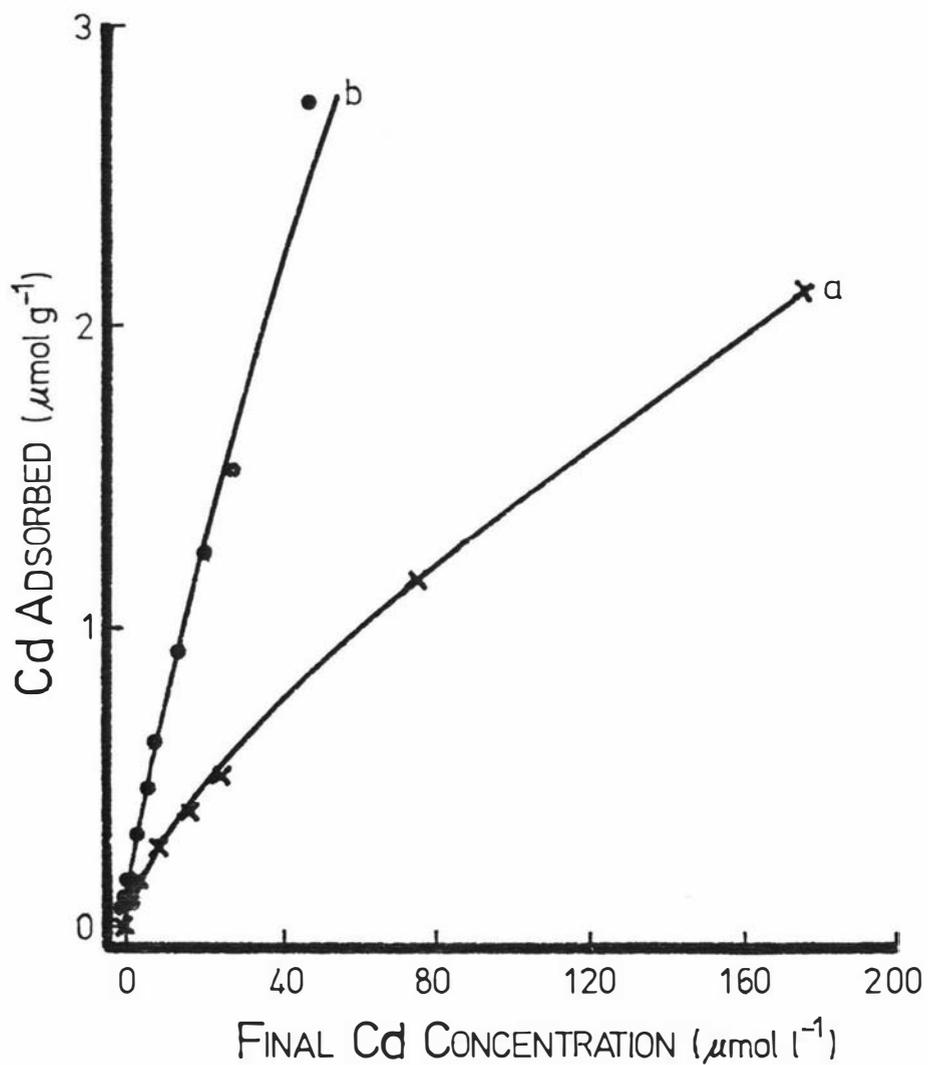


Figure 2.4 Isotherms (40 hr) for the adsorption of Cd by Okaihau (a) and Tokomaru (b) topsoils from  $3 \times 10^{-2} \text{M NaCl}$ .

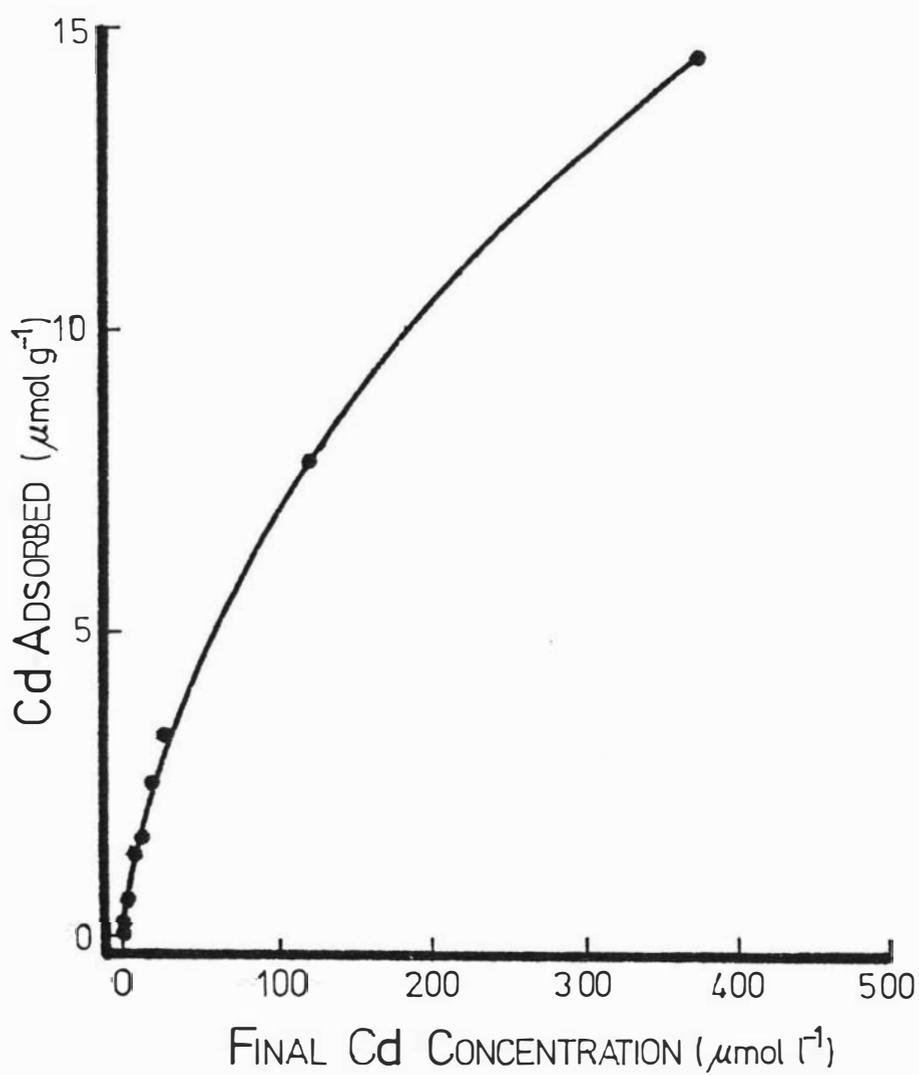


Figure 2.5 Isotherm (40 hr) for the adsorption of Cd by Egmont brown loam topsoil from  $3 \times 10^{-2}$  M NaCl.

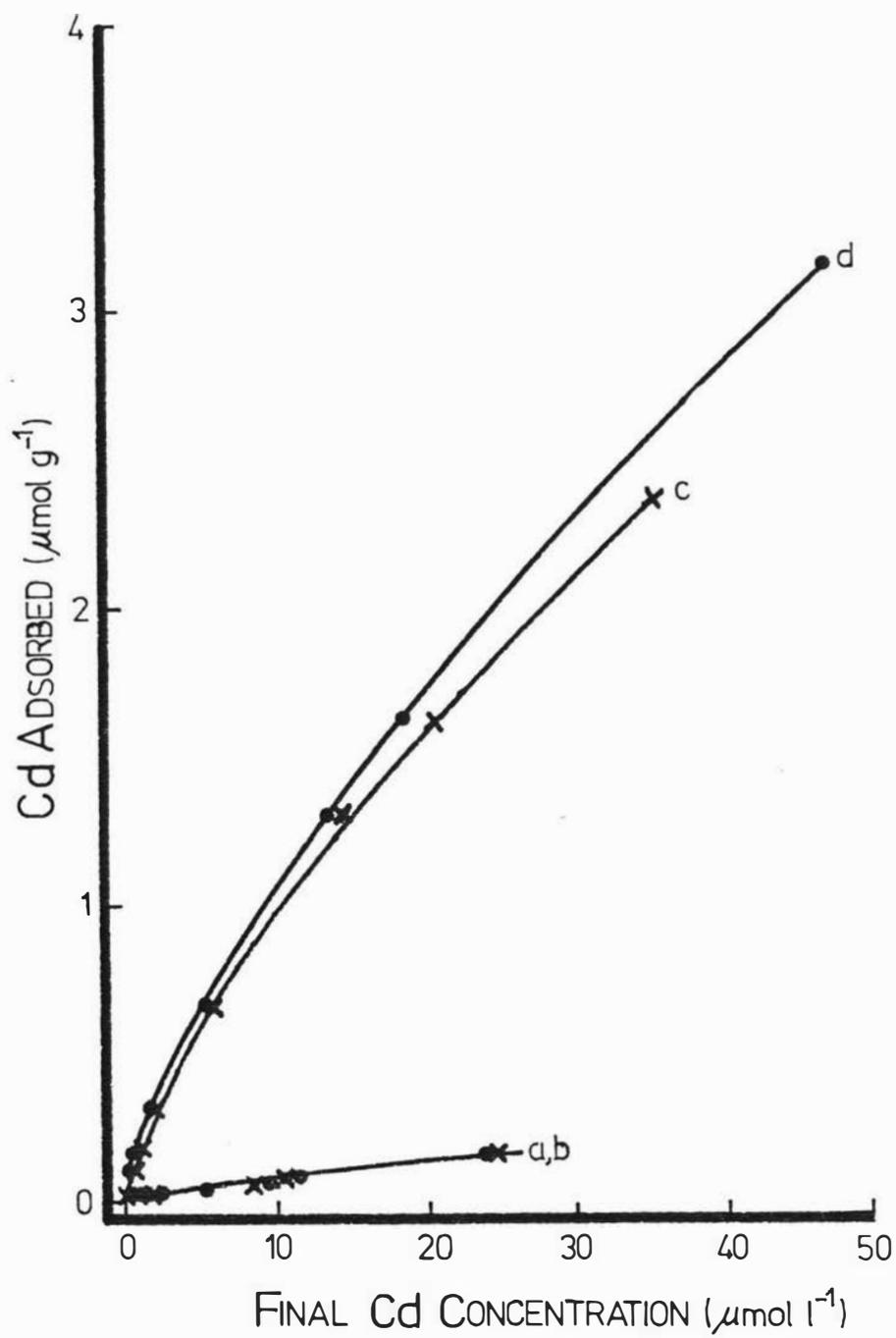


Figure 2.6 Isotherms (40 hr) for the adsorption of Cd from  $3 \times 10^{-2}$  M NaCl by Tokomaru (a), Okaihau (b), Egmont (c) and Makerua (d) subsoils.

Table 2.3 Amounts of Zn and Cd adsorbed by soils, and the ratio of Zn to Cd adsorbed from  $3 \times 10^{-2}$  M NaCl after 40 hr. at two final solution concentrations

		Zn Adsorbed		Cd Adsorbed		Zn:Cd Adsorbed	
		$\mu\text{mol g}^{-1}$		$\mu\text{mol g}^{-1}$			
Final solution concentration. $\mu\text{mol l}^{-1}$		2.5	40	2.5	40	2.5	40
<u>SOIL</u>							
OKAIHAU gravelly clay	Ah	0.125	1.100	0.080	0.715	1.6	1.5
	Bcs	0.053	0.561	0.030	0.195	1.8	2.9
TOKOMARU silt loam	Ah	0.325	2.700	0.285	2.145	1.1	1.3
	Btg	0.043	0.595	0.022	0.220	2.0	2.7
EGMONT brown loam	Ah	0.550	4.700	0.325	3.550	1.7	1.3
	Bwl	0.650	3.800	0.360	2.560	1.8	1.5
MAKERUA peaty silt loam	Oh	0.180	2.784	0.300	2.845	0.60	0.97

subsoils in the order Tokomaru  $\leq$  Okaihau  $<$  Makerua  $<$  Egmont for Zn and Tokomaru  $\leq$  Okaihau  $<$  Egmont  $<$  Makerua for Cd (Table 2.3). Except for the Egmont soil, topsoils generally adsorbed more Zn and Cd than subsoils (see Table 2.3) at both final solution concentrations, possibly indicating the high adsorption capacity of organic matter for Zn and Cd. The higher level of iron oxides in the Egmont B horizon (c.f. A horizon - See Table 2.4) may account for the larger amounts of Zn and Cd adsorbed, at low final solution concentrations, by the subsoil compared to the topsoil.

For the mineral soils more Zn was adsorbed, at the same final solution concentrations, than Cd the ratios ranging from 1.9 to 2.9 on a molar basis (Table 2.3). For the Makerua soil a relative preference for Cd was apparent, with ratios less than 1.0 occurring at both final solution concentrations.

#### 2.4.2 Relationship of Zn and Cd adsorption to soil properties

Values for pH, organic carbon, cation-exchange capacity, exchangeable bases, total exchangeable bases, base saturation and percent clay, silt and sand for the Ah, Oh and B horizons of the four soils used in this study are given in Table 2.4.

With the limited number of soils involved in this study, relationships between amounts of Zn and Cd adsorbed and soil properties would be difficult to establish, and statistical investigations are precluded.

Strong correlations have been found between soil pH and the adsorption of Zn and Cd by soils (Shuman, 1975; Shah Singh, 1979) and solution pH and Cd adsorption by soil clays (Tiller et al., 1979). It is generally found that adsorption of Zn and Cd increases with increasing pH. However, as the pH values for soils used in the present study do not cover a very wide range, pH differences would be unlikely

Table 2.4 Soil properties of possible importance in Zn and Cd adsorption

Soil	Horizon	pH	Organic Carbon %	Short-range order Fe (Tamms-oxalate) mmol 100 g <sup>-1</sup>	CEC me%	Exchangeable bases					Clay %	Silt %	Sand %	
						K me%	Na me%	Mg me%	Ca me%	TEB me%				B.S. %
OKAIHAU gravelly clay	Ah	5.2	5.76	3.5*	17.85	0.66	1.61	0.73	3.48	6.48	36.3	35	27	38
	Bcs	5.0	2.02	9.0*	7.35	0.32	0.67	0.17	2.42	3.58	48.7	56	29	15
TOKOMARU silt loam	Ah	5.9	2.40	4.6*	11.75	1.05	0.62	2.50	5.87	10.04	85.5	23	68	9
	Btg	5.1	0.50	3.7*	7.85	0.48	0.86	1.63	3.45	6.42	81.8	30	62	8
EGMONT brown loam	Ah	5.6	7.34	10.1 <sup>†</sup>	31.70	0.27	1.17	2.15	12.75	16.34	51.6	28	21	51
	Bw1	6.0	3.18	19.5 <sup>†</sup>	19.15	0.10	0.86	0.53	6.22	7.71	40.3	25	22	53
MAKERUA peaty silt loam	Oh	4.8	11.81	n.d.	47.90	1.02	1.85	7.15	20.35	30.37	63.4	37	60	3

\* Hope, 1977.

<sup>†</sup> Ryden, 1975.

to account for the observed differences in Zn and Cd adsorption. In fact, the only relationship that could be observed between pH and Zn and Cd adsorption was for the subsoils, where the high pH in the Egmont subsoil was related to the highest adsorption of Zn and Cd. The Okaihau and Tokomaru subsoils had similar, low pH values and adsorbed correspondingly less Zn and Cd. A similar relationship with pH was not apparent for the topsoils, however.

Whereas pH has been shown to be positively correlated with Zn and Cd adsorption in previous studies, the use of pH as a single indicator for Zn and Cd adsorption capacity of soils is likely to be of limited predictive value because of the large number of factors known to be related to Zn and Cd adsorption, some of which may override pH effects.

Organic carbon and organic matter have both been related to the adsorption of Zn (Shuman 1975; Udo et al., 1976; Singh and Sekhon, 1977) and Cd (John, 1971; Levi-Minzi et al., 1976; Singh and Sekhon, 1977a; Shah Singh, 1979). The organic carbon values for the soils used in this study covered an approximately twenty-fold range (Table 2.4). The subsoils which contain the lower amounts of organic carbon also generally adsorbed smaller quantities of both Zn and Cd than did the higher organic carbon topsoils (Figs. 2.1 - 2.6 and Table 2.3). The relatively high adsorption of Zn and Cd noted for the Egmont subsoil could partially result from the relatively high organic carbon content found for this soil. However, Makerua peaty silt loam which has the highest organic carbon content, did not adsorb higher amounts of Zn and Cd than either the Egmont topsoil or subsoil, both of which have lower organic carbon contents. To further complicate the situation however, it is noted that the Makerua soil also possessed

the lowest pH of all soils in this study, a fact which may reduce the adsorption potential of the soil. Thus, organic carbon content is only one of a number of soil factors which are known to contribute to Zn and Cd adsorption.

The cation-exchange capacity (CEC) of soils has been positively correlated to both the adsorption maxima and bonding energy of Zn (Shuman, 1975; Sidhu et al., 1977a; Singh and Sekhon, 1977) and Cd (John, 1971; Levi-Minzi et al., 1976; Singh and Sekhon, 1977a; Navrot et al., 1978; Shah Singh, 1979) for many soils, although some authors have not always found positive correlations between CEC and Zn and Cd adsorption (Udo et al., 1970; John, 1972). As for pH, a general relationship could be observed between CEC of the subsoils and Zn and Cd adsorption at both concentrations. For example Egmont subsoil, of relatively high CEC, adsorbs more Zn and Cd than the lower CEC Tokomaru and Okaihau subsoils. A general trend in the same direction was noted for the topsoils. The Makerua soil did not conform to this pattern. Undoubtedly, the variable charge components of volcanic ash and organic soils make for difficulty in directly measuring and correlating CEC with adsorption properties.

It has been reported that the clay content of soil influences the CEC of soil (Shuman, 1975; Sidhu et al., 1977) and is also significantly correlated with the amounts of Zn adsorbed by soils (Shuman, 1975; Sidhu et al., 1977; Singh and Sekhon, 1977) and similarly for Cd (John, 1972; Singh and Sekhon, 1977a). It is generally concluded that as the % clay increases, the adsorption maxima for Zn and Cd adsorption also increases. However, for the soils used in this study, the % clay showed no such relationship, thus, Egmont soils which showed the highest Zn and Cd adsorption did not

contain the highest clay contents. The type of clay present may be more important than the amount. Additionally, in this study, there was no clear relationship between short range order Fe (related to hydrous oxide content of soils) and adsorption of Zn and Cd by the soils investigated.

Although, as discussed above, many soil properties are probably important for Zn and Cd adsorption by soils, it is difficult to determine which, if any, of the major soil properties dominate the adsorption process. This is because many soil properties are closely interrelated. For example, in the present study, the high amount of Zn and Cd adsorption found for the Egmont soil may be due to a high content of organic matter coupled with a 'relatively' high pH.

No further attempts were made to explore the relationship between soil composition or properties and Zn and Cd adsorption behaviour in this study. Rather, the approach adopted was to investigate adsorption mechanisms using soils and synthetic soil components with a view to obtaining information on the nature of the adsorption process itself. Such studies form the basis of the remaining chapters. It was with this experimental approach in mind that the contrasting soils were initially selected for the study.

CHAPTER THREE

DEVELOPMENT AND EVALUATION OF A METHOD FOR  
SIMULTANEOUS EXTRACTION AND CONCENTRATION  
OF Zn AND Cd FROM SOIL EXTRACTS

3.1 Introduction

A technique for concentrating low amounts of Zn and Cd prior to analysis by atomic absorption was developed for the following reasons:

1. To enable the study of Zn and Cd adsorption by soils and synthetic oxides at low additions of Zn and Cd. At these low additions, equilibrium solution concentrations of Zn and Cd were often  $< 2.5 \mu\text{mol l}^{-1}$  and  $< 2.0 \mu\text{mol l}^{-1}$  respectively.
2. To determine extractable Zn and Cd contents of soils often within the range  $0.0015$  to  $0.153 \mu\text{mol g}^{-1}$  and  $0.00009$  to  $0.0062 \mu\text{mol g}^{-1}$  respectively. Similarly, low total Cd levels in soils ( $0.0089$  to  $0.027 \mu\text{mol g}^{-1}$  (Swaine, 1955)) often require concentration.

The two most common techniques that have been used for concentrating Zn and Cd are ion-exchange and solvent extraction procedures. The use of flameless atomic absorption techniques, such as graphite furnace or carbon rod atomisation analysis, often makes concentration of Zn and Cd unnecessary. However, this technique was not available for the present study.

Some general aspects of the procedures for extracting and concentrating Zn and Cd are discussed below.

### 3.2 Solvent Extraction

A chelating agent can be used to extract Zn or Cd from aqueous solution into an organic solvent. Concentration is then achieved by using a smaller volume of the organic solvent, relative to the original aqueous sample (Thorn and Ludwig, 1962). The methods can be tailor-made for a particular metal by varying the nature of the complexant and extraction conditions.

The commonest procedures used for Zn and Cd employ ammonium pyrrolidine dithiocarbamate (APDC) as the complexing agent and methylisobutyl ketone (MIBK) as the solvent (Mulford, 1966; Brooks et al., 1967; de Vries et al., 1975) or 1,5 diphenylthiocarbazone (dithizone) with carbon tetrachloride or chloroform (Westöö, 1963; Williams et al., 1972; Gajan et al., 1973).

#### 3.2.1 APDC/MIBK

An APDC/MIBK procedure was used for concentrating Zn from sea water (Brooks et al., 1967) and Cd from plant material (de Vries et al., 1975). The extraction of heavy metals by APDC/MIBK is unaffected by extraction ratios (Munro, 1968). The recommended optimum pH for Cd is around pH 3.3, with recovery decreasing as pH increases above this value (de Vries et al., 1975). For Zn, the optimum extraction is achieved at a pH of between 4 and 5 (Brooks et al., 1967) with no extraction occurring below pH 2.5. When using the APDC/MIBK procedure, the conditions of pH, extraction ratios and matrix should be matched for samples and standards (Munro, 1968).

The APDC/MIBK method is reported to be fast and relatively free from interferences by other metal ions, with good precision and repeatability (Mulford, 1966; Brooks et al., 1967; de Vries et al., 1975).

The use of the solvent MIBK is convenient because it can be directly aspirated into a A.A. spectrophotometer. In addition, as with many other organic solvents, the presence of MIBK enhances the absorption signal over that for aqueous samples. This "solvent effect" (Mulford, 1966; Brooks et al., 1967; Yamamoto et al., 1972) is thought to be due to the formation of smaller-sized droplets during aspiration, than occurs for aqueous solutions. These smaller-sized droplets are better able to pass through the burner mixing chamber without condensing, thereby delivering more sample to the flame.

Oien and Gjerdingen (1977) used an APDC/MIBK extraction system to determine Cd in soils, but found the atomic absorption readings to be unstable. The procedure was improved by using APDC/chloroform at pH 3.0 after first removing Fe with acetylacetone and chloroform at pH 3.0. The APDC/chloroform extract was digested with acid to destroy the APDC and chloroform and the residue was then redissolved in dilute acid and analysed for Cd by atomic absorption.

### 3.2.2 Dithizone

Although 1,5 diphenylthiocarbazone (dithizone) has been recommended for the colorimetric determination of both Zn and Cd (Sandell, 1959), its use for metal ion concentration prior to atomic absorption analysis is less well documented.

Yamamoto et al. (1972) used dithizone for the extraction of Cd from standard solutions. Chlorinated solvents, such as carbon tetrachloride, were avoided because of their incomplete combustion in the flame and the formation of toxic decomposition products (e.g. phosgene). Five different solvents, i.e., MIBK, ethyl propionate, n-butyl acetate, nitroethane and nitrobenzene were used over the pH range 3.5 to 10.0 and all showed complete extraction of the Cd-dithizonate complex.

Few interferences were reported for this method.

Addition of diphenylthiocarbazone and acetyl acetone to an ethyl propionate/8-quinolinol extraction system was found necessary before Zn and Cd could be effectively extracted from aqueous solutions (Sachdev and West, 1970). With this extraction procedure several metal ions, including Zn and Cd, could be extracted within the pH range of 5.0 to 7.0. No interferences were found for Zn and Cd analysis.

#### 3.2.2.1 Dithizone/chloroform

Dithizone/chloroform has been used to concentrate and extract Cd from plant and soil extracts (Ure and Mitchell, 1976) and foodstuffs (Gajan et al., 1973). A pH range 8.0 to 9.0 was chosen to minimise Zn and Cu extraction (Ure and Mitchell, 1976). High concentrations of Zn and Cu interfere with Cd extraction, probably as a result of competition for the dithizone reagent. Increasing the concentrations of dithizone overcomes this problem. The Cd levels were then determined by carbon-rod atomisation directly on the dithizone/chloroform extract (Ure and Mitchell, 1976) or by back-extraction of Cd with dilute acid and analysis of Cd by conventional atomic absorption (Gajan et al., 1973). Both methods gave repeatable results and were suitable for routine use.

#### 3.2.2.2 Dithizone/carbon tetrachloride

A dithizone/carbon tetrachloride method has been used to extract Zn from organic material (Westöo, 1963), and Cd from plant and soil extracts (Williams et al., 1972) under a range of pH conditions.

Westöo (1963), Sandell (1959) and Morrison and Freiser (1957)

reported quantitative extraction and concentration of Zn under acidic pH conditions, Zn being determined colorimetrically, after addition of appropriate masking agents to reduce interference from other metal/dithizonate complexes.

The extraction of Cd from plant and soil extracts was carried out under alkaline conditions (Morrison and Freiser, 1957; Williams et al., 1972). Adequate recoveries of added Cd from both plant and soil extracts were reported, with good limits of detection (Williams et al., 1972). For Cd analysis the Cd/dithizonate complex was decomposed by hot acid digestion. The residue was then redissolved in dilute acid, and the solutions analysed by atomic absorption (Williams et al., 1972).

### 3.3 A Method for Simultaneous Zn and Cd Determination

In this section, results are presented for a method that was designed to simultaneously extract and concentrate Zn and Cd from dilute solutions in a single operation. The procedure was designed to achieve a ten-fold concentration of Zn and Cd from aqueous solutions or soil extracts. The method uses dithizone and carbon tetrachloride. The Zn and Cd was extracted into the organic phase then back-extracted into a small volume of hydrochloric acid.

#### 3.3.1 Procedure

To a 50-ml aliquot of the solution to be analysed, in a 100-ml beaker, add 10 ml of 0.5M sodium acetate buffer, and 1 ml of 10% (w/v) hydroxylammonium chloride solution. The hydroxylammonium chloride solution is used to prevent the oxidation of dithizone (Sandell, 1959) during extraction. Adjust pH to 4.50 with redistilled hydrochloric

acid or ammonia solution using a pH meter, and then quantitatively transfer the solution to a separating funnel.

Cd and Zn are extracted in two successive extractions using 5-ml aliquots of the dithizone extracting solution (0.01% w/v in carbon tetrachloride). The extraction is accomplished by vigorous shaking of the separating funnel, by hand, for 1 minute. The two phases separate on standing, after which the organic phase is run off into a second separating funnel. After combination of the two extracts, Zn and Cd are then back-extracted into the aqueous phase by the addition of 5 ml of 0.01M hydrochloric acid, again shaking for 1 minute. The Zn and Cd concentrations can then be determined using AAS. Zn and Cd standards, ranging from 0 to 30.6  $\mu\text{mol Zn l}^{-1}$  and 0 to 17.8  $\mu\text{mol Cd l}^{-1}$ , are prepared using the concentration procedure on Zn and Cd solutions prepared in deionised water over the concentration ranges of 0 to 3.06  $\mu\text{mol Zn l}^{-1}$  and 0 to 1.78  $\mu\text{mol Cd l}^{-1}$ .

### 3.4 Assessment of the Performance of the Procedure

#### 3.4.1 Effect of extraction pH

Earlier work with dithizone used acidic conditions for Zn extraction (Morrison and Freiser, 1957; Sandell, 1959; Westöö, 1963) and alkaline conditions for Cd extraction (Morrison and Freiser, 1957; Williams and David, 1972; Gajan et al., 1973; Ure and Mitchell, 1976). However, the alkaline extraction of Cd was used to minimise the extraction of Zn and other cations (Ure and Mitchell, 1976) which interfere with the colorimetric finish used for Cd analysis.

In order to simultaneously extract Zn and Cd it is necessary to utilise one set of conditions of pH and buffer type. Yamamoto et al. (1972) reported complete extraction of Cd over a range of pH 3.5 to 10.0 and

Sachdev and West (1970) reported that Zn and Cd can be extracted quantitatively between pH 5.0 and 7.0.

Thus, to determine a single pH at which complete recovery of both Zn and Cd occurred, the recovery of 0.038  $\mu\text{mol}$  Zn and 0.022  $\mu\text{mol}$  Cd from 50 ml of deionised water was measured at unit pH increases over the pH range 3.0 to 11.0. The buffers used to maintain the desired pH were: 0.50M sodium acetate (pH 3.0 to 7.0), 0.35M sodium citrate (pH 8.0 to 9.0) and 0.48M potassium sodium tartrate (pH 10.0 to 11.0). Five replicates for each pH and each addition of Zn and Cd were used. The efficiency of extraction was assessed by comparison with Cd and Zn standards which were also prepared in acidified deionised water. These aqueous standards had not undergone the extraction and back-extraction procedure and were approximately ten times more concentrated than the original sample solutions.

#### 3.4.2 Recovery of Zn and Cd from water

The simultaneous recovery of Zn and Cd from deionised water was determined by extracting and concentrating the metals from solutions containing 0.0038, 0.0077 and 0.0153  $\mu\text{mol}$  Zn and 0.0022, 0.0045 and 0.0089  $\mu\text{mol}$  Cd using the procedure given in Section 3.3.1 (i.e., pH 4.50 with sodium acetate buffer). Three replicates were used and recovery efficiencies determined as in Section 3.3.1.

#### 3.4.3 Recovery of Zn and Cd from soil extracts

Four soils of contrasting composition, sampled at 0-10 cm depth, were selected to provide a range of possible interfering substances which might affect the efficiency of recovery of Zn and Cd by the procedure. The soils used, with an indication of the major soil constituents of interest given in parenthesis, were Egmont brown loam

(allophane; organic matter); Okaihau gravelly clay (crystalline and short-range order iron oxides); Makerua peaty silt loam (organic matter) and Tokomaru silt loam (crystalline layer silicates). Further details of the soils used are given in Chapter 2.

For each soil 20 g was extracted with 200 ml of  $1 \times 10^{-2}$  M calcium chloride solution, by shaking on an end-over-end shaker (40 r.p.m.) for 2 hr in a 250-ml polycarbonate bottle at  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . The suspension was centrifuged at 12,500 r.p.m. for 10 min at  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$  using a Sorvall RC 2B refrigerated supercentrifuge, and the supernatant filtered through pre-washed millipore ( $< 0.45 \mu\text{m}$ ) filters. A 50-ml aliquot of the soil extract was then taken for Zn and Cd extraction and concentration using the dithizone procedure. Recoveries of 0.0153 and 0.038  $\mu\text{mol}$  Zn and 0.0089 and 0.022  $\mu\text{mol}$  Cd added to soil extracts immediately prior to extraction and concentration were assessed. There were three replicates for each level of addition of Cd and Zn, and for each soil. Recovery efficiency was assessed from the difference in Zn and Cd contents of the soil extracts for the spiked and unspiked samples.

#### 3.4.4 Variability of the procedure

The variability of the amounts of Zn and Cd extracted and concentrated from calcium chloride extracts of Makerua peaty silt loam and New Plymouth black loam was assessed using the procedure described. These soils have been described in Section 2.2.1. Within-day variability was investigated using eighteen (18) replicate determinations, and between-day variability using triplicate determinations on each of five consecutive days. The results were statistically analysed using one-way analysis of variance.

### 3.5 Results and Discussion

The effects of extraction pH on the quantitative and simultaneous recovery of Zn and Cd from deionised water are shown in Table 3.1. The recovery of 0.038  $\mu\text{mol}$  Zn and 0.022  $\mu\text{mol}$  Cd was essentially quantitative over the pH range 4.0 - 7.0, using the sodium acetate buffer, with recovery efficiencies ranging from 92 to 102%. On the basis of these results an extraction pH of 4.50, with the sodium acetate buffer, was chosen for all subsequent studies. The use of a single pH value for the simultaneous extraction and concentration of Zn and Cd contrasts with the findings of previous studies (Morrison and Freiser, 1957; Williams, David and Iismaa, 1972) advocating an alkaline extraction pH for Cd and an acidic extraction pH for Zn (Morrison and Freiser, 1957; Westöf, 1963). The dithizone methods described by Morrison and Freiser (1957) and Sandell (1959) were designed for the colorimetric analysis of Zn and Cd. Other metal cations known to interfere with the procedure must be removed and because Zn and Cd form the same type of complex with the dithizone reagent, it is necessary to determine Zn and Cd separately. Thus, conditions of extraction, i.e., acid pH for Zn extraction and alkaline pH for Cd extraction, were chosen to enable the separate determination of both. The different pH conditions, together with the use of masking agents, allowed for the full extraction and determination of Zn and Cd.

In this present study essentially complete recoveries of the low levels of Zn (0.0038 - 0.0153  $\mu\text{mol}$ ) and Cd (0.0022 - 0.0089  $\mu\text{mol}$ ) added to deionised water were obtained using the developed procedure. The recoveries ranged from 90 to 100% at the three different levels of Zn and Cd used, as shown in Table 3.2, in a deionised water system.

Table 3.1 Effect of extraction pH on recovery of 0.038  $\mu\text{mol}$  Zn and 0.022  $\mu\text{mol}$  Cd from deionised water

pH	Recovery, %	
	Zn	Cd
3.0	56	65
4.0	102	102
5.0	98	98
6.0	98	92
7.0	98	98
8.0	89	102
9.0	88	95
10.0	87	89
11.0	2	2

Table 3.2 Effect of level of addition of Zn and Cd on recovery from deionised water

Zinc			Cadmium		
Added Zn $\mu\text{mol}$	Recovered Zn $\mu\text{mol}$	Recovery %	Added Cd $\mu\text{mol}$	Recovered Cd $\mu\text{mol}$	Recovery %
0.0038	0.0038	100	0.0022	0.0022	100
0.0077	0.0070	92	0.0045	0.0040	90
0.0153	0.0144	94	0.0089	0.0084	94

Similar high recoveries were also obtained from the calcium chloride extracts of the four different soils (Table 3.3), indicating little or no interference from soluble soil constituents.

The analysis of variance results, presented in Table 3.4, show that the extraction and concentration procedure gave repeatable results for the eighteen extractions of Zn and Cd, from the two soil samples, performed on the same day i.e., acceptable within-day variability. The analysis of variance results (Table 3.4) also showed no significant differences in amounts of Zn and Cd extracted from the two soil samples on five consecutive days, i.e., acceptable between-day variability. The results for  $\text{CaCl}_2$  extractions of Zn and Cd extracted both on a single day and on five consecutive days were similar, and variability for within- and between-day extractions for each soil was not significant. Thus, the method was shown to be reliable and consistent.

The method developed for the extraction of Zn and Cd is efficient, simple and rapid, with the sensitivity of the procedure being essentially that of the atomic absorption spectrophotometer.

Table 3.3

Recovery of Zn and Cd added to calcium chloride extracts of soils

Soil	Zinc			Cadmium		
	Added $\mu\text{mol}$	Net recovery $\mu\text{mol}$	Recovery %	Added $\mu\text{mol}$	Net recovery $\mu\text{mol}$	Recovery %
Egmont brown loam	0.0153	0.0168	110	0.0089	0.0097	110
	0.0380	0.0382	100	0.0220	0.0244	110
Makerua peaty silt loam	0.0153	0.0145	95	0.0089	0.0093	105
	0.0380	0.0375	98	0.0220	0.0231	104
Tokomaru silt loam	0.0153	0.0145	95	0.0089	0.0088	100
	0.0380	0.0344	90	0.0220	0.0230	104
Okaihau gravelly clay	0.0153	0.0153	100	0.0089	0.0090	102
	0.0380	0.0352	92	0.0220	0.0228	103

Table 3.4 Within- and between-day variability in amounts of Zn and Cd extracted from soils by calcium chloride

Soil	Source of Variation	Zinc		Cadmium	
		$\mu\text{mol g}^{-1}$	Anova <sup>*</sup> Results	$\mu\text{mol g}^{-1}$	Anova <sup>*</sup> Results
Makerua peaty silt loam	Within-day	0.0038 $\pm$ 0.0003	†	0.00020 $\pm$ 0.00004	n.s.
	Between-day	0.0036 $\pm$ 0.0002		0.00027 $\pm$ 0.00008	
New Plymouth black loam	Within-day	0.0136 $\pm$ 0.0009	n.s.	0.00024 $\pm$ 0.00003	n.s.
	Between-day	0.0145 $\pm$ 0.0008		0.00026 $\pm$ 0.00003	

Anova<sup>\*</sup> = analysis of variance

n.s. = not significant

† = P < 0.05

CHAPTER FOUR

ADSORPTION OF Zn AND Cd BY  
SOILS AND SOIL COMPONENTS

4.1 Introduction

Adsorption is thought to be an important process controlling the concentrations of Zn (Ellis and Knezek, 1972; Quirk and Posner, 1975) and Cd (Tiller et al., 1979) in the soil solution.

Although in many previous studies adsorption processes in soils have been described using Langmuir equations, often very high loadings of Zn and Cd have been used with resultant high concentrations of these cations in the equilibrium solution phase, e.g., up to  $1529 \mu\text{mol Zn l}^{-1}$  (Singh and Sekhon, 1977) and  $890 \mu\text{mol Cd l}^{-1}$  (John, 1972; Singh and Sekhon, 1977a). These concentrations of Zn and Cd are high by comparison with normal soil solution values, which are commonly  $< 1.0 \mu\text{mol l}^{-1}$  for Zn (Russell, 1973) and  $< 0.012 \mu\text{mol l}^{-1}$  for Cd (Navrot et al., 1978). Also a variety of shaking times (Udo et al., 1970; John, 1972; Shuman, 1975; 1976; Levi-Minzi et al., 1976) have been used, and, with the exception of Singh and Sekhon (1977, 1977a) who used 0.1M KCl as a support medium to keep ionic strength constant, adsorption experiments have mostly been carried out in deionised water. Therefore, it is difficult to compare the findings of different workers and to elucidate common adsorption mechanisms and adsorption characteristics operating at the naturally low concentrations of Zn and Cd occurring in most field situations.

Previous studies using the Langmuir adsorption approach have shown a single linear relationship for Zn and Cd adsorption (Udo et al., 1970;

John, 1972; Singh and Sekhon, 1977; Singh and Sekhon, 1977a).

However, these studies, using high Zn and Cd additions may have failed to detect the occurrence of a second population of adsorption sites, operating at lower equilibrium concentrations. For example, using Zn additions as low as  $30.6 \mu\text{mol Zn l}^{-1}$  Shuman (1975) found that Zn adsorption data was best described by two linear relationships, each described by a separate Langmuir equation.

In the present study, Zn and Cd adsorption by a range of soils was investigated. These soils were chosen to include components, such as organic matter, Fe and Al hydrous oxides and layer silicates, likely to be important in the adsorption of Zn and Cd. A special feature of this work was that adsorption reactions between soils and added Zn and Cd were investigated over equilibrium solution concentration ranges similar to those likely to be encountered under 'normal' field conditions. Hydrous metal oxides have been used extensively to investigate Zn and Cd adsorption reactions (Gadde and Laitinen, 1974; Quirk and Posner, 1975; Forbes et al., 1976) in order to determine the adsorption mechanisms. The composition and surface characteristics of hydrous metal oxides are relatively well-known (Parks and de Bruyn, 1962; Quirk and Posner, 1975). In the present study, Langmuir parameters for Zn and Cd adsorption by Fe gel were compared to those for soil adsorption in an attempt to validate the use of Fe gel as a model for soil systems. Furthermore, Fe gel prepared from recrystallised  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  so as to be relatively free of Zn and Cd impurities, was used in adsorption experiments to investigate adsorption at extremely low loadings in order to detect the existence or otherwise of any high affinity adsorption sites. The number of separate Langmuir equations that can be resolved from plots of the experimental data can give an indication of the potential number of different populations of adsorption sites present on the adsorbent.

For example, this approach has been successfully used for P sorption (Ryden et al., 1977) wherein the three separate Langmuir regions obtained were interpreted as three different sorption mechanisms.

## 4.2 Methods

### 4.2.1 Kinetic studies

In this section, the method used to assess the effect of equilibration time on Langmuir parameters is described. Because the model to be applied to experimental adsorption data has been derived for equilibrium conditions, and since equilibrium for Zn and Cd adsorption by soils is not reached in short term laboratory equilibration studies then some estimate of equilibrium conditions would be required.

Soil samples from the Makerua topsoil and from the Okaihau subsoil were used to investigate the rate of decrease of solution Zn and Cd concentrations following the addition of Zn and Cd. These particular soils were chosen to ascertain whether similar adsorption kinetics for Zn and Cd applied for soils with very different chemical and mineralogical compositions. The Makerua soil contains high amounts of organic matter (Table 2.4) and the Okaihau soil contains high amounts of Fe oxides (New Zealand Soil Bureau, 1968).

In all these adsorption studies, the losses of Zn and Cd from solution are generally assumed to be equivalent to uptake by soil. To check on this, controls were prepared using low concentrations of Zn and Cd, i.e.,  $0.153 \mu\text{mol Zn l}^{-1}$  and  $0.089 \mu\text{mol Cd l}^{-1}$ , in the same matrix  $3 \times 10^{-2} \text{M NaCl}$  but with no soil added. These were shaken in the polycarbonate tubes for the 40 hr total equilibration period. All

solutions were then analysed for Zn and Cd. The results indicated that Zn and Cd are neither adsorbed nor released from the centrifuge tubes to any significant extent (See results in Appendix 1). Therefore, any decrease in Zn and Cd concentration is attributed to adsorption by the particular adsorbent under investigation.

Two levels of addition of Zn and Cd (Table 4.1) were used for each soil and adsorption of Zn and Cd by the two soils was investigated over a total adsorption period of 240 hr. The extent of adsorption with time was measured at 24-hr intervals. The different additions of Zn and Cd added to the two soils were chosen so that the final solution concentrations of Zn and Cd, after 240 hr equilibration, were similar for each soil, to enable a comparison of the rates of attainment of equilibrium. A 5-g sample of each soil was shaken with 40 ml of  $3 \times 10^{-2} \text{M}$  NaCl (after aliquots of Zn or Cd had been added) in 50-ml polycarbonate centrifuge tubes on an end-over-end shaker at  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . Because shaking may induce particle breakdown, the amount of adsorption of Zn and Cd by soils shaken for longer periods may be affected by other than kinetic factors. For instance, the effect of mechanical disruption of soil aggregates may produce a greater surface area leading to more Zn and Cd adsorption. To circumvent this problem all tubes in this experiment were shaken for the same total time (240 hr), although the time of contact between the  $\text{Zn}^{2+}$  or  $\text{Cd}^{2+}$  and soil ranged from 24 to 240 hr. This common total shaking time was achieved by placing all tubes on the shaker at the start of the experiment and adding the aliquots containing the Zn or Cd at the required number of hours (equilibration time) before the end of the shaking period.

#### 4.2.2 Time-dependent and equilibrium adsorption isotherms

As already mentioned, Langmuir adsorption theory applies to systems

Table 4.1 Initial additions of Zn and Cd used  
to study adsorption kinetics

Soil	Low addition		High addition	
	Zn $\mu\text{mol g}^{-1}$	Cd $\mu\text{mol g}^{-1}$	Zn $\mu\text{mol g}^{-1}$	Cd $\mu\text{mol g}^{-1}$
Makerua peaty silt loam	0.030	0.090	1.53	3.06
Okaihau gravelly clay	0.015	0.010	0.31	0.31

at equilibrium. Because many adsorption reactions in soil exhibit fast initial kinetics followed by slow continuing adsorption (Shah Singh, 1979), and as most adsorption studies are carried out at times shorter than those required to reach equilibrium, the problem is to obtain the equilibrium values of Zn and Cd concentration. To obtain these values the extrapolation method used by Ryden and Syers (1975) for P sorption by soils was investigated. The method requires that plots of solution P concentration against the reciprocal of time (i.e.,  $\frac{1}{t}$ ) be linear. By extrapolation to  $\frac{1}{t} = 0$  (i.e.,  $t = \infty$ ), an estimate of the "true equilibrium" P concentration can be obtained. To obtain equilibrium isotherms for Zn and Cd, 5-g samples of soil were equilibrated with a range of ten different additions of Zn and Cd, to produce for each soil, final concentrations of Zn or Cd in solution within the range 0.2 to 300  $\mu\text{mol l}^{-1}$ . The experiment was conducted in  $3 \times 10^{-2} \text{M NaCl}$  at a soil:solution ratio of 1:8 using polycarbonate centrifuge tubes. NaCl was used as the matrix solution to maintain a constant ionic strength and overcome any effects of variable soil electrolyte content on the ionic strength of the solution. The tubes were shaken on an end-over-end shaker (40 r.p.m.) at  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for one of four equilibration times, viz., 24, 48, 96 and 144 hr. After equilibration the tubes were centrifuged at 15,000 r.p.m. at  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for 5 min. in a Sorvall RC-5 refrigerated supercentrifuge. The supernatant solutions were filtered (Millipore  $< 0.45 \mu\text{m}$ ) and analysed for Zn and Cd contents. A reciprocal time plot of adsorption data was prepared according to the method of Ryden and Syers (1975), an example of which is shown in Fig. 4.1, for Okaihau gravelly clay subsoil at different levels of added Zn (shown in Fig. 4.1). Unfortunately, the data obtained from this plot did not lie on the one straight line and

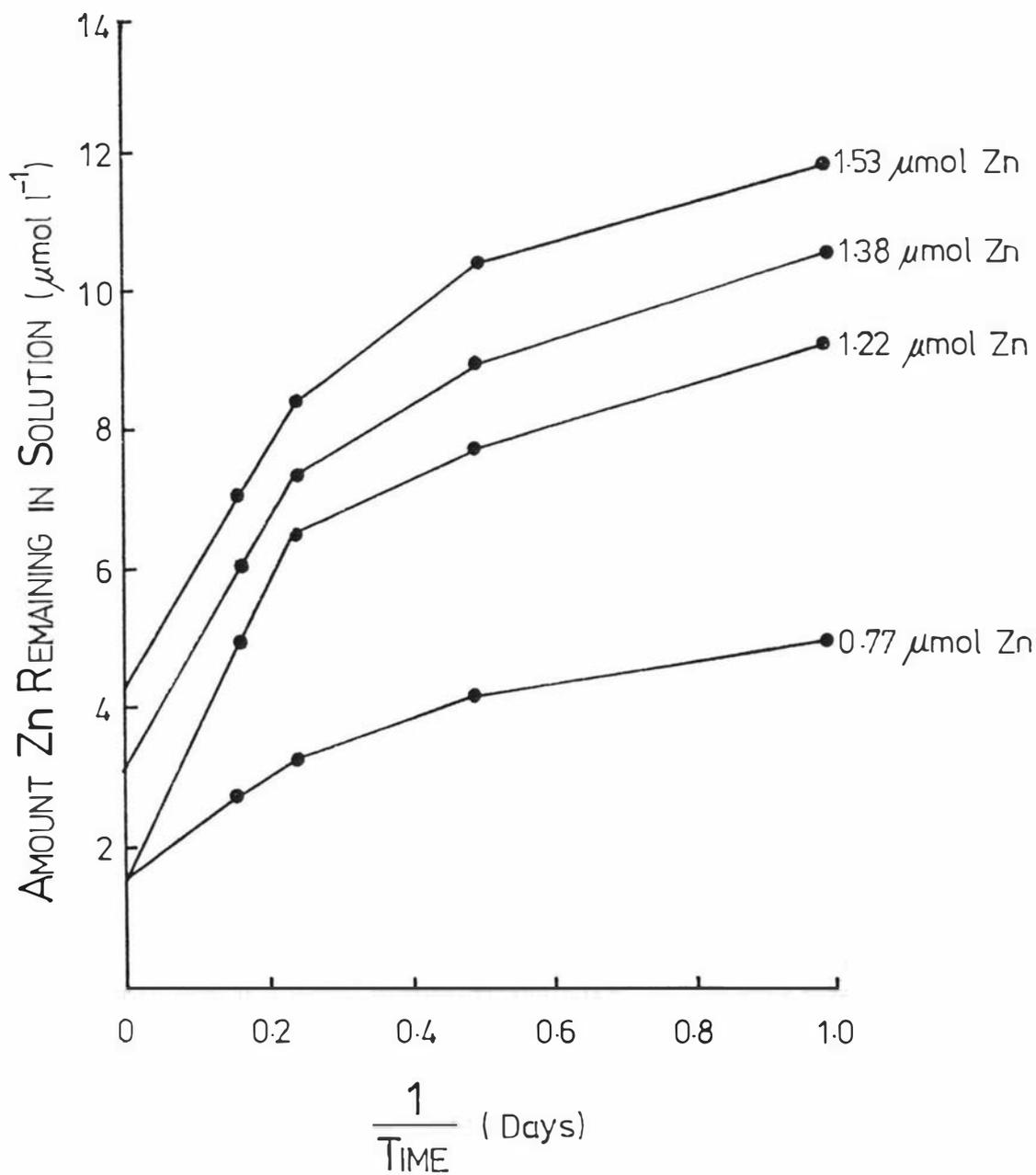


Figure 4.1 Reciprocal time plot of Zn in solution during adsorption of added Zn by Okaihau gravelly clay subsoil

therefore no simple linear extrapolation could be performed. The same was true for all other soils, although the plots are not shown.

These results are unlike those found for P by Ryden and Syers (1975) and therefore necessitated another approach to the problem. A practical alternative was to compare the Langmuir adsorption constants obtained at various equilibration times. For this investigation, samples from the same two soils (Makerua peaty silt loam soil, and Okaihau gravelly clay subsoil) were used at equilibration times of 120, 144, and 192 hr.

The adsorption characteristics of Zn and Cd adsorption at 120 hr, 144 and 192 hr were then compared to those obtained at 40 hr, the objective here being to check whether 40-hr isotherms might be a reasonable approximation of those obtained at longer equilibration times.

For all equilibration times, ten levels of addition of Zn and Cd were used, with final solution concentrations ranging between 0.2 and 300  $\mu\text{mol Zn or Cd l}^{-1}$ .

#### 4.2.3 40-hr adsorption isotherms

A series of 40-hr adsorption isotherms were carried out using the same general procedure outlined in Section 4.2.2. Data were obtained, for both Zn and Cd, for the Makerua topsoil, Okaihau gravelly clay, Tokomaru silt loam and Egmont brown loam top and subsoils. Properties of these soils and reasons for their choice have been previously outlined in Chapter 2 of this study. In all experiments 154  $\mu\text{mol NaN}_3 \text{ l}^{-2}$  (Mann and Quastel, 1946) was present in each tube to limit microbial growth.

#### 4.2.4 "Native-adsorbed"\* Zn and Cd

In all adsorption experiments with soils, the amount of adsorbed Zn or Cd present on the soil surface at any time will depend on both:

- a. The amount of native-adsorbed initially on the soil surface at the commencement of the experiment, and
- b. The amount adsorbed during the course of the experiment.

Although there is no accepted method for determining native-adsorbed Zn and Cd, in this study 1M HCl was used to extract this category of adsorbed Zn and Cd from soils. A 2-g sample of each soil was extracted with 40 ml 1M HCl by shaking, in 50 ml polycarbonate centrifuge tubes, for 16 hrs on an end-over-end shaker (40 r.p.m.) at  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . The samples were then centrifuged (15,000 r.p.m. at  $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for 5 min), filtered (Millipore  $< 0.45 \mu\text{m}$ ), and analysed for Zn and Cd by A.A.S. For two of the soils (Egmont brown loam topsoil and subsoil) subsequent evaluation of the adsorption data (Section 4.3.2.1) suggested that native-adsorbed Zn and Cd may have been overestimated and for these two an alternative milder extractant,  $2.0 \times 10^{-2} \text{CuSO}_4 \cdot 7\text{H}_2\text{O}$  was used.

#### 4.2.5 Experiments with synthetic Fe gel and allophane

##### 4.2.5.1 Adsorption experiments

For Zn and Cd adsorption studies 5-ml aliquots of Fe gel, containing 50 mg gel were removed from the continuously stirred suspension

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\* In this study, the term "native-adsorbed" Zn and Cd is used to indicate the amount of Zn and Cd present on adsorption sites prior to additions made in the laboratory. These could derive from a number of sources including parent material, and fertiliser addition.

of the stock gel suspension. The solid:solution ratio used was 1:800 and the adsorption determinations were carried out in a matrix of  $3 \times 10^{-2}$  M NaCl. A 40-hr equilibration time was used.

Studies of Zn and Cd adsorption onto purified Fe gel were carried out to investigate adsorption at low Zn and Cd loadings on the gel. To accomplish this, very low initial additions of Zn and Cd were used to give correspondingly low final solution concentrations. For example, adsorption data for Zn were obtained for five additions of Zn which gave final concentrations of from 0.064 to 0.510  $\mu\text{mol Zn l}^{-1}$  and five additions which gave final solution concentrations between 1.87 to 30.20  $\mu\text{mol Zn l}^{-1}$ . For Cd, the final solution concentrations for six additions ranged from 0.056 to 0.50  $\mu\text{mol Cd l}^{-1}$  and for a further five additions from 2.50 to 26.69  $\mu\text{mol Cd l}^{-1}$ . The initial pH of the matrix solution was pH 6.40 prior to addition of Zn or Cd but no attempt was made to maintain the pH during adsorption.

For Zn and Cd adsorption by allophane, use of the same 5-ml aliquot produced a solid:solution ratio of 1:670, because the allophane was 60 mg gel per 5-ml aliquot. Otherwise, the same conditions for the adsorption experiment were used as for the Fe gel. Whereas the same additions of Zn and Cd were made they resulted in different final solution concentrations.

#### 4.2.5.2 Effect of pH on Zn and Cd adsorption by Fe gel

The effect of pH on adsorption of Zn and Cd by Fe gel was determined over a range of final equilibrium pH values. The major objective was to investigate the effect of pH on the adsorption parameters determined by resolution of Langmuir isotherm plots. In order to obtain adsorption isotherms at several different pH values, the

following procedure was used: Zn or Cd was adsorbed by Fe gel from a matrix of  $3 \times 10^{-2}$  M NaCl, at 10 different levels of addition of Zn or Cd. Each addition of Zn or Cd was repeated for gel samples at 4 different initial pH values within the range pH 5.0 to pH 6.0. The initial pH of the matrix solutions was adjusted using  $1 \times 10^{-3}$  M and  $1 \times 10^{-3}$  M HCl or  $1 \times 10^{-3}$  M and  $1 \times 10^{-2}$  M NaOH. The solid:solution ratio was 1:800 and the equilibration time was 40 hr. After adsorption, the suspensions were centrifuged, filtered, and the equilibrium pH of the supernatant solution measured. The supernatant solution was then analysed for Zn or Cd contents. The amounts of Zn or Cd adsorbed were obtained by difference between initial and final concentrations.

Plots of amounts of Zn or Cd adsorbed against final pH of the supernatant for each addition of Zn or Cd were then prepared. Examples of such plots for Zn adsorption are shown for four additions of Zn in Fig. 4.2. Two final pH values were selected on the linear portions of these curves. (See points a and b on Fig. 4.2). In the case of the example shown in Fig. 4.2, the pH values chosen for Zn were pH 5.45 (point a) and 5.60 (point b). The amounts of Zn adsorbed for the four additions are indicated by points  $c_1 - c_4$  on the y-axis for pH 5.45, and points  $d_1 - d_4$  for pH 5.60. This procedure, when used for the ten actual additions of Zn and Cd made, generated a series of adsorption data at a fixed final pH. This data was then plotted as a separate adsorption isotherm and resolved using the Langmuir treatment.

Because of the difficulty in controlling the final equilibrium pH with any adsorption reaction, when different additions of Zn or Cd are made the above method is used to obtain adsorption data for a range of different additions of Zn or Cd, at fixed equilibrium pH values. The method described has been used previously by Kinniburgh et al. (1975,

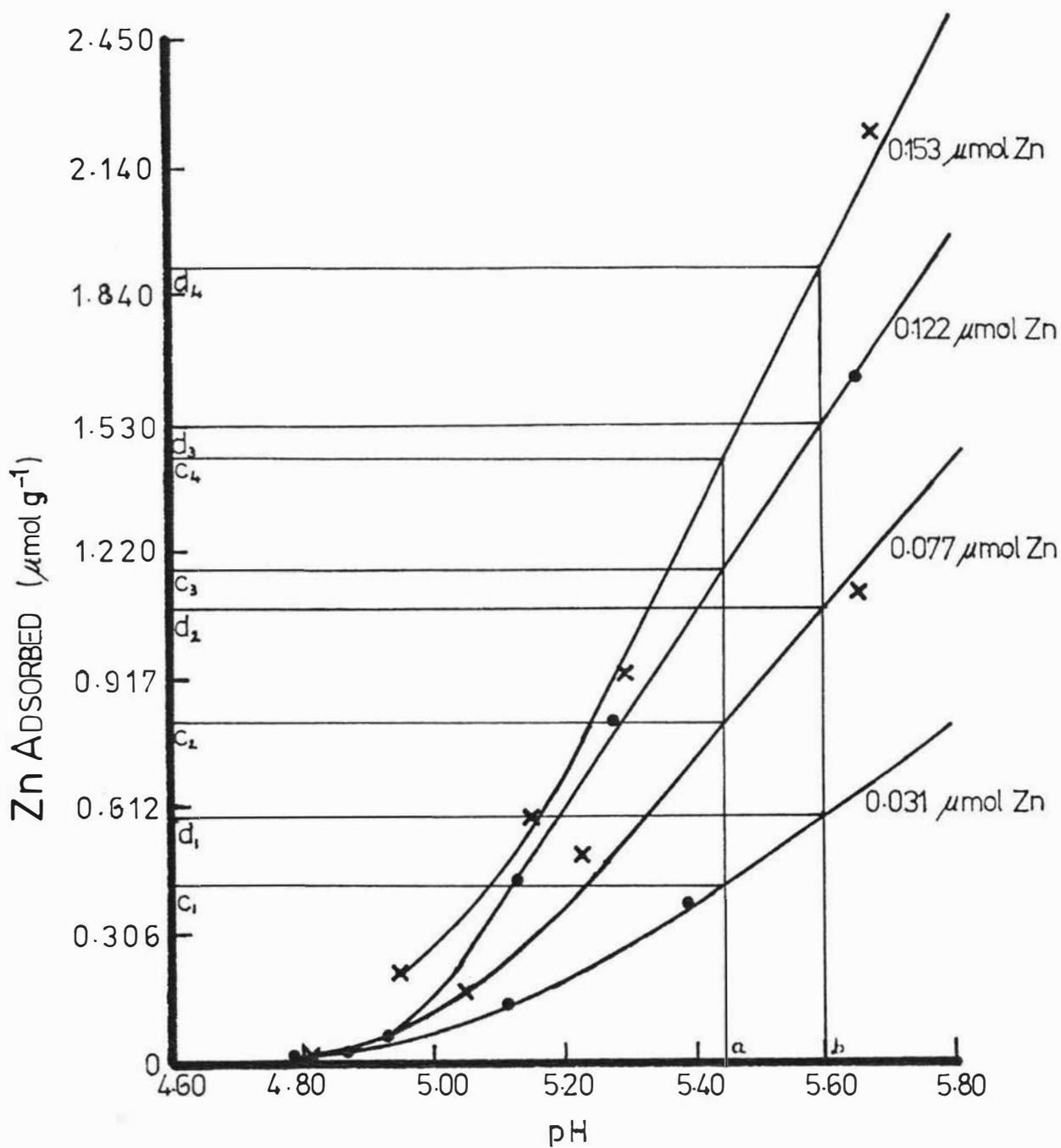


Figure 4.2

Effect of final pH on amount of Zn adsorbed by Fe gel from  $3 \times 10^{-2} \text{M NaCl}$  after 40 hr, at different additions of Zn

1976), for the adsorption of Ca, Cd, Co, Cu, Mg, Ni, Pb, Sr and Zn by hydrous oxides.

### 4.3 Results and Discussion

#### 4.3.1 Effect of time of equilibration on Zn and Cd adsorption

In Section 4.2.1 it was established that Zn and Cd were not adsorbed by the polycarbonate tubes during equilibration, so in all future discussions any losses of these metals from solution is interpreted as uptake by the adsorbent under study.

The initial uptake of both Zn and Cd at both the low and high levels of addition of Zn and Cd for each soil was rapid. Within the first 12 hr of equilibration loss from solution was virtually complete, as shown in Figs. 4.3 and 4.4. Closer examination of the data (Figs. 4.5 and 4.6) for the Okaihau subsoil revealed a gradual decrease in solution concentration for both Zn and Cd which continued right up to 240 hr at the high levels of addition. A smaller change, (i.e., decrease in solution concentration) occurred for Cd over the period 24 to 240 hr. There were no trends in Zn or Cd concentrations at the low levels of addition after 24 hr.

For the Makerua soil, concentrations of Zn and Cd were essentially constant after 96 hours, at both levels of Zn and Cd addition. The different kinetics of adsorption noted for Makerua and Okaihau soils may relate to their different compositions. The rapid equilibrium with the Makerua soil may represent the situation of readily-accessible absorbing sites such as on soil organic matter. The slower adsorption kinetics observed for Okaihau soil may indicate the presence of a number

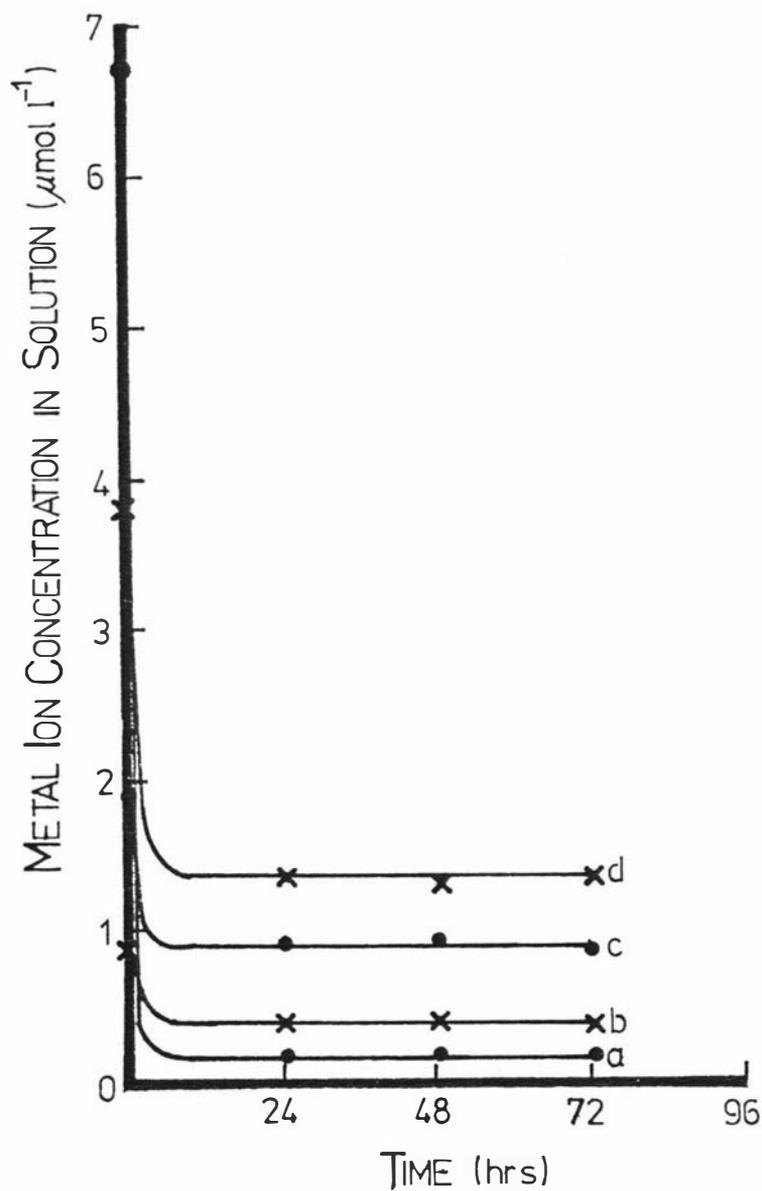


Figure 4.3 Effect of time of equilibration at low initial solution concentrations of Zn and Cd for adsorption of Zn and Cd by Makerua topsoil and Okaihau subsoil

- a:  $0.090 \mu\text{mol Cd g}^{-1}$  added to Makerua topsoil
- b:  $0.010 \mu\text{mol Cd g}^{-1}$  added to Okaihau subsoil
- c:  $0.015 \mu\text{mol Zn g}^{-1}$  added to Okaihau subsoil
- d:  $0.030 \mu\text{mol Zn g}^{-1}$  added to Makerua topsoil.

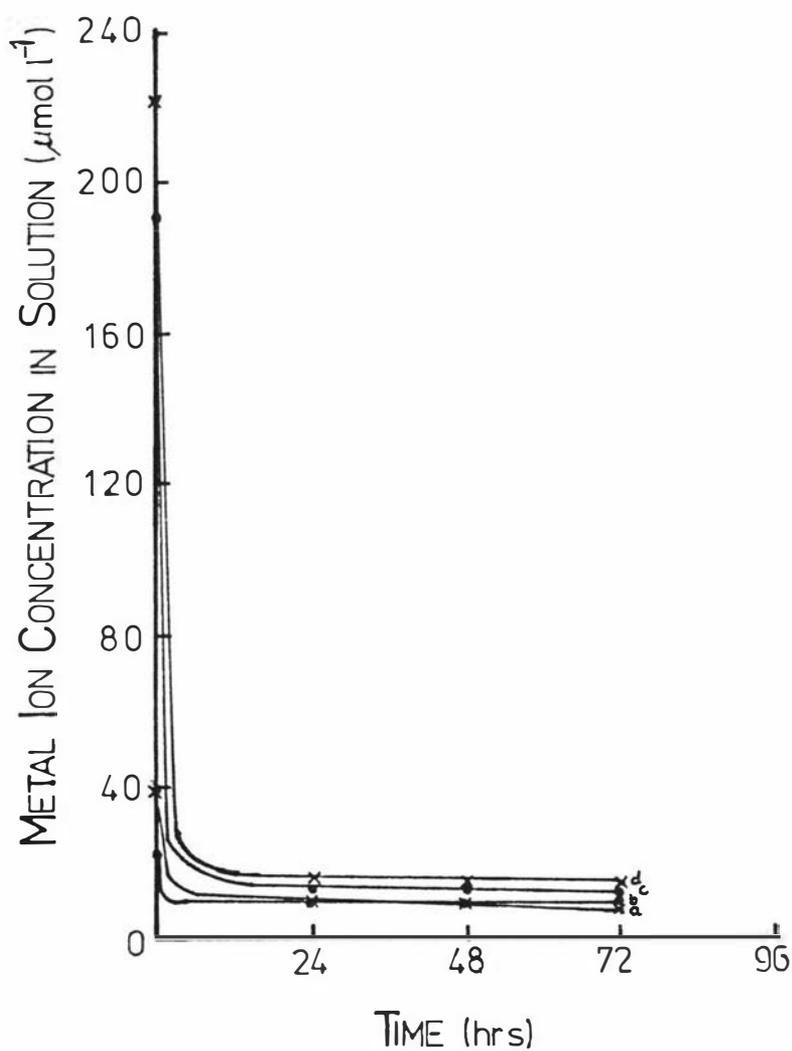


Figure 4.4 Effect of time of equilibration at high initial solution concentrations of Zn and Cd for adsorption of Zn and Cd by Makerua topsoil and Okaihau subsoil

- a:  $1.53 \mu\text{mol Zn g}^{-1}$  added to Makerua topsoil
- b:  $0.31 \mu\text{mol Cd g}^{-1}$  added to Okaihau subsoil
- c:  $0.31 \mu\text{mol Zn g}^{-1}$  added to Okaihau subsoil
- d:  $3.06 \mu\text{mol Cd g}^{-1}$  added to Makerua topsoil

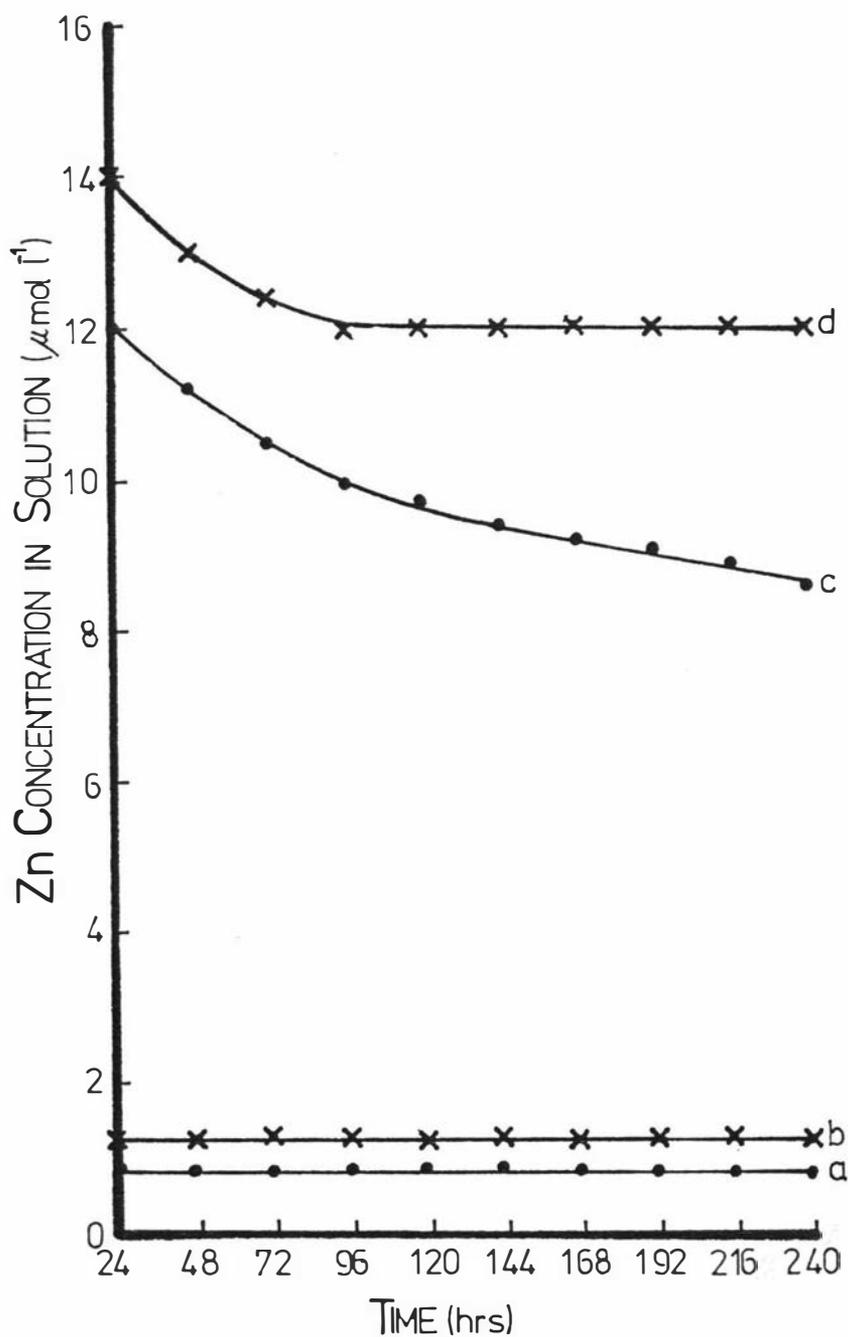


Figure 4.5 Effect of time of equilibration on solution Zn concentrations for Makerua topsoil and Okaihau subsoil

- a:  $0.015 \mu\text{mol Zn g}^{-1}$  added to Okaihau subsoil  
 b:  $0.030 \mu\text{mol Zn g}^{-1}$  added to Makerua topsoil  
 c:  $0.31 \mu\text{mol Zn g}^{-1}$  added to Okaihau subsoil  
 d:  $1.53 \mu\text{mol Zn g}^{-1}$  added to Makerua topsoil

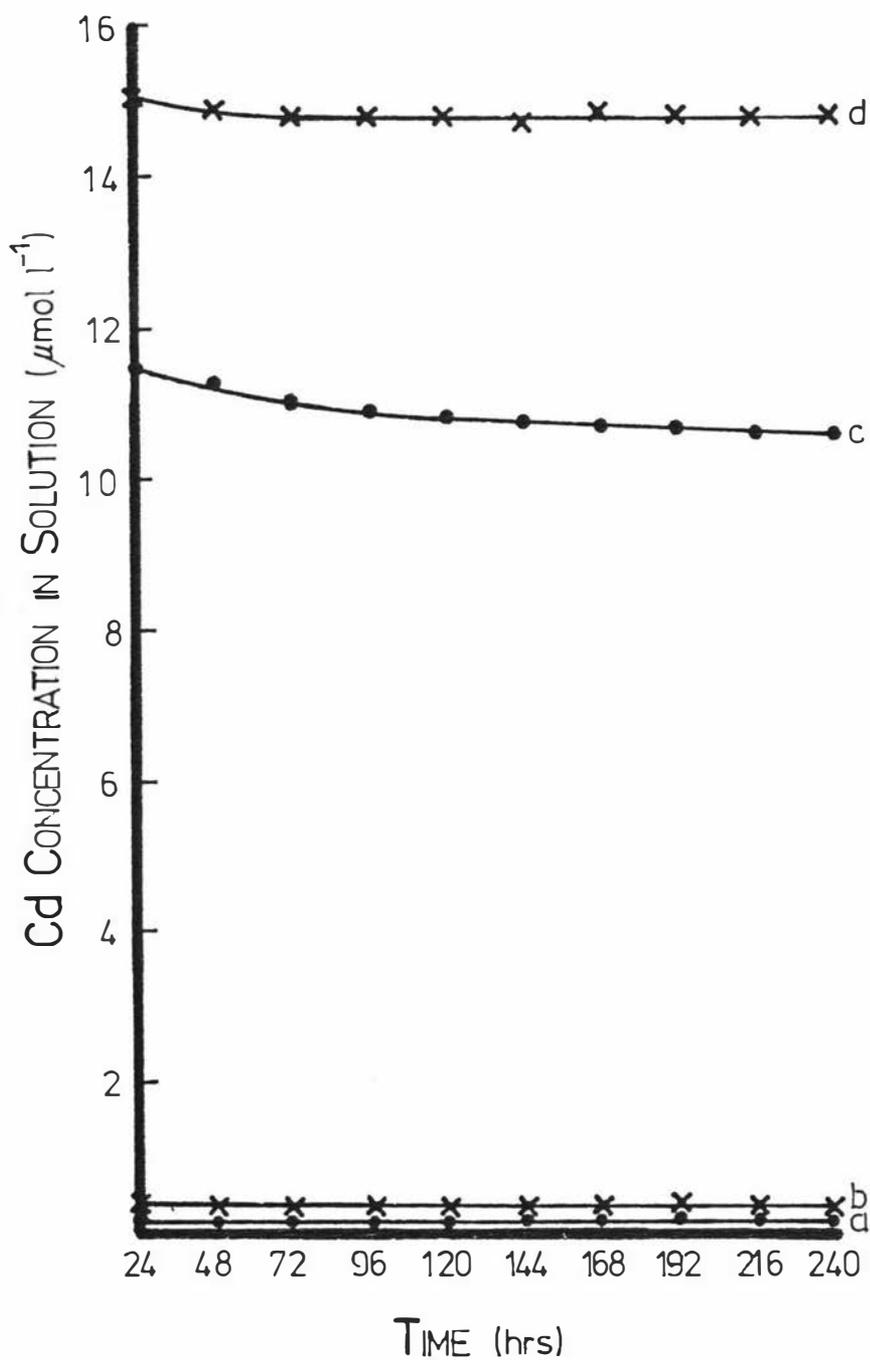


Figure 4.6 Effect of time of equilibration on solution Cd concentrations for Makerua topsoil and Okaihau subsoil

- a:  $0.090 \mu\text{mol Cd g}^{-1}$  added to Makerua topsoil
- b:  $0.010 \mu\text{mol Cd g}^{-1}$  added to Okaihau subsoil
- c:  $0.31 \mu\text{mol Cd g}^{-1}$  added to Okaihau subsoil
- d:  $3.06 \mu\text{mol Cd g}^{-1}$  added to Makerua topsoil

of less accessible (internal) sites onto which Zn and Cd diffuse slowly from exterior positions; this process is sometimes referred to as "absorption" (Ryden et al., 1977a). Whilst the process of absorption by hydrous oxides does not appear to have been invoked as an explanation for the continuing slow adsorption of Zn or Cd, the phenomenon has been suggested for P on Fe gel, on other hydrous oxides and on soils (McLaughlin et al., 1977; Ryden et al., 1977a). Further investigation into the occurrence of an absorption process for Zn and Cd with hydrous Fe oxides is discussed in a later chapter (Chapter 6).

#### 4.3.2 Evaluation of Zn and Cd adsorption isotherms

##### 4.3.2.1 Evaluation of isotherms using the Langmuir equation

The Langmuir equation was applied to 40, 120, 144 and 192 hr adsorption data for Makerua, Okaihau, Tokomaru, and Egmont topsoil and subsoil samples.

The reciprocal form of the Langmuir equation used to describe the experimental data was:

$$\frac{1}{X} = \frac{1}{kbc} + \frac{1}{b} \quad (4.1)$$

where X = the amount of Zn or Cd adsorbed, c = the final Zn or Cd solution concentration, b = the adsorption maximum and k = a constant related to the free energy of the adsorption reaction. The use of reciprocal plots allowed better evaluation of the data points at low final solution concentration values (i.e., higher reciprocal concentration values).

Evaluation of experimental data for Zn and Cd adsorption by soils using the Langmuir approach requires that all Zn and Cd present on soil surfaces be taken into account. Native-adsorbed Zn and Cd values can be included by adding the appropriate amounts of Zn or Cd to the amounts

(X values) of Zn or Cd adsorbed for each soil (as determined experimentally). A consideration of the amounts of native-adsorbed Zn and Cd becomes especially important at low surface loadings when native-adsorbed Zn or Cd obviously represents a higher proportion of the total amount adsorbed than is the case at higher loadings.

For all four soils used in this study, plots of the adsorption data for 40 hr to 192 hr equilibration times did not conform to a single linear plot (See Figs. 4.7 to 4.10 for typical plots). Only at final solution concentrations of less than  $2.5 \mu\text{mol Zn l}^{-1}$  and  $2.0 \mu\text{mol Cd l}^{-1}$  could the data be adequately described by a single Langmuir equation. The amounts adsorbed at these low final solution concentrations (high  $\frac{1}{c}$  values) were thus attributed to adsorption by one population of sites termed 'region I'. At higher solution concentration values (low  $\frac{1}{c}$  values), the experimental data deviated from the single linear relationship (Figs. 4.7 to 4.10). Thus it appeared that the description of the adsorption data required a more complex mathematical equation. Therefore a second linear region, to accommodate the amounts of Zn and Cd adsorbed at the high solution concentrations was postulated.

The two regions can be mathematically described by two separate Langmuir equations, each equation having its own adsorption maximum (b value) and binding energy (k value) terms. As the adsorption data in this study is described by more than one Langmuir equation, a method for assessing the appropriate parameters for the different populations of sites is required. Such a method based on that used by Ryden et al. (1977) for P sorption, is described in Appendix 2.

In a system containing more than one type of adsorption site, it is assumed that adsorption will preferentially take place at sites of

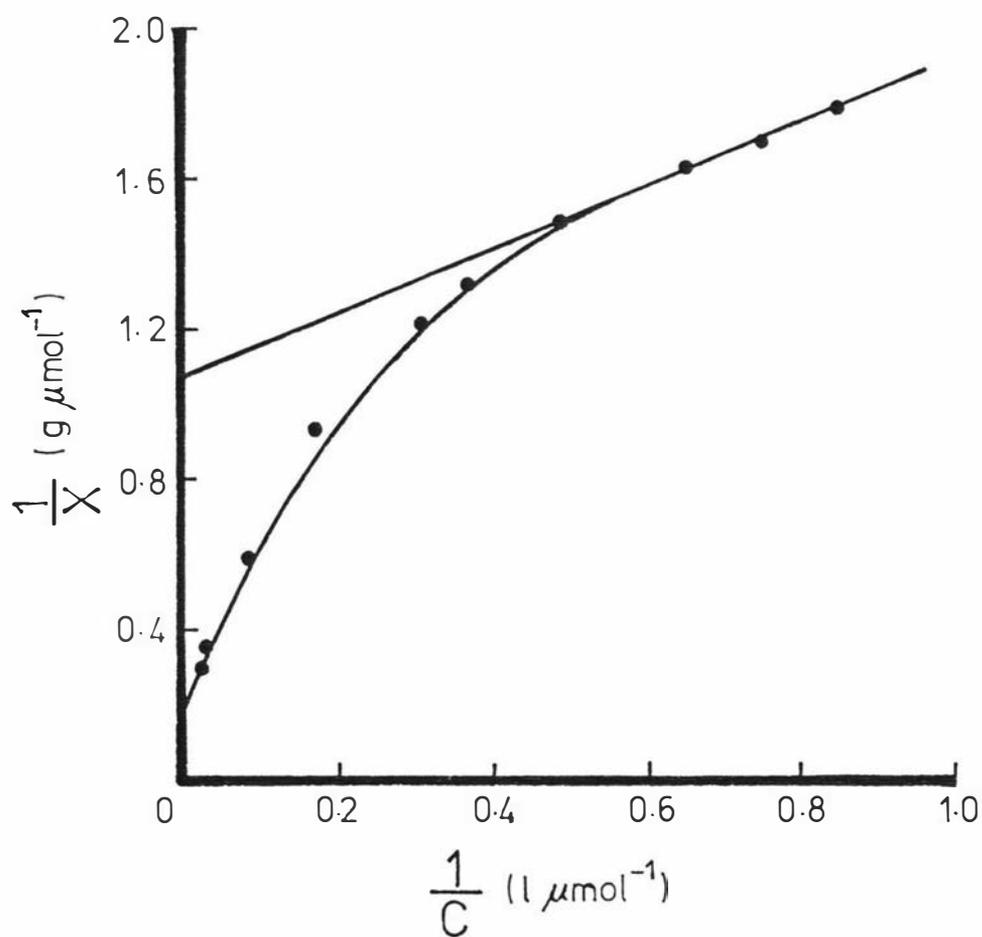


Figure 4.7 Reciprocal plots of amounts of Zn adsorbed by Makerua peaty silt loam topsoil against equilibrium Zn concentrations

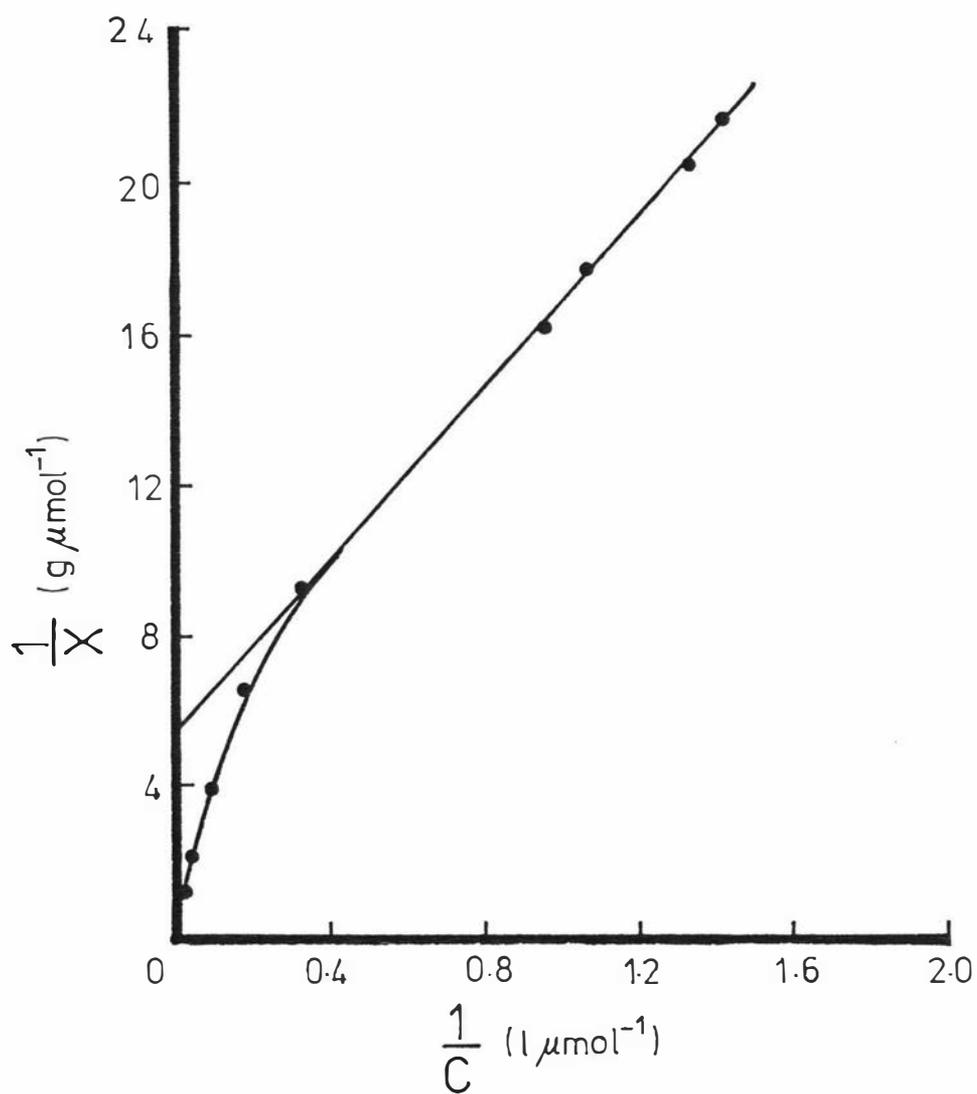


Figure 4.8 Reciprocal plots of amounts of Zn adsorbed by Okaihau gravelly clay sub-soil against equilibrium Zn concentrations

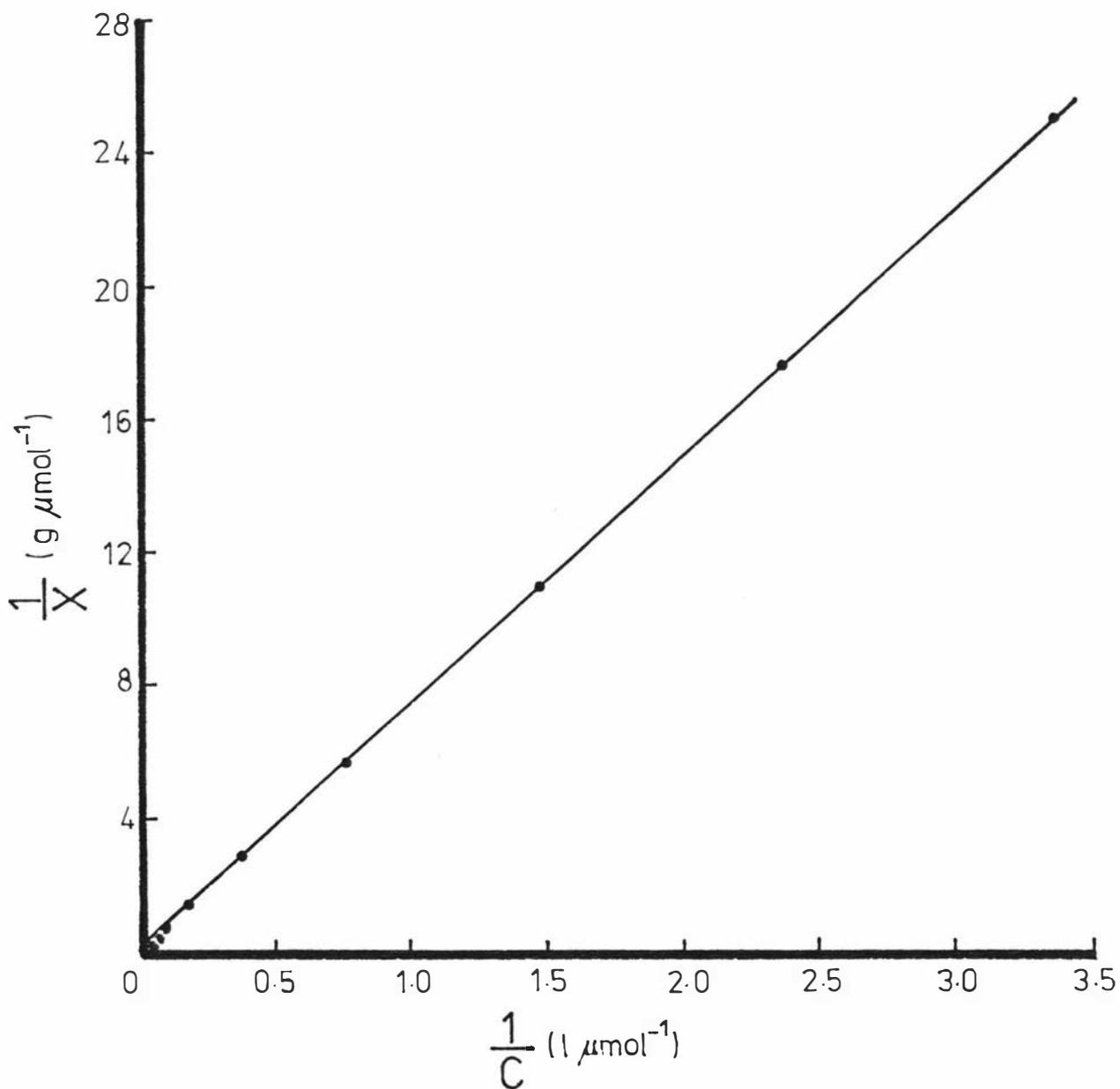


Figure 4.9 Reciprocal plots of amounts of Cd adsorbed by Makerua peaty silt loam topsoil against equilibrium Cd concentrations

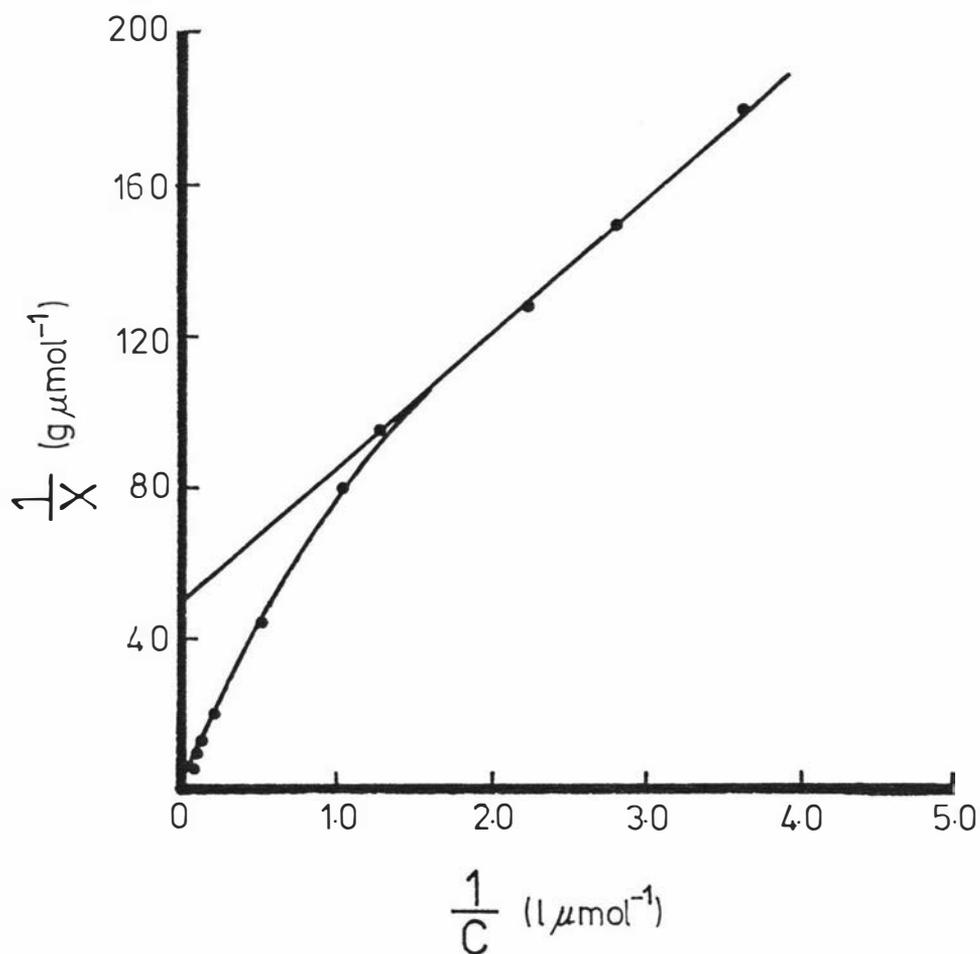


Figure 4.10 Reciprocal plots of amounts of Cd adsorbed by Okaihau gravelly clay subsoil against equilibrium Cd concentrations

highest binding energy, initially at low saturations of available adsorption sites. At all final solution concentrations, it appears reasonable to suggest that some adsorption takes place on both postulated populations of sites. It is reasonable to propose that at lower equilibrium solution concentrations of Zn and Cd, adsorption will predominantly take place on one population of sites and at higher final concentrations of Zn and Cd, adsorption occurs on a second population of sites. In order to obtain the Langmuir constants (b and k values) for each of the two regions a reiterative process involving successive approximations of b and k values was used. The method of successive approximations is outlined in Appendix 2 and the first step in the process is shown in Figs. 4.7 to 4.10 for Makerua peaty silt loam topsoil and Okaihau gravelly clay subsoils. In each case, a reasonable approximation of the adsorption data could be obtained using two Langmuir equations. Although the data for Cd adsorption by the Makerua soil (Fig. 4.9) is not as well-defined as for the other soils, the data can be resolved into two regions.

At each equilibrium concentration of Zn or Cd, the amounts of Zn or Cd assigned to the two regions can be summed to give the total amount adsorbed. If the resolution has been successful the isotherm derived by plotting the calculated amounts adsorbed versus equilibrium concentrations should be equivalent to the original experimental isotherm. A typical comparison of "derived" and actual adsorption isotherms for Zn and Cd adsorption by Okaihau gravelly clay subsoil is shown in Figs. 4.11 and 4.12.

The "derived" isotherm deviates from the experimental data points by no more than 5% at each equilibrium concentration of Zn and Cd for all soils used. Thus, adsorption isotherms for Zn and Cd on soil

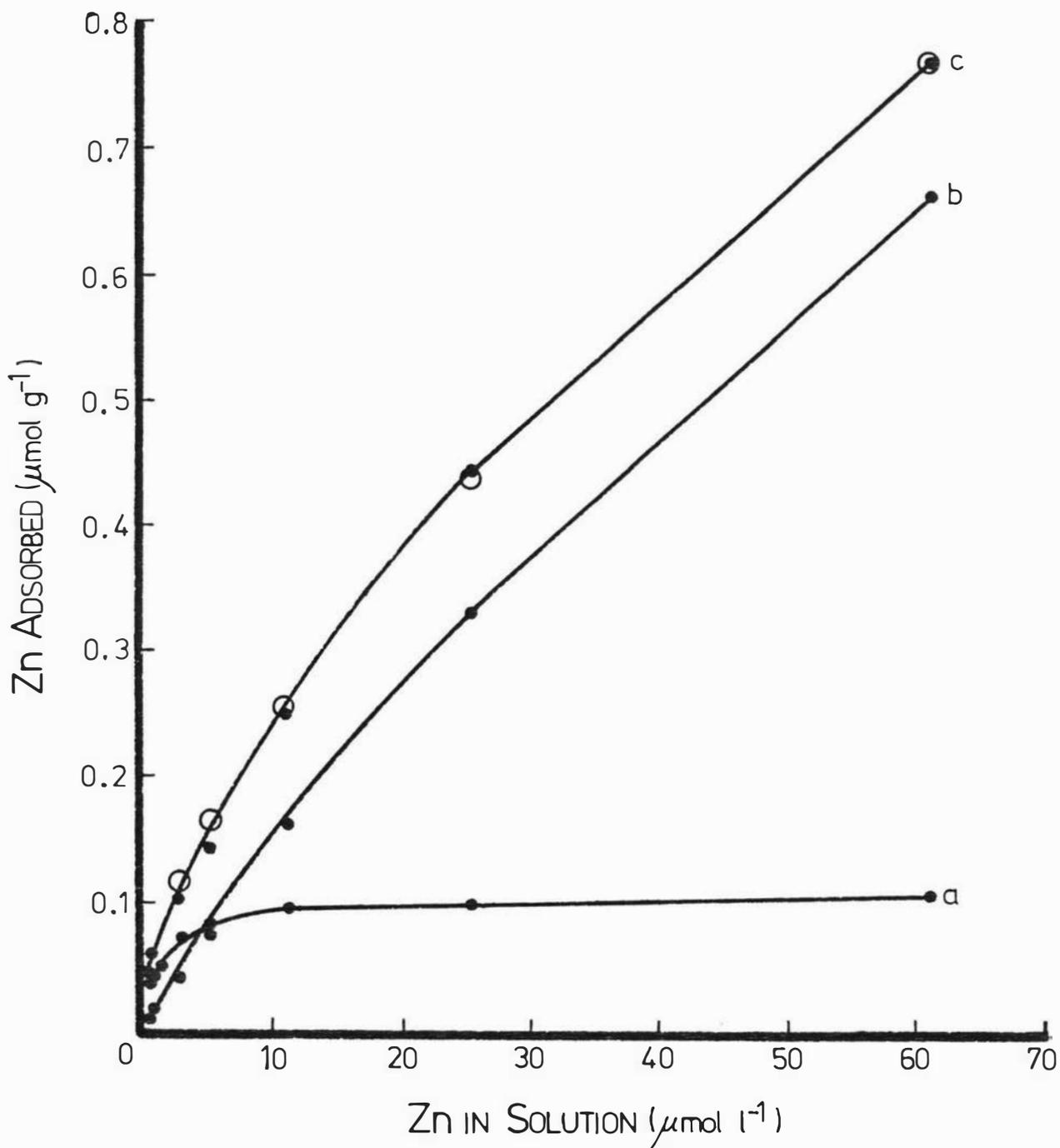


Figure 4.11

Plots of Zn adsorption (40 hr) by Okaihau gravelly clay subsoil showing actual (c), resolved (region I (a) and region II (b)) and recombined (o) isotherms

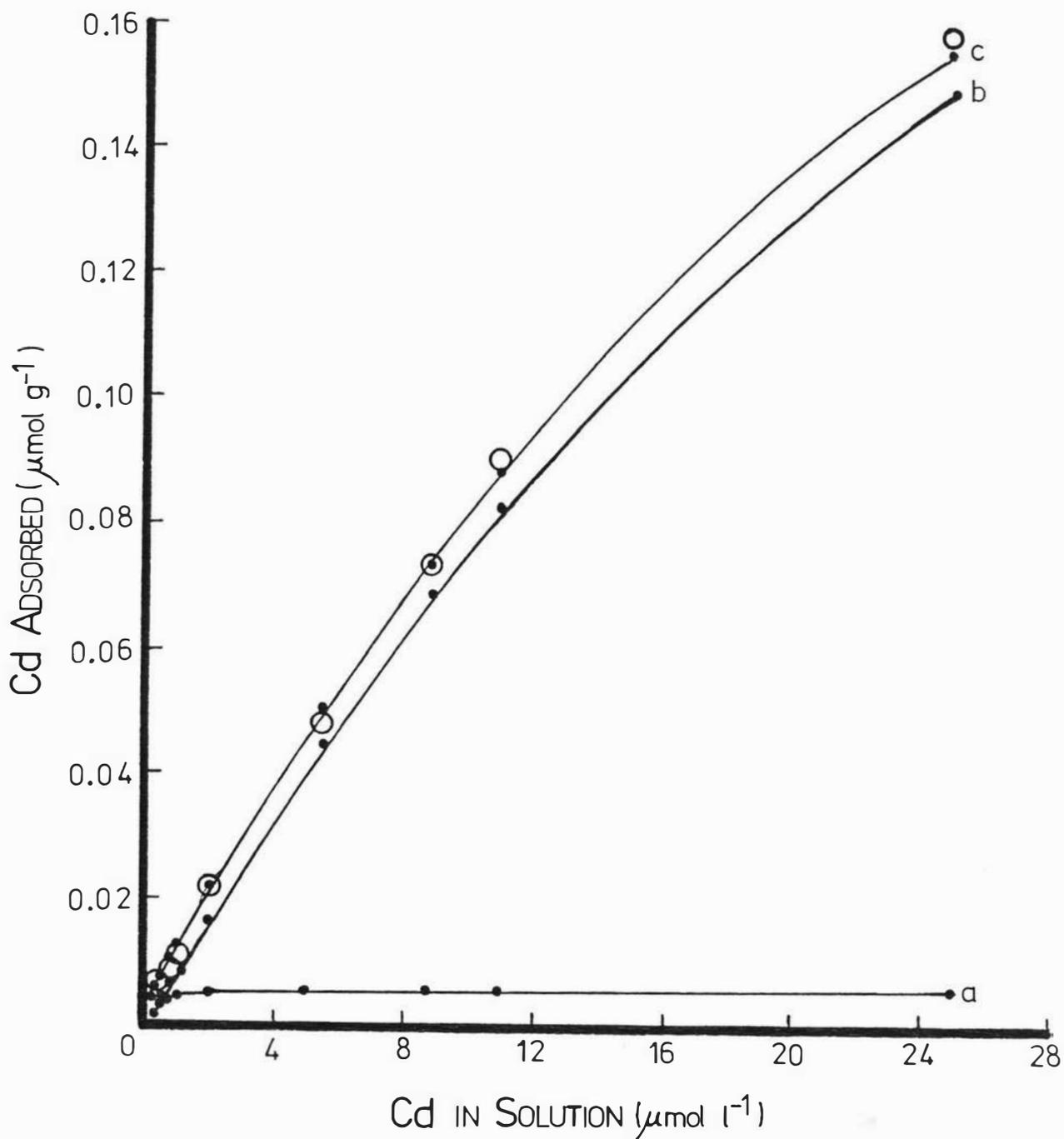


Figure 4.12

Plots of Cd adsorption (40 hr) by Okaihau gravelly clay subsoil showing actual (c), resolved (region I (a) and region II (b)) and recombined (o) isotherms

samples over the final equilibrium concentration range 0 - 300  $\mu\text{mol Zn or Cd l}^{-1}$  can be closely approximated by the use of a Langmuir model based on the existence of two populations of sites.

#### 4.3.2.2 Free energies of adsorption

Free energies of adsorption ( $\Delta G$  values) were derived for all soils studied, using the respective Langmuir constants according to the relationship (4.2):

$$\Delta G = -RT \ln k \quad (4.2)$$

where  $k$  = the Langmuir constant relating to binding energy.

The validity of this requires discussion.

For the adsorption of non-electrolytes by ideal surfaces at equilibrium, the fractional surface coverage ( $\theta$ ), is given by the equation:

$$\frac{\theta}{1-\theta} = Kc \quad (\text{Graham, 1953}) \quad (4.3)$$

where  $K$  = equilibrium constant for the adsorption reaction

$c$  = equilibrium concentration.

This assumes that all activity coefficients are unity and activity coefficients for filled and unfilled sites are the same (Graham, 1953).

Equation (4.3) is of the same form as the Langmuir equation:

$$\frac{x}{b} = \frac{kc}{1+kc} \quad (4.4)$$

if  $\frac{x}{b} = \theta$  = fractional surface coverage, Equation (4.3) may be rearranged to give:

$$\frac{\frac{x}{b}}{1 - \frac{x}{b}} = kc \quad (4.5)$$

where  $k$  is the ratio of rate constants for the forward and reverse reactions and is analogous to an equilibrium constant (Moore, 1962).

Equation (4.5) is now in the same form as equation (4.3) with  $k$  equivalent to  $K$ , the equilibrium constant. The equilibrium constant ( $K$ ) is related to the free energy of adsorption ( $\Delta G$ ) for a reaction by the equation:

$$\Delta G = -RT \ln K \quad (\text{Stumm and Morgan, 1970}) \quad (4.6)$$

As the equilibrium constant,  $K$ , and the Langmuir coefficient,  $k$ , are analogous (Moore, 1962) and if equation (4.6) is valid, then it is also valid to determine  $\Delta G$  values from the Langmuir constant ( $k$ ), using equation (4.2).

However, these present studies deal with adsorption of electrically-charged species, and apart from chemical forces, coulombic and solvation forces are also involved in the adsorption process. The free energy becomes the sum of the free energies of chemical and coulombic attractions and solvation energy (which is usually negligible compared to the former pair (Huang, 1975)) and this free energy of adsorption may be given as:

$$\Delta G_{\text{Total}} \approx \Delta G_{\text{Chemical}} + \Delta G_{\text{Coulombic}} + \Delta G_{\text{Solvation}} \quad (4.7)$$

(James and Healy, 1972)

If the Langmuir constant ( $k$ ) is used for calculation of  $\Delta G$  values, then  $\Delta G_{\text{Total}}$  depends on  $\Delta G_{\text{Chemical}}$ , the chemical affinity between reactants, and  $\Delta G_{\text{Coulombic}}$ , the electrostatic affinity between reactants, which depends on the amount of adsorption (Aveyard and Haydon, 1973).  $\Delta G_{\text{Coulombic}}$  will change as adsorption changes, and so  $\Delta G_{\text{Total}}$  will alter unless  $\Delta G_{\text{Coulombic}}$  is small compared to  $\Delta G_{\text{Chemical}}$ . When there is a strong chemical interaction between adsorbing ion and surface, i.e., a high  $\Delta G_{\text{Chemical}}$ , then the  $\Delta G_{\text{Total}}$  value will be more a measure of the chemical affinity of the surface for the adsorbed ion.

Hence,  $\Delta G$  values obtained from the Langmuir coefficients ( $k$  values) will give a measure of the chemical affinity of the adsorption

surfaces of the soil for adsorbed Zn and Cd.

#### 4.3.3 Comparison of 40, 120, 144, 192 hr adsorption isotherms for Zn and Cd adsorption by Makerua peaty silt loam topsoil and Okaihau gravelly clay subsoil

The determination of equilibrium adsorption isotherms, as discussed in Section 4.2.2, was not possible in the present study. In order to establish the validity of 40-hr adsorption isotherms for obtaining Langmuir constants and free energies of adsorption, the effect of time of equilibration on the Langmuir adsorption parameters ( $b$  and  $\Delta G$  values) was investigated using Makerua peaty silt loam topsoil and Okaihau gravelly clay subsoil. As explained earlier, these two soils of contrasting composition were used to examine whether soil composition affects the kinetics of adsorption and the validity of using short equilibration times in subsequent adsorption experiments.

The adsorption maxima ( $b$  values) and free energies of adsorption ( $\Delta G$  values) for Zn adsorption by Makerua and Okaihau soils are given in Table 4.2 for 40, 120, 144, and 192 hr adsorption isotherms. Table 4.3 shows the same information for Cd.

For both Zn and Cd, and for both soils, the  $b$  and  $\Delta G$  values obtained at different times of equilibration were essentially the same for each region. The variation in the data presented in Tables 4.2 and 4.3 is due more to experimental error which is implicit in the determination of amounts of Zn and Cd remaining in solution after adsorption, rather than to errors in positioning the line of best fit through data points to obtain the  $b$  and  $k$  values by successive approximation. The intercepts and slopes, which are used to obtain  $b$  and  $k$  values, respectively, by the method of successive approximation, were in the present study determined, both by regression analysis and

Table 4.2 Effect of time of equilibration on the adsorption parameters for Zn adsorption by Makerua and Okaihau soils

Soil	Adsorption parameter	40 hr	120 hr	144 hr	192 hr
Makerua Oh	$b_I$ ( $\mu\text{mol g}^{-1}$ )	0.61	0.48	0.49	0.46
	$b_{II}$ ( $\mu\text{mol g}^{-1}$ )	15.29	15.29	16.99	12.74
	$\Delta G_I$ ( $\text{KJmol}^{-1}$ )	-36.2	-37.9	-37.9	-38.0
	$\Delta G_{II}$ ( $\text{KJmol}^{-1}$ )	-21.6	-21.8	-21.4	-22.3
Okaihau Bcs	$b_I$ ( $\mu\text{mol g}^{-1}$ )	0.11	0.13	0.12	0.15
	$b_{II}$ ( $\mu\text{mol g}^{-1}$ )	2.47	2.78	2.78	2.64
	$\Delta G_I$ ( $\text{KJmol}^{-1}$ )	-33.2	-33.2	-33.3	-32.7
	$\Delta G_{II}$ ( $\text{KJmol}^{-1}$ )	-21.5	-21.7	-21.7	-21.8

Table 4.3 Effect of time of equilibration on the adsorption parameters  
for Cd adsorption by Makerua and Okaihau soils

Soil	Adsorption parameters	40 hr	120 hr	144 hr	192 hr
Makerua Oh	$b_I$ ( $\mu\text{mol g}^{-1}$ )	0.89	0.59	0.45	0.59
	$b_{II}$ ( $\mu\text{mol g}^{-1}$ )	17.79	17.79	17.79	17.79
	$\Delta G_I$ ( $\text{KJmol}^{-1}$ )	-28.4	-29.2	-29.5	-29.1
	$\Delta G_{II}$ ( $\text{KJmol}^{-1}$ )	-20.0	-20.4	-20.5	-20.3
Okaihau Bcs	$b_I$ ( $\mu\text{mol g}^{-1}$ )	0.007	0.007	0.009	0.010
	$b_{II}$ ( $\mu\text{mol g}^{-1}$ )	0.42	0.41	0.56	0.68
	$\Delta G_I$ ( $\text{KJmol}^{-1}$ )	-36.9	-36.8	-36.3	-35.8
	$\Delta G_{II}$ ( $\text{KJmol}^{-1}$ )	-24.6	-24.9	-23.6	-23.2

by lines drawn by "inspection" through the data points. This latter technique was shown to produce virtually identical values for slopes and intercepts (Table 4.4), and this method was adopted for all subsequent analyses.

Allowing for the errors associated with the determination of experimental data points, the  $b$  and  $\Delta G$  values for 40-hr, 120-hr, 144-hr and 192-hr adsorption isotherms for both Makerua and Okaihau soils are considered as acceptably similar.

As time of equilibration appeared to have little obvious effect on the adsorption parameters obtained for the soils, 40-hr adsorption isotherms were used, in place of either longer-term adsorption isotherms or equilibrium adsorption isotherms, to determine adsorption parameters. This shorter equilibration time offered the advantage of expediency, without any major loss in accuracy of results and facilitated the handling of a large number of samples.

#### 4.3.4 40-hr adsorption isotherms

Results discussed in the previous Section 4.3.3 suggest that adsorption parameters derived from 40-hr adsorption isotherms are likely to be similar to those derived under equilibrium conditions. However, an adsorption maximum may never be reached even with longer times of equilibration because of the possibility of absorption of the adsorbed Zn and Cd. Absorption will be discussed in a later chapter (Chapter 6).

In order to compare and contrast Zn and Cd adsorption characteristics for Makerua, Egmont, Tokomaru, and Okaihau soils, 40-hr isotherms were determined. Typical 40-hr Zn and Cd isotherms obtained for the Oh horizon of Makerua peaty silt loam, the Ah and Bwl horizon of Egmont brown loam, the Ah and Btg horizon of Tokomaru silt loam, and

Table 4.4 Comparison of slopes and intercepts fitted by regression analysis and by "inspection" for Zn and Cd adsorption by Okaihau topsoil

		Curve fitted by:	
		regression analysis	"inspection"
Zn	<u>Region I</u>		
	Slope	0.0072	0.0075
	Intercept	0.1570	0.1520
	<u>Region II</u>		
	Slope	0.0363	0.0364
	Intercept	0.0021	0.0020
Cd	<u>Region I</u>		
	Slope	0.0231	0.0233
	Intercept	0.0830	0.0800
	<u>Region II</u>		
	Slope	0.0541	0.0542
	Intercept	0.0017	0.0014

the Ah and Bcs horizon of Okaihau gravelly clay are illustrated in Figs. 2.1 to 2.6. These isotherms were all of the L-type, according to the classification of Giles et al. (1960), this being the most commonly found type for liquid-solid systems. It is typical in situations where a limit to adsorption occurs at the completion of a monolayer of surface coverage.

Resolution of the experimental data revealed the existence of at least two adsorption regions with adsorption in each fitting a single Langmuir equation. For all soils, adsorption in region I was dominant at low final solution concentrations, i.e., up to approximately  $2.0 \mu\text{mol Zn or Cd l}^{-1}$ , and region II dominant at final solution concentrations above approximately  $2.0 \mu\text{mol Zn or Cd l}^{-1}$ .

For the Okaihau gravelly clay subsoil, region I for Zn was virtually saturated at a final solution concentration of  $10 \mu\text{mol Zn l}^{-1}$  (Fig. 4.11) and for Cd at  $2.0 \mu\text{mol Cd l}^{-1}$  (Fig. 4.12), while for adsorption in region II, saturation was not attained even at final solution concentrations of  $60 \mu\text{mol Zn l}^{-1}$  and  $26 \mu\text{mol Cd l}^{-1}$ .

This finding of saturation of region I at such low final solution concentrations ( $2$  and  $10 \mu\text{mol Cd or Zn l}^{-1}$ ), for all soils studied, illustrates the importance of investigating adsorption of Zn and Cd at low additions, and hence at low equilibrium Zn and Cd concentrations. Obtaining adsorption isotherms from data points at high additions of Zn and Cd, which offers the convenience of working at high final solution concentrations, could fail to detect the existence of high energy adsorption sites at low surface coverage. For example, Udo et al. (1970) using high additions of Zn, which produced final solution concentrations of from  $15.3$  to  $458 \mu\text{mol Zn l}^{-1}$  and John (1972) studying Cd adsorption at high final solution concentrations of  $3.56$  to

14.24  $\mu\text{mol Cd l}^{-1}$ , found the experimental data could be described with a single Langmuir equation, and not two equations as found in the present study.

#### 4.3.4.1 k and $\Delta G$ values for Zn and Cd adsorption by soils

Values for the Langmuir constants b (adsorption maximum) and k (coefficient related to the binding energy) and also the free energies of adsorption, i.e.,  $\Delta G_{\text{I}}$  and  $\Delta G_{\text{II}}$  for Zn and Cd are given in Tables 4.5 and 4.6. The k and  $\Delta G$  values for both Zn and Cd are always higher for region I than for region II, suggesting that Zn or Cd adsorbed in region I is more tightly held than in region II.

A statistical analysis of  $\Delta G_{\text{I}}$  and  $\Delta G_{\text{II}}$  values was carried out using both a t-test and a combined one-way analysis of variance. Both tests showed a highly significant difference (1% significance) between the  $\Delta G_{\text{I}}$  and  $\Delta G_{\text{II}}$  values, across all soils.

Although  $\Delta G$  values give no evidence of adsorption mechanism, the significant difference between the  $\Delta G$  values for regions I and II obtained for all soils suggests that different adsorption processes may well be operating in each region. Assuming that the chemical term,  $\Delta G_{\text{Chemical}}$ , is the dominant component in the free energy expression (Equation 4.7), then region I represents those sites for which a higher affinity exists between the surface and adsorbate than occurs in region II. This holds for both Zn and Cd, and on all soils examined. The  $\Delta G$  values obtained in this study are greater than those reported for the chemisorption of cations from aqueous solution by hydrous oxides (James and Healy, 1972). Thus, the large, negative  $\Delta G$  values found are hereafter considered as indicating chemisorption reactions, with region I being the stronger of the two.

Table 4.5 Langmuir parameters (b,k) and free energies of adsorption ( $\Delta G$ ) for Zn adsorption by Okaihau, Tokomaru and Egmont and Makerua topsoils and subsoils

Soil Horizon	Adsorption Maxima		Binding Energy		Free Energy of Adsorption*	
	$b_I$ $\mu\text{mol g}^{-1}$	$b_{II}$	$k_I$ $l\mu\text{mol}^{-1}$	$k_{II}$ $\times 10^{-2}$	$\Delta G_I$ $\text{KJ mol}^{-1}$	$\Delta G_{II}$
Okaihau Ah	0.10	7.65	133.0	0.36	-34.7	-20.2
Tokomaru Ah	0.44	15.29	26.6	0.48	-30.8	-20.9
Egmont Ah	1.12	27.80	30.0	0.37	-31.1	-20.2
Makerua Oh	0.61	15.29	244.0	0.70	-36.2	-21.6
Okaihau Bcs	0.11	2.47	71.2	0.61	-33.2	-21.5
Tokomaru Btg	0.08	2.35	116.5	0.74	-34.4	-21.9
Egmont Bwl	0.25	7.28	257.1	2.53	-36.3	-24.9
					$\Delta \bar{G}_I: -33.8 \pm 0.9$	$\Delta \bar{G}_{II}: -21.6 \pm 0.7$

\* Statistical analysis of free energy of adsorption data:

t test

t = 11.53 for 12 d.f.

F test (analysis of variance)

F = 43.11 for 1 and 12 d.f.

0.1% significance level, t = 4.32 •• Highly significant difference between  $\Delta G_I$  and  $\Delta G_{II}$  values.

1% significance level, F = 9.33 •• highly significant difference.

Table 4.6 Langmuir parameters (b,k) and free energies of adsorption ( $\Delta G$ ) for Cd adsorption by Okaihau, Tokomaru and Egmont and Makerua topsoils and subsoils

Soil Horizon	Adsorption maxima		Binding energy		Free energy of adsorption <sup>*</sup>	
	$b_I$ $\mu\text{mol g}^{-1}$	$b_{II}$	$k_I$ $1 \mu\text{mol}^{-1}$	$k_{II}$ $\times 10^{-2}$	$\Delta G_I$ $\text{KJ mol}^{-1}$	$\Delta G_{II}$
Okaihau Ah	0.11	6.36	38.6	0.29	-31.7	-19.6
Tokomaru Ah	0.17	11.86	48.6	0.47	-32.2	-20.8
Egmont Ah	0.48	17.45	17.5	0.76	-29.7	-22.0
Makerua Oh	0.89	17.79	10.1	0.34	-28.4	-20.0
Okaihau Bcs	0.006	0.42	338.2	2.21	-36.9	-24.6
Tokomaru Btg	0.006	1.98	291.3	0.37	-36.6	-20.2
Egmont Bw1	0.27	17.79	87.8	0.42	-33.7	-20.5
					$\Delta \bar{G}_I: -32.7 \pm 1.2$	$\Delta \bar{G}_{II}: -21.1 \pm 0.7$

\*Statistical analysis of free energy of adsorption data:

t test

t = 8.44 for 12 d.f. 0.1% significance level, t = 4.3

F-test (analysis of variance)

F = 70.83 for 1 and 12 d.f.

∴ Highly significant difference between  $\Delta G_I$  and  $\Delta G_{II}$  values. 1% significance level F = 9.33

∴ Highly significant difference

As the  $\Delta G$  values within each region, for all soils, were not significantly different, this suggested that the same adsorption mechanism may be operating, within each region, for the various soils.

Distinct similarities were noted for the  $\Delta G$  values in both regions for both Zn and Cd adsorption for all soils. Comparison of the mean values for  $\Delta G_I$  of both Zn and Cd (Tables 4.5 and 4.6) by all soils showed that in region I both were adsorbed with similar binding energies. This was also true for adsorption in region II and shows certain similarities in adsorption processes of both ions by all soils. This important finding is the result of the detailed comparison of Zn and Cd adsorption in the one study, utilising realistic Zn and Cd loadings on soil surfaces.

Although several other studies have reported results of Zn and Cd adsorption by soils (Table 4.7) most authors obtained only one region of adsorption (Udo et al., 1970; John, 1972; Levi-Minzi et al., 1976; Singh and Sekhon, 1977; 1977a). A two-region model was suggested by Shuman (1975) and Shukla and Mittal (1979) for Zn adsorption by soils with the two regions exhibiting different  $k$  and  $b$  values. No such findings for Cd have been reported in the literature to date.

In fact, the  $k$  values reported in the literature for Zn and Cd adsorption by soils appear to correlate more closely to the values found for region II in this present study. This would be predicted from the magnitude of the additions made in many previous adsorption studies.

#### 4.3.4.2 $b$ values for Zn and Cd adsorption by soils

For all soils, adsorption maxima for topsoils were greater than for the corresponding subsoils. This was true for both Zn and Cd in both regions. A comparison of the organic carbon content of each

Table 4.7 Ranges of adsorption maxima (b values) and adsorption energy constants (k values) for Zn and Cd adsorption by soils, as reported in the literature

	Langmuir constants		Reference
	$k$ $l\mu\text{mol}^{-1}$	$b$ $\mu\text{mol g}^{-1}$	
Zinc	$0.0016 \times 10^{-4} - 0.0088 \times 10^{-4}$	13.6 - 78.0	Udo et al. (1970)
	0.055 - 0.519 ( $k_I$ )	3.7 - 6.9 ( $b_I$ )	Shuman (1975)
	0.0009 - 0.0016 ( $k_{II}$ )	7.8 - 39.8 ( $b_{II}$ )	
	0.0026 - 0.0046	14.5 - 49.0	Singh and Sekhon (1977)
	0.89 - 1.06 ( $k_I$ )	20.0 - 24.7 ( $b_I$ )	Shukla and Mittal (1979)
	$5.3 \times 10^{-4} - 5.6 \times 10^{-4}$ ( $k_{II}$ )	2610 - 2800 ( $b_{II}$ )	
	0.266 - 1.32 ( $k_I$ )	0.08 - 1.12 ( $b_I$ )	Present study
	0.004 - 0.025 ( $k_{II}$ )	2.35 - 27.80 ( $b_{II}$ )	
Cadmium	0.0031 - 0.0275	70.6 - 106.0	John (1972)
	0.0062 - 0.0252	27.0 - 94.5	Levi-Minzi et al. (1976)
	0.0018 - 0.0106	6.5 - 22.0	Singh and Sekhon (1977a)
	0.0038 - 0.0253	42.0 - 89.0	Navrot et al. (1978)
	0.10 - 3.38 ( $k_I$ )	0.006 - 0.89 ( $b_I$ )	Present study
	0.003 - 0.022 ( $k_{II}$ )	0.42 - 17.79 ( $b_{II}$ )	

soil to the  $b_I$  and  $b_{II}$  values for Zn and Cd adsorption by each soil (Table 4.8) showed that, in general, the soils with the higher organic matter contents, i.e., the topsoils, also had the higher  $b$  values. Other workers have found high positive correlations between  $b$  values for Zn and Cd and organic matter content (John, 1971; Levi-Minzi et al., 1976; Singh and Sekhon, 1977). However, organic matter content is generally related to many other soil properties such that cause and effect relationships are often difficult to establish.

The differences in the other soil properties given in Table 2.4 do not readily explain the differences in Zn and Cd adsorption between the soils studied. There was no obvious relation found between short-range order (Tamms oxalate) Fe and adsorption maxima for Zn and Cd for soils, although it has been proposed by Jenne (1968) that Fe oxides can exert a disproportionate influence on trace element adsorption by soils and sediments. In view of the general consensus in the literature that Fe oxides play some role in adsorption of metal cations, the investigation continued using synthetic Fe gel.

#### 4.3.5 Zn and Cd adsorption by synthetic hydrous metal oxides

##### 4.3.5.1 Description of Zn and Cd adsorption by Fe gel using Langmuir equations

Whereas it has been suggested that the adsorption of anions, such as P and Mo, by soils and hydrous oxides can be best described using a three-region model (Hope, 1977; Ryden et al., 1977), in the present study Zn and Cd adsorption by soils was adequately described with a two-region model. Given that soils already contain native-adsorbed Zn and Cd, the possibility was considered that a third region for Zn and Cd adsorption might exist at very low solution concentrations

Table 4.8

Comparison of % organic carbon and short-range order Fe to  
b values for adsorption of Zn and Cd by soils

Soil	Organic Carbon %	Short-range order Fe (Tamms-Oxalate) $\mu\text{mol } 100\text{g}^{-1}$	Zn		Cd	
			$b_{\text{I}}$ $\mu\text{mol g}^{-1}$	$b_{\text{II}}$ $\mu\text{mol g}^{-1}$	$b_{\text{I}}$ $\mu\text{mol g}^{-1}$	$b_{\text{II}}$ $\mu\text{mol g}^{-1}$
Makerua Oh	11.8	n.d.	0.61	15.29	0.89	17.79
Egmont Ah	7.3	10.1	1.12	27.80	0.48	17.45
Okaihau Ah	5.8	3.5	0.10	7.65	0.11	6.36
Egmont Bw1	3.2	19.5	0.25	7.28	0.27	17.79
Tokomaru Ah	2.4	4.6	0.44	15.29	0.17	11.86
Okaihau Bcs	2.0	9.0	0.11	2.47	0.006	0.42
Tokomaru Btg	0.5	3.7	0.08	2.35	0.006	1.98

of Zn and Cd. To investigate the likelihood of a third region for Zn and Cd adsorption, Fe gel was used as an adsorbent. The advantage of using this adsorbent was that Fe gel can be prepared relatively free of Zn and Cd impurities, hence allowing adsorption to be investigated at low additions.

40-hr adsorption isotherms with final solution concentrations of from 0.089 to 0.229  $\mu\text{mol Zn l}^{-1}$  and 0.047 to 0.178  $\mu\text{mol Cd l}^{-1}$  gave no indication of any deviation in region I adsorption as would occur if a third population of adsorbing sites was operating at low surface coverages. The experimental data are shown in Figs. 4.13 and 4.14.

The reciprocal plots show the first step in the successive approximation of b and k values as described in Appendix 2. Two separate Langmuir equations adequately described the experimental data for adsorption of both Zn and Cd by Fe gel, as was found earlier for the soils in this study. Thus, unlike the situation for P and Mo (Hope, 1977; Ryden et al., 1977) no evidence was found for a third region either in soils or Fe gel. Also, no evidence can be found in the literature for three region models for cation adsorption by synthetic or natural adsorbents.

The next stage in the investigation (Section 4.3.5.2) was to examine the possibility of using synthetic components as model adsorbents for Zn and Cd. Hydrous Fe, Al and Mn oxides are suspected to be important in trace element adsorption (Jenne, 1968) and have been previously used as models for predicting adsorption by soils (Bowden et al., 1973; Gadde and Laitinen, 1974; Forbes et al., 1976).

#### 4.3.5.2 40-hr adsorption isotherms for Fe gel and allophane

In this study 40-hr adsorption isotherms were obtained for Zn and Cd adsorption by Fe gel and allophane. The isotherms were

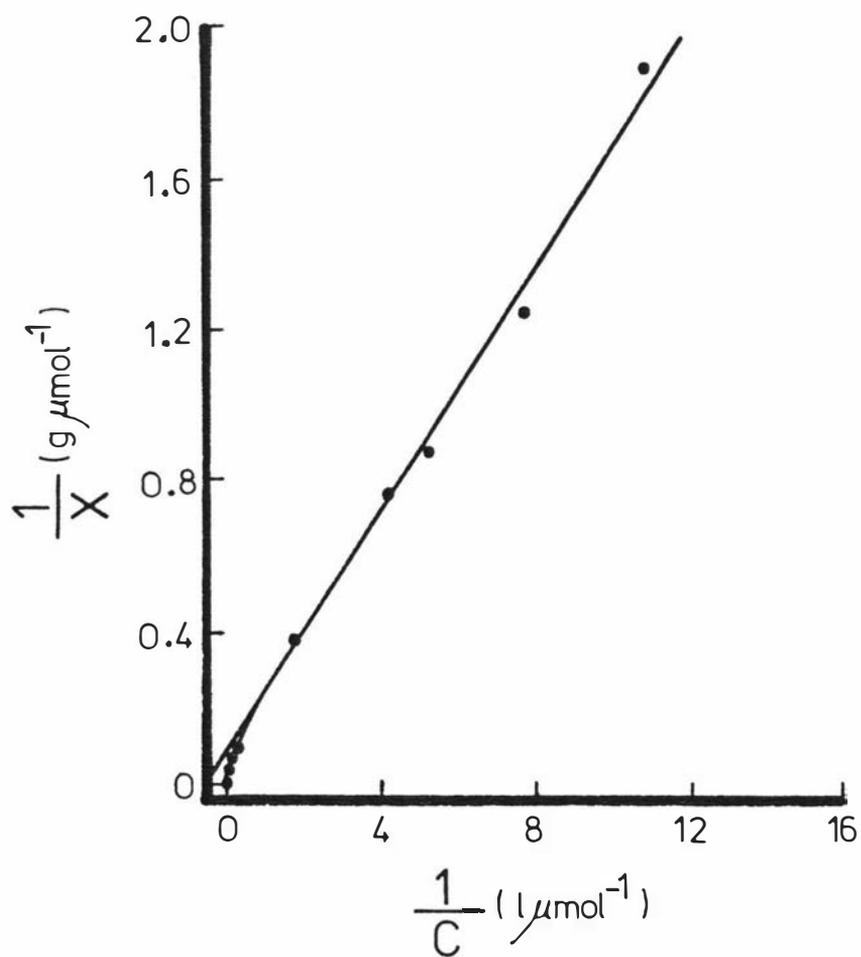


Figure 4.13 Reciprocal plot of adsorption data (40 hr) for Zn adsorption by Fe gel showing linear relationship at low final solution concentrations

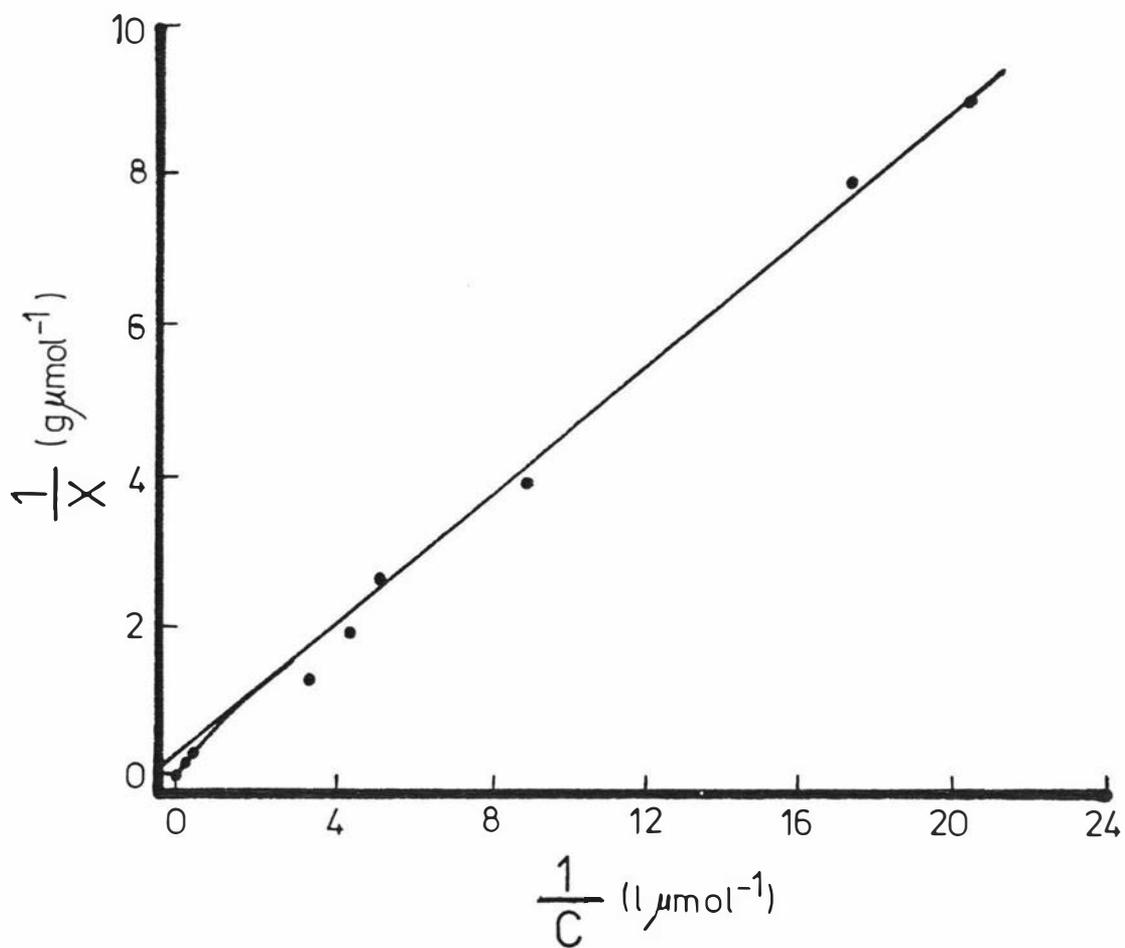


Figure 4.14 Reciprocal plot of adsorption data (40 hr) for Cd adsorption by Fe gel showing linear relationship at low final solution concentrations

obtained at the pH attained (pH 6.40) when the required aliquot of synthetic gel was added to  $3 \times 10^{-2}$  M NaCl matrix solution. The solution pH was not controlled during adsorption. Adsorption isotherms for Zn and Cd adsorption by synthetic Fe gel and allophane are shown in Figs. 4.15 and 4.16 respectively. Again the adsorption isotherms for both Zn and Cd adsorption by Fe gel and allophane were of the L-type (Giles et al., 1960).

As found for the soils, two regions were found for Zn and Cd adsorption onto both Fe gel and allophane with the smaller amounts adsorbed on the higher binding energy sites. Sufficient data points were obtained in the low final solution concentration range ( $<2 \mu\text{mol Zn or Cd l}^{-1}$ ) to enable successive approximations (Appendix 2) of b and k values to be carried out. Values derived for b, k and  $\Delta G$  are shown in Table 4.9.

The b values indicated that synthetic Fe gel adsorbed greater amounts of Zn than did synthetic allophane (on a  $\mu\text{mol Zn g}^{-1}$  gel basis), especially for region I (c.f.  $b_I$  values). The  $b_{II}$  values for Zn are also larger for Fe gel than for allophane. Similarly, b values for Cd indicated greater adsorption by Fe gel than by allophane in both regions. These findings suggest that Fe gel presents more adsorption sites than does allophane (Regions I and II) for both Zn and Cd. (Kalbasi et al.(1978) have previously shown that at comparable pH values aluminium oxides absorb considerably less Zn than iron oxides). The  $\Delta G$  values obtained for Zn and Cd adsorption were higher in region I for allophane compared to Fe gel, but similar in region II. The Langmuir parameters, together with the  $\Delta G$  values, derived as shown earlier, were then compared for Fe gels, allophane and soils. Table 4.10 shows that for both Zn and Cd the  $\Delta G_I$  and  $\Delta G_{II}$  values for Fe gel and the  $\Delta G_{II}$  values for

Table 4.9 Adsorption parameters for Zn and Cd adsorption by Fe gel and allophane gel from  $3 \times 10^{-2}$  M NaCl (pH 6.40, 40 hr)

		$b_I$	$b_{II}$	$k_I$	$k_{II}$	$\Delta G_I$	$\Delta G_{II}$
		$\mu\text{mol g}^{-1}$		$l\mu\text{mol}^{-1} \times 10^{-2}$		$\text{kJ mol}^{-1}$	
Fe Gel	Zn	6.95	66.48	91.7	2.2	-33.8	-24.6
	Cd	0.80	52.34	288.0	1.1	-36.6	-22.9
Allophane	Zn	0.41	25.48	361.0	1.7	-37.2	-24.0
	Cd	0.09	8.90	6.3	0.91	-38.5	-22.5

Table 4.10 Comparison of Langmuir parameters and free energies of adsorption for Zn and Cd adsorption by Fe gel and soils

	$b_I$	$b_{II}$	$k_I$	$k_{II}$	$\Delta G_I$	$\Delta G_{II}$
	$\mu\text{mol g}^{-1}$		$l \mu\text{mol}^{-1} \times 10^{-2}$		$\text{kJ mol}^{-1}$	
<u>Zinc</u>						
Mean Soil Value	$0.39 \pm 0.14$	$11.16 \pm 3.42$	$125.5 \pm 35.6$	$0.83 \pm 0.29$	$-33.8 \pm 0.8$	$-21.9 \pm 0.7$
Fe gel	6.95	66.48	91.7	2.2	-33.8	-24.6
Allophane	0.41	25.48	361.0	1.7	-37.2	-24.0
<u>Cadmium</u>						
Mean Soil Value	$0.28 \pm 0.12$	$10.52 \pm 3.75$	$194.3 \pm 67.3$	$0.69 \pm 0.26$	$-32.7 \pm 1.2$	$-21.1 \pm 0.7$
Fe gel	0.87	52.34	288.1	1.1	-36.6	-22.9
Allophane	0.09	8.90	629.0	0.91	-38.5	-22.5

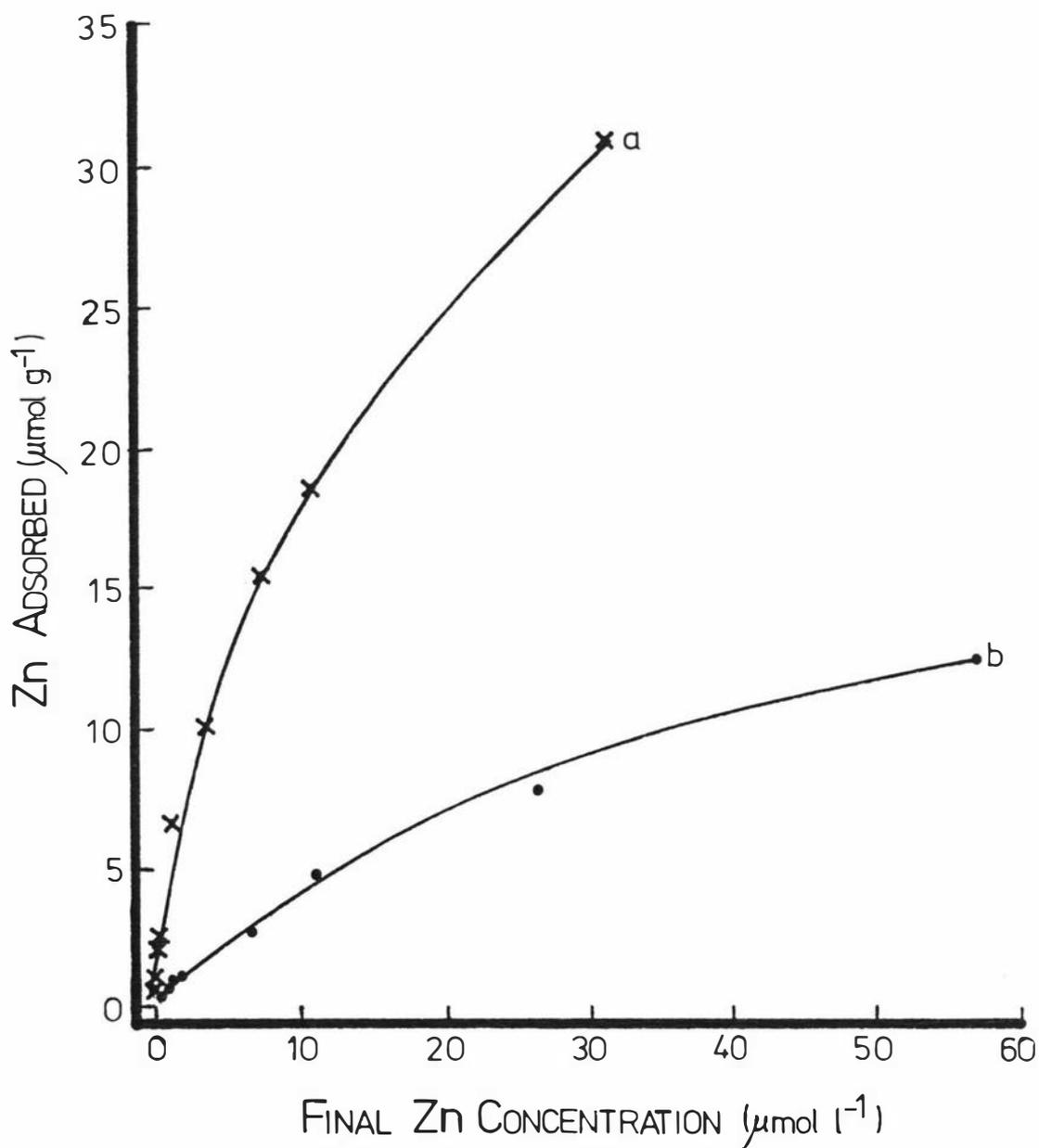


Figure 4.15 Isotherms for the adsorption of Zn by Fe gel (a) and allophane gel (b) from  $3 \times 10^{-2} \text{ M NaCl}$  after 40 hr at pH 6.40 over the final concentration range of 0 - 60  $\mu\text{mol Zn l}^{-1}$

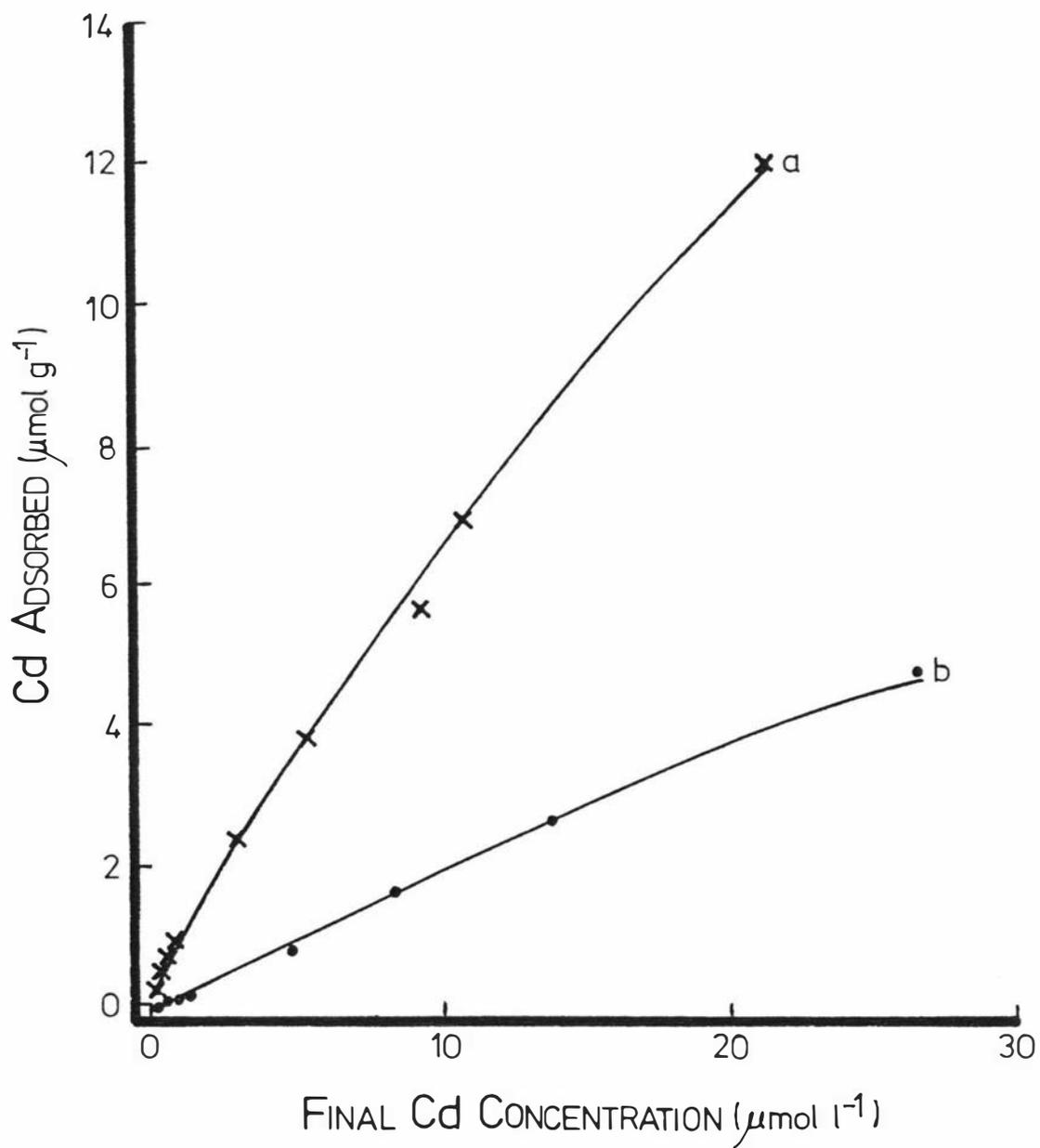


Figure 4.16 Isotherms for the adsorption of Cd by Fe gel (a) and allophane gel (b) from  $3 \times 10^{-2} \text{M}$  NaCl after 40 hr at pH 6.40 over the final concentration range of 0 - 30  $\mu\text{mol Cd l}^{-1}$

allophane were not significantly different from the mean values for free energies of adsorption for all soils. The  $\Delta G_I$  values for allophane for Zn and Cd adsorption were higher than those for soils and Fe gel, suggesting tighter binding of Zn and Cd adsorbed in region I for allophane. The similarities between the  $\Delta G$  values for Fe gel and soils suggest the possibility that similar adsorption processes may operate for both types of adsorbents. The use of Fe gel as a model for Zn and Cd adsorption by soils has been suggested previously (Bowden et al., 1973; Forbes et al., 1976). The agreement between  $\Delta G$  values for Zn and Cd adsorption by soils and Fe gels in this study lends further support to this suggestion. The use of gels facilitates investigations into many aspects of adsorption which would be more difficult to achieve using whole soils. For example, the effects of pH on Zn and Cd adsorption are conveniently undertaken in the simpler gel system. The results obtained for such an investigation are outlined below.

#### 4.3.5.3 The effect of pH on Zn and Cd adsorption by Fe gel

The effect of pH on adsorption of Zn and Cd by Fe gel was assessed from a series of 40 hr adsorption experiments carried out at different pH values. 40-hr adsorption isotherms are shown in Figs. 4.17 and 4.18 and the data were analysed according to the procedure described in Section 4.2.5.2.

Plots of Zn or Cd adsorbed against pH for ten different levels of addition of Zn or Cd were constructed. From these, the amounts of Zn and Cd adsorbed by Fe gel at selected pH values could be obtained by interpolation. The final solution concentration for each amount

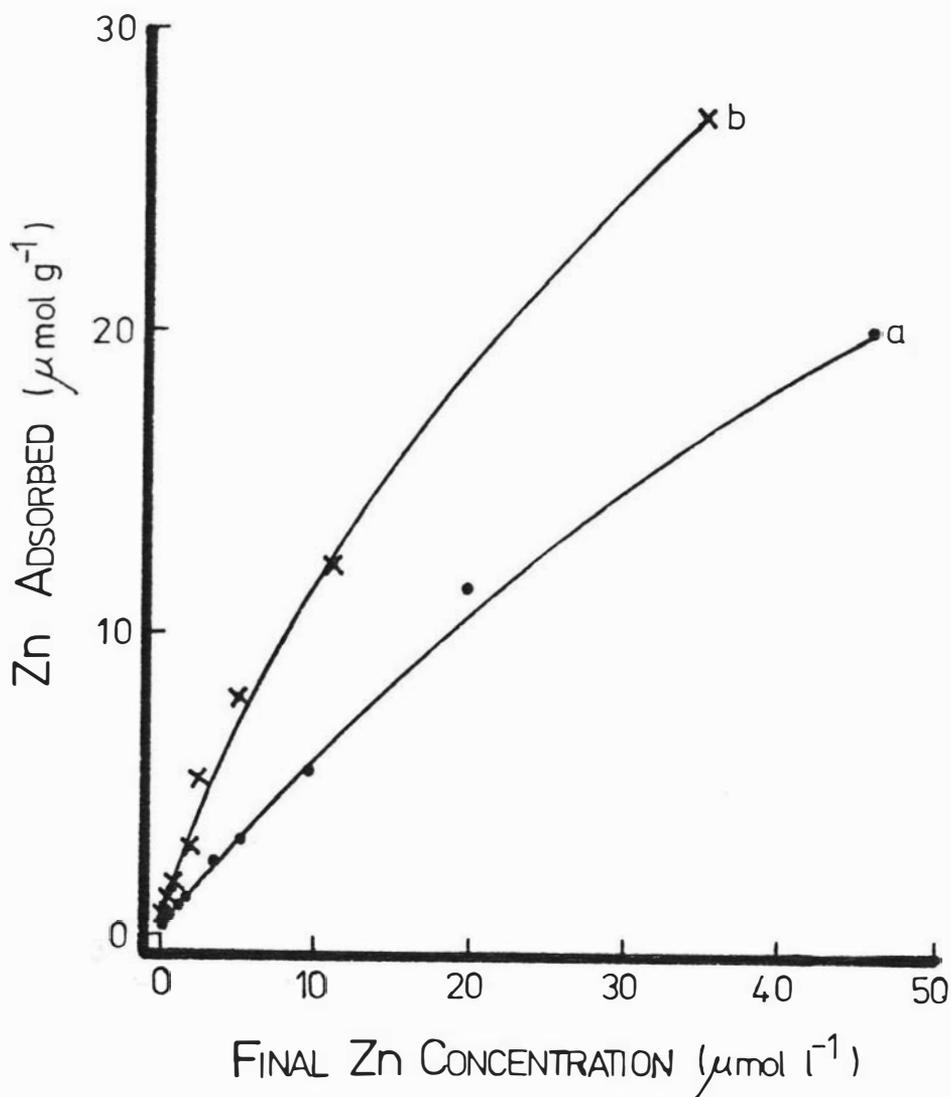


Figure 4.17 Zinc adsorption isotherms (40 hr) determined at different pHs for the adsorption of Zn by Fe gel from  $3 \times 10^{-2} \text{ M NaCl}$  over the final solution concentration range of 0 - 46  $\mu\text{mol Zn l}^{-1}$

a = pH 5.45

b = pH 5.60

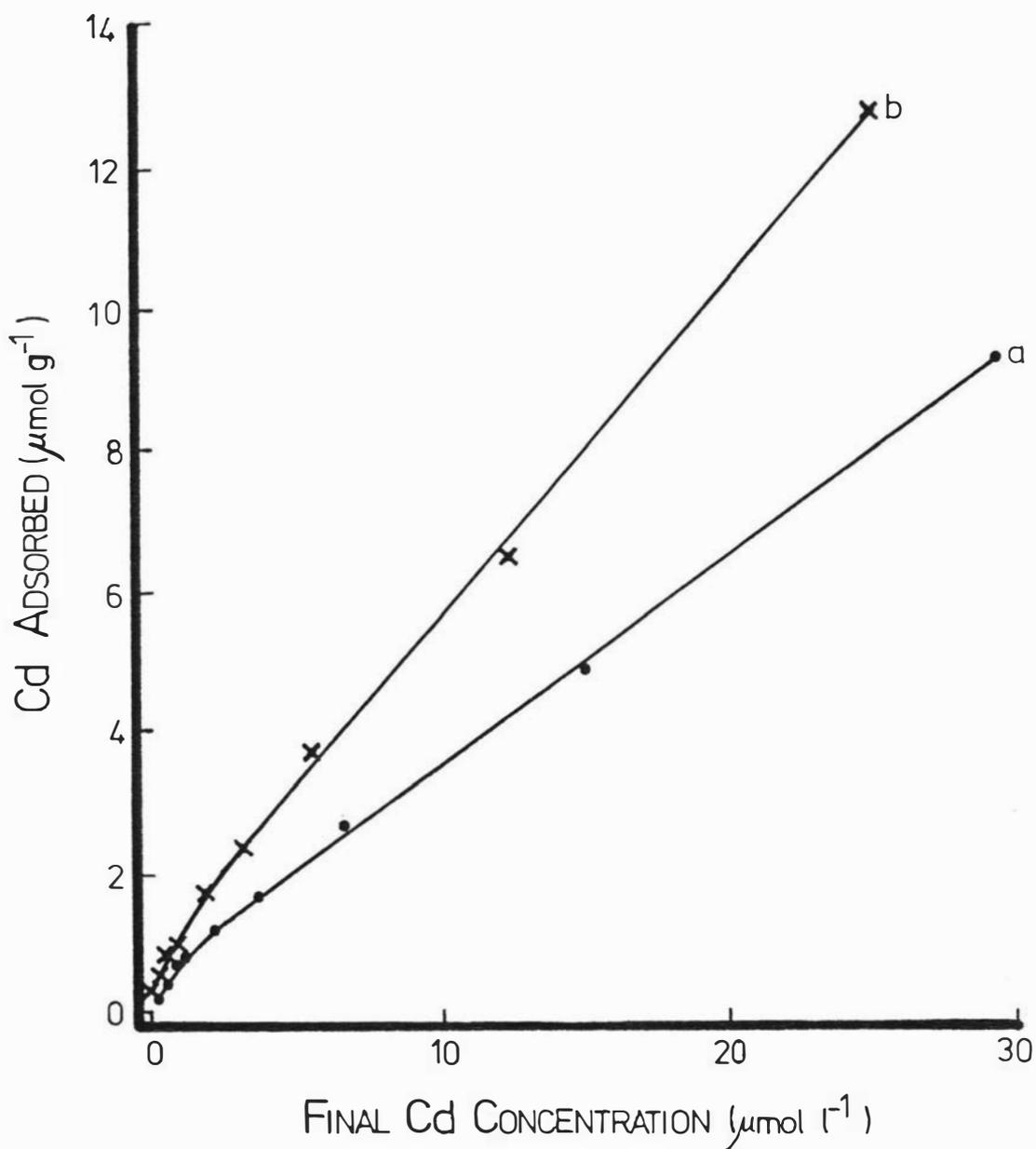


Figure 4.18 Cd adsorption isotherms (40 hr) determined at different pHs for the adsorption of Cd by Fe gel from  $3 \times 10^{-2} \text{ M NaCl}$  over the final solution concentration range of  $0 - 30 \mu\text{mol Cd l}^{-1}$

a = pH 5.60

b = pH 5.70

of Zn or Cd adsorbed at the selected pH was calculated as the difference between the amount adsorbed by the gel and the initial known level of addition of Zn or Cd (See Section 4.2.5.2). The pH values selected for Zn adsorption were pH 5.45 and pH 5.60 and for Cd adsorption pH 5.60 and pH 5.70. These pHs were chosen to include the linear portion of the experimental curves of amounts Zn or Cd adsorbed versus pH (See Fig. 4.2). As the linear portions covered slightly different pH ranges for Zn and Cd adsorption, the isotherms for Zn and for Cd were determined at the pH values given above. ...

Adsorption parameters, summarized in Table 4.11 show that as pH increases adsorption maxima increase for both Zn and Cd and for both regions. Although adsorption maxima change, the  $\Delta G$  values do not significantly alter (Section 4.3.3). Thus, the effect of increasing pH is to increase the amounts adsorbed, but not the free energies of adsorption.

#### 4.3.6 Summary

Data for the adsorption of Zn and Cd by soils, Fe gel and allophane was described in this study by the use of a two-region model, one region covering adsorption at low equilibrium solution concentrations and the other at higher concentrations. Treatment of the adsorption data using the Langmuir approach allowed calculation of parameters such as adsorption maxima (b values), constants relating to binding energy (k values) and values for the free energies of adsorption ( $\Delta G$  values) for each of the two regions. For both Zn and Cd adsorption by all soils used, no significant differences were found in  $\Delta G$  values within a region, but there was a highly significant difference found between regions. For Fe gel, and for both Zn and Cd, the  $\Delta G$  values for

Table 4.11

Parameters describing Zn and Cd adsorption (40 hr) by Fe gel

from  $3 \times 10^{-2}$  M NaCl at two pH values

pH	$b_I$	$b_{II}$	$k_I$	$k_{II}$	$\Delta G_I$	$\Delta G_{II}$
	$\mu \text{ mol g}^{-1}$		$1 \mu \text{ mol}^{-1} \times 10^{-2}$		$\text{kJ mol}^{-1}$	
Zinc						
5.45	3.06	101.94	26.0	0.47	-30.5	-20.8
5.60	7.46	117.62	22.0	0.61	-30.3	-21.4
Cadmium						
5.60	0.71	59.31	182.0	0.56	-35.5	-21.3
5.70	0.85	118.62	306.0	0.46	-36.8	-20.8

adsorption are similar to those obtained for the soils used, suggesting certain similarities in adsorption of both cations.

Although the use of Langmuir adsorption equations does not give specific information on mechanisms of adsorption by soils or Fe gel, the partitioning of Zn and Cd adsorption into two 'regions' indicates the likely existence of two different populations of adsorption sites and hence allows for the possibility that two adsorption mechanisms may be operating in the adsorption process.

In Chapter 5, Fe gel is used for the further investigation of Zn and Cd adsorption.

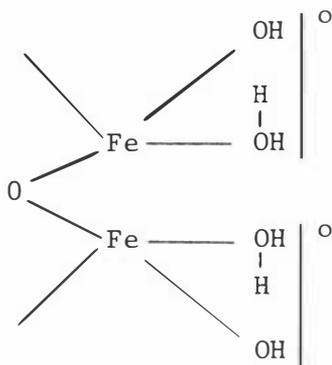
CHAPTER FIVE

## MECHANISMS FOR Zn AND Cd ADSORPTION

## BY SYNTHETIC Fe GEL

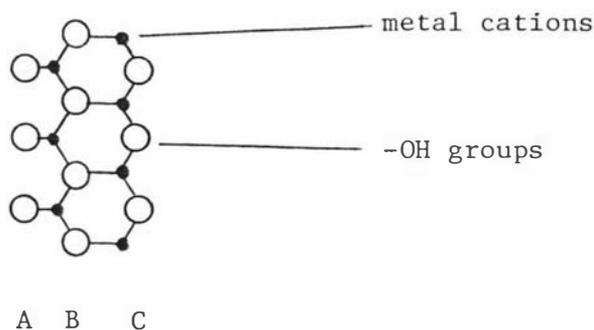
5.1 Introduction

Hydrous oxides of Fe, Al and Mn play an important role in the adsorption of many cations by soils (Jenne, 1968; Shuman, 1976). Synthetic materials provide convenient model surfaces for the study of metal cation adsorption (Mitchell et al., 1964) and hydrous Fe oxides, such as Fe gel, have found extensive use for investigating the mechanisms involved (Bowden et al., 1973; Bar-Yosef et al., 1975; Forbes et al., 1976; Bowden et al., 1977; Kalbasi et al., 1978). According to Quirk and Posner (1975) the surface of hydrous metal oxides can be considered as:

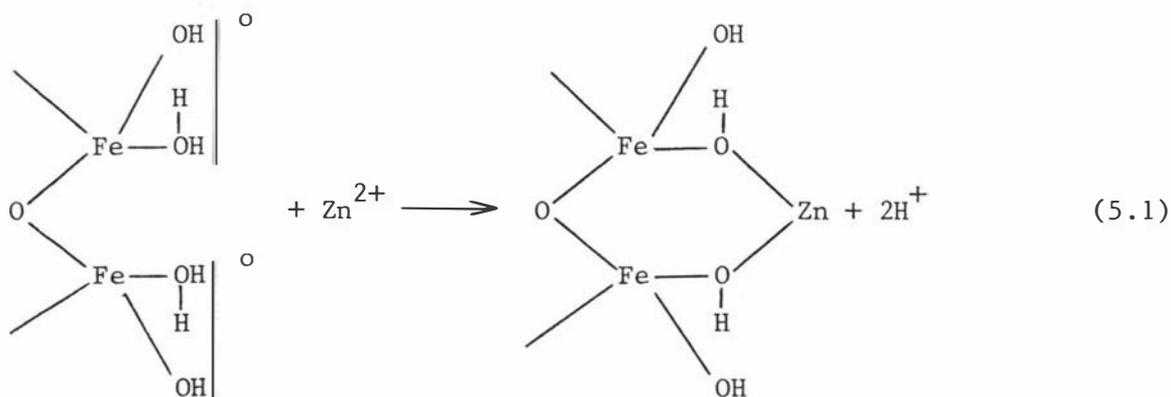


The  $-OH$  and  $-OH_2$  groups are shown co-ordinately bonded to only one metal cation, (Fe, Mn, or Al) in the oxide. Such singly co-ordinated  $-OH$  groups are thought to be involved in adsorption reactions with anions and cations, whereas the same groups shared between two or three metal cations are not considered to be involved in adsorption reactions (Parfitt et al., 1977; 1977a). A plan of the (100) face of goethite shows the singly co-ordinated  $-OH$  groups and 3- and 2- co-ordinated

-OH groups as A, B and C, respectively (Parfitt and Russell, 1977):



For hydrous oxides, the ratio of  $\text{-OH}_2$  to  $\text{-OH}$  groups depends on pH (Parks and de Bruyn, 1962) with the proportion of  $\text{-OH}_2$  groups increasing relative to  $\text{-OH}$  groups as pH decreases, thereby increasing the net positive charge on the surface. However, at common soil pH values the number of positive sites would be far fewer than the number of neutral sites (Forbes et al., 1976). The  $\text{-OH}_2$  and  $\text{-OH}$  groups are considered to be part of the hydrous oxide surface (Parfitt and Russell, 1977) and replacement of these groups by adsorbing ions (i.e., anions) occurs as a ligand-exchange, or chemisorption, reaction in which the bonding is covalent. However, unlike the situation for anion adsorption, cation adsorption can not involve replacement of whole groups, only the protons, e.g.,



(Quirk and Posner, 1975)

Recently, the suggestion has been made that two mechanisms for Zn and Cd adsorption could occur, involving monodentate and bidentate complexes (Quirk and Posner, 1975; Kalbasi et al., 1978). The formation of a typical bidentate complex is shown in equation (5.1). Monodentate complex formation involves the adsorption of a monovalent complex ion, e.g.,  $\text{ZnCl}^+$  (Kalbasi et al., 1978). Over the pH range 5.93 - 6.96 and for an initial addition of  $306 \mu\text{mol Zn g}^{-1}$ , more Zn was adsorbed on the hydrous Fe oxide by the bidentate than the monodentate mechanism (Kalbasi et al., 1978). This finding would appear to be in conflict with those obtained in Chapter 4, of this study. Although two populations of sites were indicated, those sites which bound Zn more tightly (high  $\Delta G$  values) constituted the smaller fraction of the total Zn adsorbed. This was true even at high surface coverages resulting from additions similar to those used by Kalbasi et al., (1978). To investigate the mechanisms for Zn and Cd adsorption in the regions indicated by the Langmuir studies (Chapter 4), studies into the effects of pH on Zn and Cd adsorption, proton release concomitant with Zn and Cd adsorption, and isotopic exchangeability and desorbability of adsorbed Zn and Cd at both low and high surface coverages were carried out.

## 5.2 Methods

Iron gel for this study was prepared according to the procedure described in Chapter 2.

### 5.2.1 Effect of pH on Zn and Cd adsorption by Fe gel

#### 5.2.1.1 Zinc adsorption by Fe gel, with no pH control

Adsorption of Zn by Fe gel from  $3 \times 10^{-2} \text{M NaCl}$  was studied

at three different initial pH values, viz., pH 5.40, 6.40, and 7.30. The initial pH values were established using dilute acid ( $1 \times 10^{-2}$  M HCl) or base ( $1 \times 10^{-2}$  M NaOH), with the gel left to stabilise at each pH for 1 hr. After adding the appropriate amount of Zn, the final volume in each reaction vessel (50-ml polycarbonate centrifuge tubes) was adjusted to 40 ml giving a solid:solution ratio of 1:800.

#### 5.2.1.2 Adsorption of Zn and Cd by Fe gel, under controlled pH conditions

In a separate experiment the effect of pH on Zn and Cd adsorption by Fe gel was investigated with the aid of an automatic titrator (Radiometer Titrator II). The titrator was coupled to a Radiometer pH meter Model 26 and a Radiometer Autoburette (Model ABU 13) and chart recorder. The titrator was used to maintain a constant pH throughout the adsorption process. When pH is not controlled in this way, the initial adsorption occurs at a relatively higher pH than the final equilibrium value. It can be argued that this might produce a different end-result to that obtained for a system maintained at constant pH throughout, depending on the reversibility of the adsorption mechanism.

Iron gel (50 mg) in  $3 \times 10^{-2}$  M NaCl was adjusted to the required pH by appropriate additions of acid ( $1 \times 10^{-3}$  M,  $1 \times 10^{-2}$  M HCl) or base ( $1 \times 10^{-3}$  M,  $1 \times 10^{-2}$  M NaOH) and allowed to pre-equilibrate for 16 hr, after which time the suspension pH was found to be reasonably constant. An aliquot of Zn or Cd, in  $3 \times 10^{-2}$  M NaCl, was delivered to the solution via a 0.2-ml micro-pipette. The final volume in the reaction vessel was 40 ml. The procedure was carried out at room temperature ( $25 \pm 2^\circ\text{C}$ ) under an atmosphere of nitrogen to exclude the possibility of carbonic acid formation from any entrained  $\text{CO}_2$  in the reaction vessel. The

suspensions in the reaction vessel were constantly stirred prior to the addition of Zn or Cd and stirring continued during the course of the experiment. Two levels of addition of Zn and Cd were used. The amounts added were chosen such that at low levels of addition, i.e.,  $2.294 \mu\text{mol Zn g}^{-1}$  and  $1.335 \mu\text{mol Cd g}^{-1}$  adsorption would be predominantly in region I, as determined from earlier results for Fe gel (Chapter 4). In this way it was planned to examine the effect of pH on the adsorption of Zn and Cd within the two regions over the pH range of approximately 5.0 to 7.5.

All suspensions were equilibrated for 1 hr after Zn or Cd addition and then centrifuged (15,000 r.p.m. for 5 min. at  $23 \pm 2^\circ\text{C}$ ), filtered ( $< 0.45 \mu\text{m}$  Millipore filters), and the filtrates were analysed for Zn and Cd.

### 5.2.2 Proton release

Adsorption of Zn and Cd by Fe oxides generally results in a decrease in the pH of the matrix solution due to the release of protons that accompanies adsorption (Quirk and Posner, 1975; Kalbasi et al., 1978). A determination of the number of protons released for each Zn or Cd ion adsorbed gives a mole ratio which can be of some assistance in elucidating the types of sites and adsorption mechanisms involved in the adsorption process.

In order to determine these mole ratios the amounts of NaOH consumed in maintaining constant pH (pH 6.40 and pH 6.80) of the Fe gel suspension were measured using the Radiometer Titrator II apparatus with the same operating conditions, as described in Section 5.2.1.2. Amounts of  $1 \times 10^{-3} \text{M}$  or  $1 \times 10^{-2} \text{M}$  NaOH consumed were recorded on the chart recorder. During the adsorption period the addition of base commenced at a fast rate (controlled by the titrator) to minimise large

pH changes resulting from Zn or Cd additions. During the later stages of the adsorption, the rate of base addition slowed as the pH remained closer to the initial and target, pH. After 1 hr of equilibration, the gel suspension was centrifuged, filtered and analysed for Zn or Cd. The amounts of Zn or Cd adsorbed were obtained by the difference between the amounts initially added and the amounts left in solution. Proton release is taken to be equivalent to the  $\mu\text{mol NaOH}$  consumed. The mole ratios were expressed as:

$$\frac{\mu\text{mol H}^+ \text{ released}}{\mu\text{mol Zn or Cd adsorbed}} = \text{Mole Ratio, R.} \quad (5.2)$$

### 5.2.3 Exchangeability of Zn and Cd adsorbed by Fe gel

The exchangeabilities of Zn and Cd adsorbed by Fe gel were determined using the isotopes  $^{65}\text{Zn}$  and  $^{109}\text{Cd}$ . Also, the effects of pH changes and level of Zn and Cd addition on the amounts of isotopically and non-isotopically exchangeable Zn and Cd were investigated.

Two levels of Zn and Cd addition were used, i.e., 2.294 and 22.94  $\mu\text{mol Zn g}^{-1}$  and 1.335 and 13.35  $\mu\text{mol Cd g}^{-1}$ . These were chosen for the same reasons given in Section 5.2.1.2, i.e., that adsorption of Zn and Cd from low additions would lead to predominantly region I adsorption, and the higher additions predominantly region II adsorption.

The method used was as follows: 5-ml aliquots of Fe gel were removed from a continuously-stirred suspension of Fe gel, and placed in 50-ml polycarbonate centrifuge tubes. Appropriate additions of Zn or Cd were added together with approximately 35 ml of  $3 \times 10^{-2}\text{M NaCl}$  solution. As exchangeability was to be studied at two different pH values, pH 6.40 and 6.80, the pH of the suspensions was adjusted to the required value by the addition of appropriate amounts of  $1 \times 10^{-2}\text{M}$

HCl or  $1 \times 10^{-2}$  M NaOH prior to adjusting the final volume of each reaction vessel to 40 ml. For each level of addition of Zn or Cd at each different pH, six replicate samples of gel were prepared. One set of triplicates was used for the isotopic exchange experiments, the other for determining the amounts of unlabelled Zn or Cd adsorbed by the gel. The samples were equilibrated for 40 hr on an end-over-end shaker (40 r.p.m.) at  $23 \pm 2^\circ\text{C}$ .

After 40-hr equilibration, the tubes were removed from the shaker and one set of triplicates for each level of addition and each pH was centrifuged at 15,000 r.p.m. in an RC-2B Sorvall Supercentrifuge at  $23 \pm 2^\circ\text{C}$  for 5 min. The supernatants were filtered through Millipore ( $< 0.45 \mu\text{m}$ ) filters and the filtrates analysed for Zn and Cd contents. From these results the amounts of unlabelled Zn and Cd adsorbed by the gel were calculated.

The second set of triplicates for each level of Zn and Cd addition and for each pH were spiked with 0.2-ml aliquots of 0.04  $\mu\text{Ci}$  of either  $^{65}\text{Zn}$  or  $^{109}\text{Cd}$ . The tubes were shaken for 1 hr to allow isotopic exchange to take place. A 1-hr equilibration time for exchange was found to be sufficient in a preliminary study (Table 5.1). Equilibration times ranging from  $\frac{1}{4}$  hr to 48 hr did not markedly affect the percent of adsorbed Zn and Cd that exchanged with the isotopes at either low or high Zn or Cd addition, thus for convenience an equilibration time of 1 hour was chosen.

The finding that exchangeability of Zn and Cd did not increase with increasing times of equilibration raises the question as to whether the non-exchangeable Zn and Cd is actually adsorbed or is in some precipitated or occluded form. The possibility of an absorption process occurring will be investigated in Chapter 6. After equilibrating

Table 5.1 Effect of time of equilibration on the isotopic exchangeability of Zn and Cd adsorbed by Fe gel

Time Allowed for Exchange hours	Isotopic Exchangeability			
	Zn		Cd	
	Low Addition	High Addition	Low Addition	High Addition
$\frac{1}{4}$	27.2	86.0	87.6	87.3
$\frac{1}{2}$	25.9	85.4	90.2	86.3
24	29.0	84.0	91.9	92.3
48	32.1	83.9	88.0	89.6

Low Zn addition:  $2.29 \mu\text{mol Zn g}^{-1}$

High Zn addition:  $22.94 \mu\text{mol Zn g}^{-1}$

Low Cd addition:  $1.34 \mu\text{mol Cd g}^{-1}$

High Cd addition:  $13.35 \mu\text{mol Cd g}^{-1}$ .

the gel samples with the isotopes for 1 hr, the tubes were centrifuged (15,000 r.p.m. at  $23 \pm 2^\circ\text{C}$  for 5 min), filtered (Millipore  $< 0.45 \mu\text{m}$  filters), and 0.2-ml aliquots transferred to plastic vials. The samples were counted with a Packard Auto-Gamma Scintillation Spectrometer Model 5285, to determine the amount of isotope remaining in solution. Standards of 0.04  $\mu\text{Ci}$  of Zn or Cd in 40 ml of  $3 \times 10^{-2}\text{M}$  NaCl were also counted.

Isotopically-exchangeable Zn or Cd was calculated using the principle of isotopic dilution, according to the following relationship:

$$\frac{\text{Exchangeable Zn or Cd on surface } (\mu\text{mol})}{\text{Zn or Cd in solution } (\mu\text{mol})} = \frac{^*\text{Zn (or } ^*\text{Cd) on surface}}{^*\text{Zn (or } ^*\text{Cd) in solution}} \quad (5.3)$$

where asterisks (\*) denote radioactive isotopes  $^{65}\text{Zn}$  and  $^{109}\text{Cd}$  in counts per minute.

The percentage exchangeability of Zn or Cd can then be calculated by the following formula:

$$\% \text{ exchangeability} = \frac{\text{Exchangeable Zn or Cd on surface}}{\text{Total Zn or Cd adsorbed on surface}} \times 100 \quad (5.4)$$

#### 5.2.4 Desorption of Zn adsorbed by Fe gel

Amounts of Zn adsorbed by Fe gel were obtained by adding Zn concentrations of 1.15, 1.18, 1.87, 2.34, 3.50, 4.68, 7.02, 11.70, 18.66, 23.40, 35.02, and 46.79  $\mu\text{mol Zn l}^{-1}$  to samples of gel (in triplicate) in a matrix of  $3 \times 10^{-2}\text{M}$  NaCl in 50-ml polycarbonate centrifuge tubes. The solid:solution ratio was 1:800, and the tubes were shaken on an end-over-end shaker (40 r.p.m.) for 40 hr, at  $23 \pm 2^\circ\text{C}$ . After a 40-hr equilibration time, the samples were centrifuged and filtered as described in Section 5.2.1.2. The filtrates were retained and analysed for Zn contents, and the amounts of Zn adsorbed by Fe gel calculated by difference. Following the decantation and filtration of the

supernatants, the tubes containing the centrifuged gel samples and residual supernatants were weighed and the weight of the entrained liquid determined. The amount of entrained Zn was calculated as the product of entrained solution (ml) and its concentration of Zn ( $\mu\text{mol ml}^{-1}$ ).

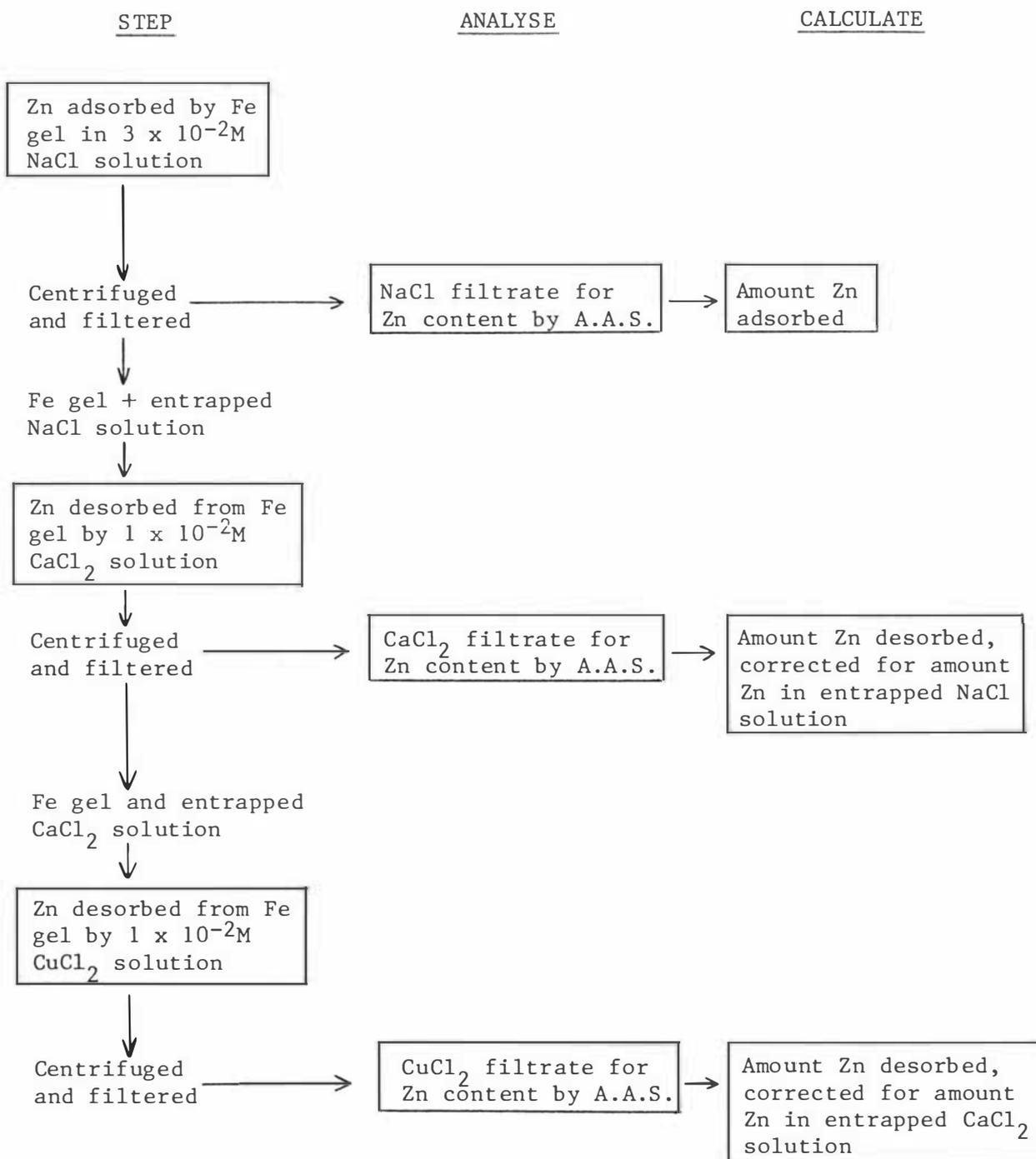
For the first desorption step, the gel samples were resuspended in 40 ml of  $1 \times 10^{-2}\text{M}$   $\text{CaCl}_2$  solution and placed on an end-over-end shaker (40 r.p.m.) for a 40-hr equilibration period. After 40 hr, the samples were centrifuged for 5 min. at 15,000 r.p.m. on an RC 2B Sorvall Super-centrifuge, and filtered through Millipore ( $0.45 \mu\text{m}$ ) filters. The filtrates were analysed for Zn contents and the amounts of Zn desorbed by  $1 \times 10^{-2}\text{M}$   $\text{CaCl}_2$  solution determined after subtracting the amounts of Zn left in the entrained NaCl solution.

A second desorption was made by resuspending the centrifuged gel samples in 40 ml of  $1 \times 10^{-2}\text{M}$   $\text{CuCl}_2$  solution and the process repeated as described for  $\text{CaCl}_2$  desorption. The amounts of Zn desorbed by  $1 \times 10^{-2}\text{M}$   $\text{CuCl}_2$  were determined after taking into account the amount of Zn initially present in the entrapped  $\text{CaCl}_2$  solution. The adsorption and desorption steps are outlined in the flow diagram, Fig. 5.1.

The concentration of the desorbing Ca and Cu solutions used was  $1 \times 10^{-2}\text{M}$  which maintained the matrix solution at the same ionic strength as the  $3 \times 10^{-2}\text{M}$  NaCl matrix solutions used for adsorption.

Ca ions were used to extract Zn and Cd because, in addition to being a common soil cation, Ca ions have the same divalent charge as Zn and Cd ions, similar ionic radii, i.e.,  $0.99 \text{ \AA}$  for Ca,  $0.74 \text{ \AA}$  for Zn and  $0.97 \text{ \AA}$  for Cd, and little tendency to form co-ordinate bonds (Cotton and Wilkinson, 1966). Therefore, if present in great excess of the amount of Zn or Cd present, the Ca ions could be expected to

Figure 5.1 Flow diagram showing the method of sequential desorption of Zn by  $1 \times 10^{-2} \text{M}$   $\text{CaCl}_2$  and  $1 \times 10^{-2} \text{M}$   $\text{CuCl}_2$  solutions



displace ions non-specifically held on soil surfaces by electrostatic attraction. Cu ions, on the other hand, are known to form large numbers of complexes with ligands co-ordinated through oxygen atoms (Cotton and Wilkinson, 1966). If present in excess amounts Cu ions could displace Zn and Cd held by co-ordinate bonds, and hence give some measure of the more specifically adsorbed Zn.

### 5.3 Results and Discussion

#### 5.3.1 Effect of pH on Zn and Cd adsorption

Fe gel possesses a variable charge surface, such that as pH increases the charge becomes more negative, and as pH decreases, it becomes more positive (Bowden et al., 1973; Bowden et al., 1977). As Zn and Cd exist as positively-charged ions in solution, it would be expected that changes in the pH-dependent charge on gel surfaces would cause either an increase or decrease in the amount of Zn or Cd adsorbed depending on whether the surface charge becomes more negative or more positive.

##### 5.3.1.1 Zn adsorption by Fe gel, under uncontrolled pH conditions

Isotherms for the adsorption of Zn by Fe gel at initial pH values of pH 5.40, 6.40 and 7.30 are shown in Fig. 5.2. Because the pH of the solution was not controlled during adsorption of Zn, equilibrium pH values were lower than the initial values, presumably due to proton release which occurred with Zn adsorption (Quirk and Posner, 1975; Forbes et al., 1976; Kalbasi et al., 1978). As expected, the decrease in pH with Zn adsorption was not the same for each level of Zn addition being dependent on the amount of Zn adsorbed. For example, at the

initial pH of 6.40, the final equilibrium pH values of matrix solutions ranged from pH 6.40 for low Zn additions (e.g., 0.83 and 1.11  $\mu\text{mol Zn g}^{-1}$ ) to pH 6.10 for the highest Zn addition (e.g., 55.60  $\mu\text{mol Zn g}^{-1}$ ). Ideally, a constant pH should be maintained throughout the adsorption process and for each level of Zn addition.

The adsorption isotherms in Fig. 5.2 show that for a given final solution concentration, more Zn was adsorbed as the equilibrium pH increased. Thus, at a final equilibrium concentration of 20  $\mu\text{mol Zn l}^{-1}$ , 0.80  $\mu\text{mol Zn g}^{-1}$  was adsorbed at pH 5.40 (curve a on Fig. 5.2), 6.50  $\mu\text{mol Zn g}^{-1}$  at pH 6.40 (curve b) and at least 55  $\mu\text{mol Zn g}^{-1}$  at pH 7.30 (curve c).

A disproportionate increase in adsorption of Zn was found as pH increased from pH 6.40 to pH 7.30, relative to that found as pH increased from pH 5.40 to pH 6.40. This effect could be due to several factors amongst which are; (a) increasing negativity of the surface, (b) faster kinetics of adsorption and (c) changing speciation of adsorbing Zn. The combined effects of (a) and (b) which result in the availability of a larger number of adsorbing sites, reduced repulsive forces between the surface and Zn (due to the reduction in positive sites on the surface) and increased electrostatic attraction, may produce more rapid adsorption and hence greater uptake of Zn in the equilibration time used. Thus, the uptake noted could be due to both (a) the presence of more sites and/or (b) increased kinetics of adsorption. In addition, the third factor involving the change in ionic species of the Zn, i.e., from a divalent to a monovalent species e.g.,  $\text{Zn(OH)}^+$ , may increase the potential for adsorption, as proposed by Bowden et al., (1973).

Whilst the data highlights the sensitivity of Zn adsorption to pH it also brings into question the validity of adsorption experiments in which pH is not controlled. As soil systems are generally better-

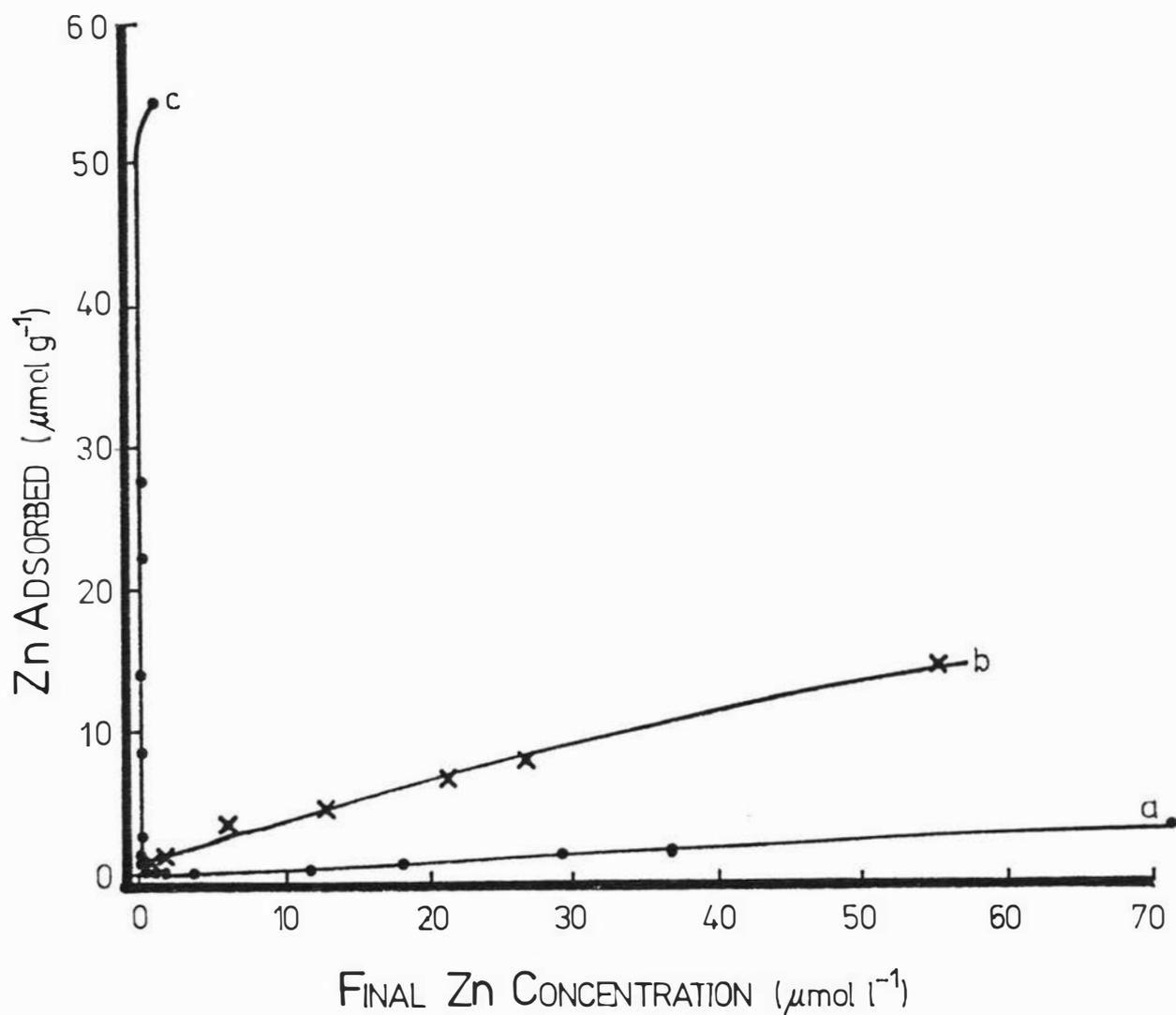


Figure 5.2 Adsorption (40 hr) of Zn by Fe gel from  $3 \times 10^{-2} M$  NaCl at three different pHs, a: pH 5.40, b: pH 6.40 and c: pH 7.30.

buffered than gels, less of a problem would be anticipated in the soil adsorption studies (Tisdale and Nelson, 1970), where pH changes would be smaller for similar amounts of Zn and Cd adsorbed.

#### 5.3.1.2 Zn and Cd adsorption by Fe gel, under controlled pH conditions

Results for Zn and Cd adsorption in the pH-controlled system (using a Radiometer pH-stat) at two different levels of addition of Zn (2.294 and 22.94  $\mu\text{mol Zn g}^{-1}$ ) and Cd (1.335 and 13.35  $\mu\text{mol Cd g}^{-1}$ ) are shown in Fig. 5.3. When amounts of adsorbed Zn and Cd are plotted against pH (Fig. 5.3), S-shaped curves result. These show that adsorption of both cations increased markedly as pH increased from pH 5.0 to pH 7.0 at the two levels of addition. Curves of similar shape over the range pH 5.0 to pH 7.5 have previously been found for Zn (Stanton and Burger, 1970; Bar-Yosef et al., 1975; Quirk and Posner, 1975; Forbes et al., 1976; Kinniburgh et al., 1976; Bolland et al., 1977; Kalbasi et al., 1978) and for Cd (Kinniburgh et al., 1976). The data presented in Fig. 5.3 suggest a similar pH response for the adsorption of Zn and Cd in regions I and II. This is clearly shown in Fig. 5.4, where the amounts of Zn or Cd adsorbed, expressed as percentages of the initial amounts added, are plotted against pH. From these results the  $\text{pH}_{50}$  values (i.e., at which 50% adsorption of initial amounts of added Zn or Cd occurs (Kinniburgh et al., 1976)) for Zn and Cd are shown in Table 5.2. Although the initial additions of Zn and of Cd are not the same (on a  $\mu\text{mol Zn or Cd g}^{-1}$  basis) the  $\text{pH}_{50}$  values for Cd adsorption by Fe gel were higher than those for Zn, i.e., the  $\text{pH}_{50}$  values at both low and high additions of Cd occurred at higher pH values than for either addition of Zn. This result may be an example of the close association that appears to exist between cation adsorption

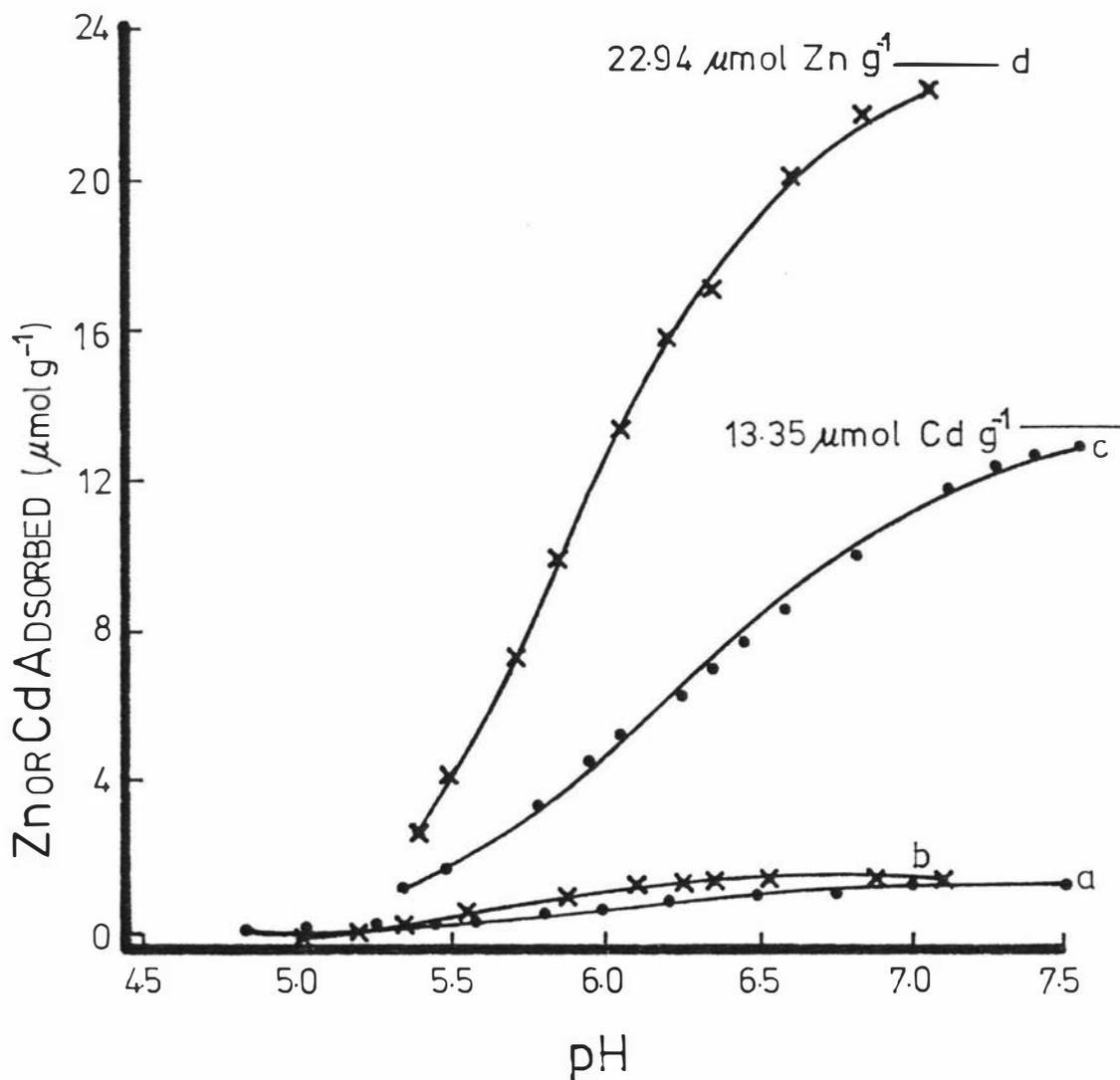


Figure 5.3 Effect of pH (controlled) on the adsorption of Zn and Cd by Fe gel in  $3 \times 10^{-2} \text{M NaCl}$

- a: 1.335  $\mu\text{mol Cd g}^{-1}$  added  
 b: 2.294  $\mu\text{mol Zn g}^{-1}$  added  
 c: 13.35  $\mu\text{mol Cd g}^{-1}$  added  
 d: 22.94  $\mu\text{mol Zn g}^{-1}$  added.

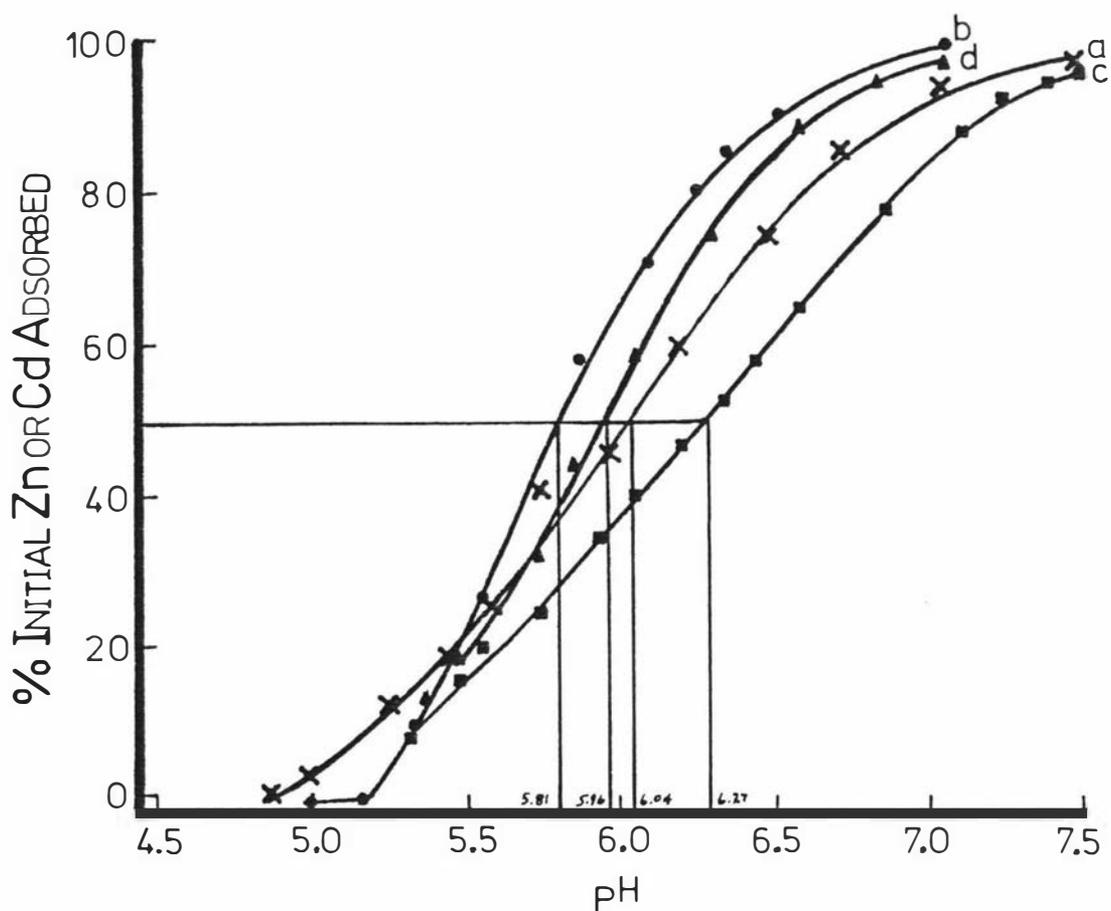


Figure 5.4 Effect of pH on percent of initial Zn or Cd added, adsorbed by Fe gel in  $3 \times 10^{-2}$  M NaCl

- a:  $1.335 \mu\text{mol Cd g}^{-1}$  added
- b:  $2.294 \mu\text{mol Zn g}^{-1}$  added
- c:  $13.35 \mu\text{mol Cd g}^{-1}$  added
- d:  $22.94 \mu\text{mol Zn g}^{-1}$  added.

Table 5.2  $\text{pH}_{50}$  values for Zn and Cd adsorption by Fe gel

Initial addition of Zn or Cd	$\text{pH}_{50}$ value
2.294 $\mu\text{mol Zn g}^{-1}$	pH 5.76
22.94 $\mu\text{mol Zn g}^{-1}$	pH 5.94
1.335 $\mu\text{mol Cd g}^{-1}$	pH 6.04
13.35 $\mu\text{mol Cd g}^{-1}$	pH 6.27

and cation hydrolysis (Kinniburgh et al., 1976). Because the cation-surface complex forms as a result of a reaction between  $\text{OH}^-$  and  $\text{M}^{2+}$  groups (Kinniburgh et al., 1975) the more covalent the  $\text{O-M}^{2+}$  bond (i.e., the higher the electronegativity of  $\text{M}^{2+}$ ) the greater the adsorption that is found at a given pH (Kinniburgh et al., 1976). Consequently, the  $\text{pH}_{50}$  values for Zn might be expected to occur at a lower pH than the  $\text{pH}_{50}$  for Cd adsorption, as the Zn has a higher electronegativity than does Cd (c.f. Allred-Rochow electronegativity values (Cotton and Wilkinson, 1966) of 1.66 for Zn and 1.46 for Cd).

Slightly lower  $\text{pH}_{50}$  values of 5.40 for Zn and 5.80 for Cd were reported by Kinniburgh et al. (1976) at a common addition of 12.6  $\mu\text{mol g}^{-1}$  of Zn and Cd to Fe gel. The same trend towards a higher  $\text{pH}_{50}$  value for Cd than for Zn was observed by those workers.

The amounts of Zn and Cd adsorbed, expressed as a percent of the initial addition, at different pH values are shown in Table 5.3 together with similar data presented by Quirk and Posner (1975) and Kinniburgh et al., (1976). Although the amounts of Zn and Cd initially

Table 5.3 A summary of published data relating to the effect of pH on percentage adsorption of Zn and Cd by iron oxides

Cation	Amount added $\mu\text{mol g}^{-1}$	Relative adsorption of Zn and Cd (%)				Reference	
		pH:	5.90	6.50	7.20		7.50
Zn	64.0		13	22	68	-	Quirk and Posner (1975)
Cd	64.0		-	23	44	53	
Zn	12.6		80	100	-	-	Kinniburgh et al., (1976)
Cd	12.6		45	78	100	-	
Zn	2.29		60	87	100	-	Present study
	22.94		47	79	100	-	
Cd	1.34		43	71	97	100	Present study
	13.35		32	57	91	100	

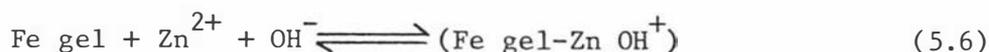
added differed for the various studies, it was generally found that at a given pH, more Zn was adsorbed by Fe gel than Cd, unless total adsorption occurred in which case, of course, no differences were found. The difficulty with expressing the data in this way (Table 5.3), is that the steep gradients that result have (see Fig. 5.4) the effect that small pH changes, which are difficult to measure accurately, can cause relatively large changes in the amounts of Zn or Cd adsorbed. However, these results clearly show that with increasing additions, the amounts of Zn or Cd adsorbed (expressed as a percent of initial addition) decrease at a particular pH within the range pH 5.0 to pH 7.0. Also more Zn is adsorbed than Cd at a given pH. These findings appear to hold true for a variety of matrices and for different additions of Zn and Cd.

### 5.3.2 Proton release

The decrease in pH of the matrix solution concomitant with Zn and Cd adsorption (Forbes et al., 1976; Kalbasi et al., 1978) is generally taken to indicate a net release of protons. The amount of base required to maintain constant pH during the adsorption of Zn or Cd is the commonest method used to determine the number of protons released. The amounts of base used in relation to the amounts of Zn and Cd adsorbed by Fe gel, in a 1-hr equilibration experiment, are shown in Fig. 5.5. Whether the base consumed was used to maintain constant pH as a result of  $H^+$  release, i.e.,



or  $OH^-$  uptake, i.e.,



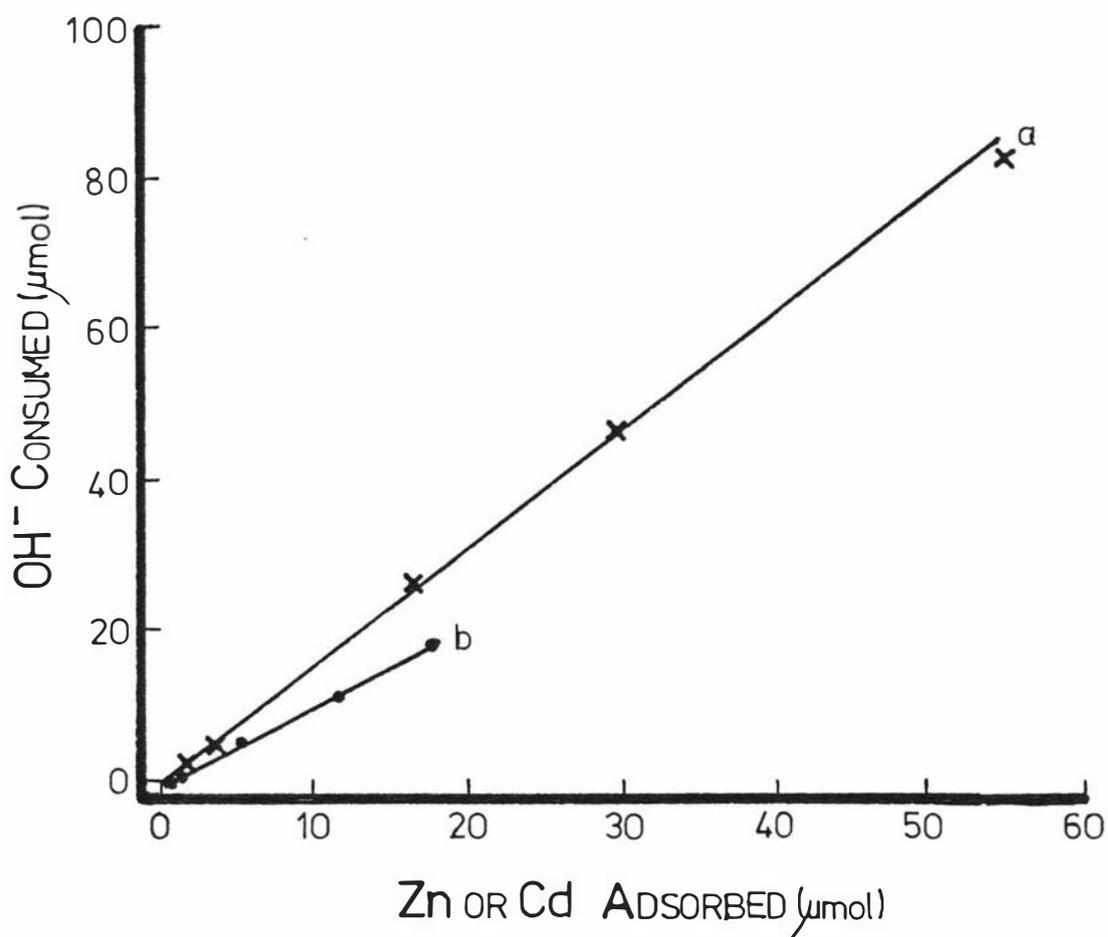


Figure 5.5

Base consumed in maintaining a constant pH (pH 6.40) during Zn (a) and Cd (b) adsorption by Fe gel from  $3 \times 10^{-2}$  M NaCl, as a function of the amount of Zn or Cd adsorbed. (Zn and Cd adsorbed and  $\text{OH}^-$  consumed expressed per gram of gel).

accompanying Zn or Cd adsorption cannot actually be determined. Mole ratios for Zn and Cd adsorption by Fe gel at two pH values, viz., pH 6.40 and pH 6.80 and at different levels of Zn and Cd addition are shown in Table 5.4. For Zn, at both these pH values, the mole ratios varied from 1.31 and 1.67 with no obvious relationship with the amounts of Zn adsorbed. In contrast, for Cd, mole ratios tended to increase with increasing adsorption, at both pH values. Mole ratios less than one, as found for Cd in this study, have also been observed by Kinniburgh et al. (1975) for Ca and Sr adsorption onto hydrous Fe oxides. These workers assumed such mole ratios to approximate 1.0 with no mechanistic explanation available for mole ratios less than unity. For Zn and Cd adsorption, in the present study, there was no marked effect of pH on mole ratios.

Taking into consideration experimental errors in pH measurements, the trends shown by the proton release data obtained in the present study indicate the likelihood of two mechanisms for Zn and Cd adsorption, one of which appears to involve a release of one proton and the other, a release of two protons.

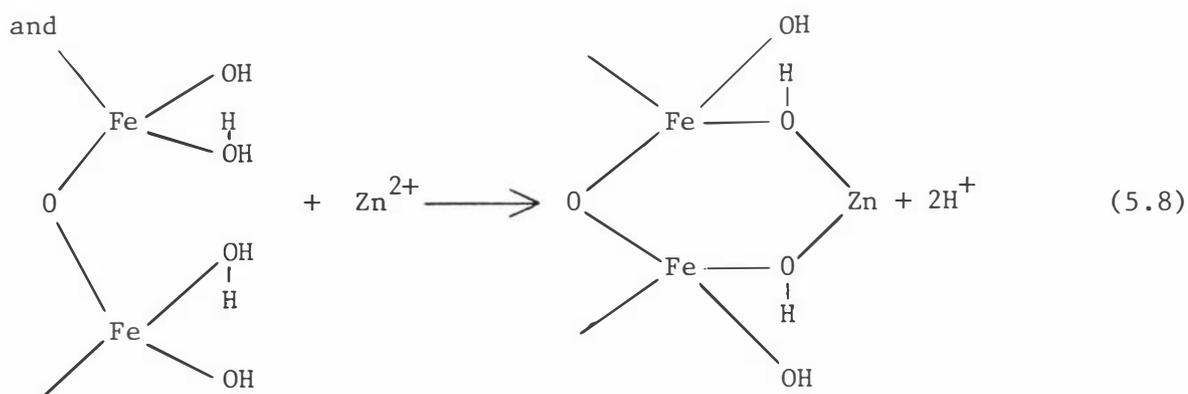
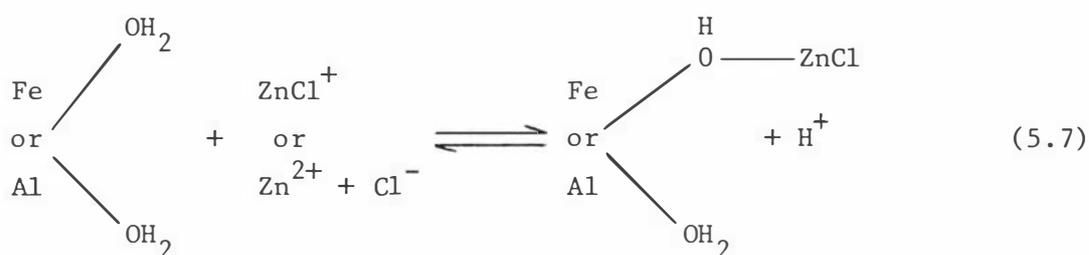
From the literature, there appears to be no general agreement as to whether one or two mechanisms exist for Zn and Cd adsorption on hydrous metal oxides and whether one or two protons are released from the surface for each Zn and Cd adsorbed.

The proton release data for Zn and Cd adsorption by Fe gel in this study are similar to results obtained for Zn on hydrous Mn oxide (Gadde and Laitinen, 1974) where the ratio found was 1.30 moles  $H^+$  released per mole Zn adsorbed (for  $1000 \mu\text{mol Zn l}^{-1}$  addition), and 1.10 for Cd (for  $1000 \mu\text{mol Cd l}^{-1}$  addition). On both hydrous Mn oxides and Fe gels,

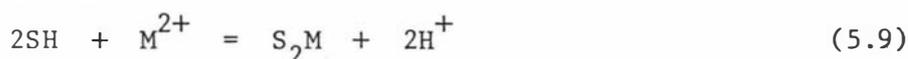
Table 5.4 Mole ratios of base consumed to Zn or Cd adsorbed, as a function of Zn or Cd concentration and pH, for Fe gel in  $3 \times 10^{-2}$  M NaCl.  
(Quantities of Zn and Cd added and adsorbed, and  $\text{OH}^-$  consumed are expressed per gram of gel).

Zn or Cd added $\mu\text{mol}$	Equilibrium Zn or Cd concentration $\mu\text{mol l}^{-1}$	Zn or Cd adsorbed (a) $\mu\text{mol}$	$\text{OH}^-$ consumed/ $\text{H}^+$ released (b) $\mu\text{mol}$	Mole ratio (b/a)	
				pH 6.40	pH 6.80
<u>Zinc</u>					
3.0	0.29	2.1	3.0	1.43	-
6.2	1.04	3.9	5.2	1.31	1.38
30.6	1.15	16.5	27.3	1.56	1.59
61.2	2.52	29.8	47.0	1.60	1.67
122.4	2.91	55.3	83.3	1.51	-
<u>Cadmium</u>					
1.8	0.79	0.82	0.68	0.80	-
3.6	1.69	1.6	1.4	0.87	1.05
17.8	10.50	6.4	6.1	0.95	1.43
35.6	23.40	11.6	12.1	1.05	1.30
71.2	27.87	17.6	19.7	1.12	-

more protons were released per mole of Zn adsorbed than for Cd. For Zn, Kalbasi et al., (1978) found the ratio to be within the range 1.53 to 1.94 for a single addition of Zn ( $306 \mu\text{mol Zn g}^{-1}$ ) over a range of pH values from 5.93 to 6.96 for Fe and Al hydrous oxides. They also explained their data with a two-mechanism model, with the first mechanism releasing one proton, and the second, two protons per Zn adsorbed. The contributions of each mechanism to the total adsorption determined the actual mole ratios obtained at each pH and for each amount of adsorbed Zn. The mechanisms proposed were:



In marked contrast to the results of this study and to those of most other workers, Forbes et al. (1976) found mole ratios of 2.2 for Zn and Cd adsorption onto goethite in a matrix of  $7.5 \times 10^{-2} \text{M NaNO}_3$ . The initial additions, however, of Zn and Cd were  $2620 \mu\text{mol l}^{-1}$  for each cation. Forbes et al. (1976) attributed the proton release data to a general interfacial reaction involving the release of two protons for every Zn adsorbed, i.e.,



### 5.3.3 Isotopic exchangeability of Zn and Cd adsorbed by Fe gel

An attempt was made to differentiate between the forms of Zn and Cd adsorbed by determining the relative proportions of isotopically and non-isotopically exchangeable Zn or Cd adsorbed on the Fe gel. The implicit assumption is that differences in isotopic exchangeability relate to differences in the strengths of binding of the adsorbed Zn or Cd.

As the relative amounts of Zn and Cd adsorbed into regions I and II (Chapter 4) depend on the level of addition, and because an increase in pH causes an increase in the total amounts adsorbed, these two variables were considered likely to affect the proportions of the two cations found within the two regions and hence the overall isotopic exchangeability of the adsorbed Zn and Cd.

The results for the exchangeability of Cd are easier to explain than those for Zn in view of the results presented in Chapter 4. The low exchangeability of Cd found at the low initial addition ( $1.78 \mu\text{mol Cd g}^{-1}$ ) may result from a higher proportion of the total Cd adsorbed being held as more tightly-bound Cd predominantly in region I. At the higher initial Cd addition the higher exchangeability occurs where relatively more Cd is adsorbed in the less tightly held region II form. pH had no apparent effect on the exchangeability of Cd at either addition, a feature that ties in well with earlier results (Section 4.3.5.3) suggesting that pH affects the amounts adsorbed rather than the binding energies of adsorption. The contrasting results noted for Zn, showing decreasing exchangeability with increasing pH yet similar exchangeabilities at each level of addition are not so readily explainable. They suggest a similar apportioning of Zn between the two regions at both additions at a fixed pH, with a shift of Zn to less

Table 5.5 Isotopic exchangeability of Zn and Cd adsorbed on Fe gel as affected by pH and level of addition

Zn			Cd		
pH	Zn addition $\mu\text{mol g}^{-1}$	Exchangeability %	pH	Cd addition $\mu\text{mol g}^{-1}$	Exchangeability %
5.85	3.06	58	5.90	1.78	76
	30.60	55		17.80	80
6.10	3.06	49	6.31	1.78	55
	30.60	49		17.80	83
6.45	3.06	36	6.63	1.78	60
	30.60	34		17.80	85
6.65	3.06	26	6.83	1.78	59
	30.60	27		17.80	83

exchangeable forms as pH increases. Such results appear to contradict the earlier findings (Chapter 4) of certain similarities between reactions of Zn and Cd.

#### 5.3.4 Desorption of adsorbed Zn from Fe gel by $\text{CaCl}_2$ and $\text{CuCl}_2$ solutions

The desorbability of adsorbed Zn was assessed using calcium and copper as competing cations.

The amounts of Zn adsorbed by Fe gel from a matrix solution of  $3 \times 10^{-2}\text{M}$  NaCl, together with the amounts sequentially desorbed by  $1 \times 10^{-2}\text{M}$   $\text{CaCl}_2$  and  $1 \times 10^{-2}\text{M}$   $\text{CuCl}_2$  solution are shown in Table 5.6. Also shown for each addition of Zn are the amounts estimated to be in regions I and II from the resolution of 40-hr adsorption data using the procedure outlined in Chapter 4. A plot of the amounts of Zn desorbed (either with Ca, or Cu after Ca) against Zn adsorbed in region II is shown in Fig. 5.6. Also shown on this graph is the sum of Ca + Cu desorbed Zn. Desorption data lying on the 1:1 bisector (shown dotted) would indicate that Ca + Cu removed only Zn adsorbed in region II, and not that adsorbed in region I. Ca did not remove all of the Zn in region II at any level of adsorbed Zn. However, Ca + Cu-desorbable Zn, approximated more closely the amounts of region II Zn for each addition of Zn (Fig. 5.6). For example, for  $2.5 \mu\text{mol Zn g}^{-1}$  adsorbed in region II,  $5.25 \mu\text{mol Zn g}^{-1}$  were desorbed by Ca + Cu, and for  $25 \mu\text{mol Zn g}^{-1}$ ,  $26 \mu\text{mol Zn g}^{-1}$  were desorbed by Ca + Cu (data from Fig. 5.6 and Table 5.6).

An important finding from the desorption studies is that the percentage of Zn desorbed was similar (76-88%) for all amounts of Zn adsorbed (Table 5.6). Hence, a relatively constant proportion (12-24%)

Table 5.6 Distribution of Zn adsorbed by Fe gel and desorption against  $1 \times 10^{-2} \text{M CaCl}_2$  and  $1 \times 10^{-2} \text{M CuCl}_2$

Equilibrium concentration of Zn after adsorption $\mu\text{mol l}^{-1}$	Amount of Zn			
	Adsorbed (total) $\mu\text{mol g}^{-1}$	Adsorbed in Region I $\mu\text{mol g}^{-1}$	Adsorbed in Region II $\mu\text{mol g}^{-1}$	Desorbed by $1 \times 10^{-2} \text{M CaCl}_2$ $\mu\text{mol g}^{-1}$
0.136	1.32	1.05	0.27	0.30
0.237	2.09	1.62	0.47	0.47
0.340	2.59	1.92	0.67	0.60
0.566	3.84	2.73	1.11	0.97
0.905	5.00	3.24	1.76	1.41
1.641	7.29	4.18	3.11	2.24
3.361	11.69	5.63	6.06	3.93
7.179	17.36	5.73	11.63	6.43
10.195	20.82	5.76	15.06	8.26
18.647	28.71	5.80	22.91	11.96
28.317	35.63	5.97	29.67	15.24

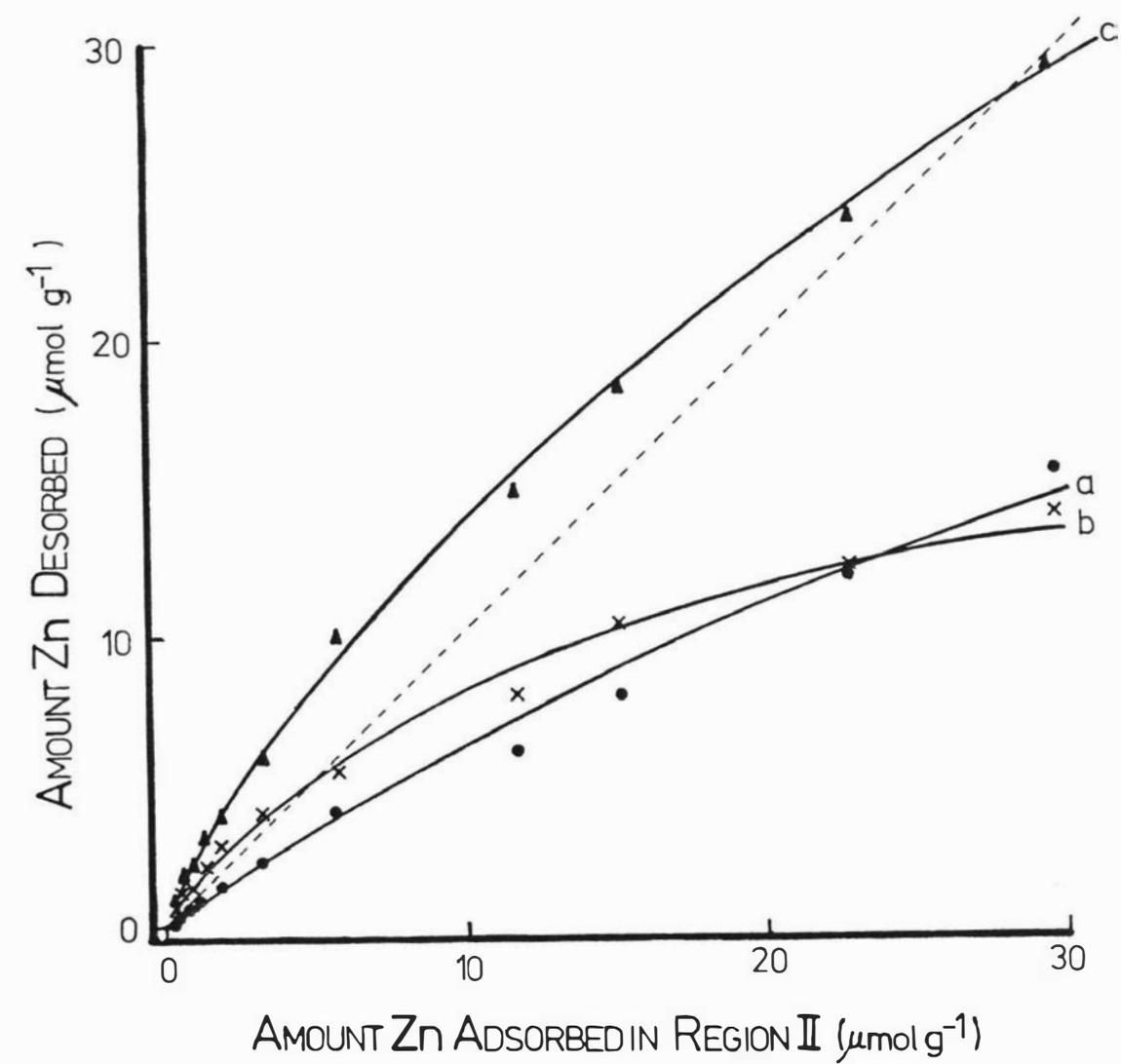


Figure 5.6 Desorption of adsorbed Zn from Fe gel by  $1 \times 10^{-2} \text{M CaCl}_2$  (a),  $1 \times 10^{-2} \text{M CuCl}_2$  after desorption by  $\text{CaCl}_2$  (b) and total amount of Zn desorbed by  $\text{CaCl}_2 + \text{CuCl}_2$  (c).

## Amount of Zn

Desorbed by $\text{CaCl}_2$ as a percentage of total adsorbed %	Desorbed by $1 \times 10^{-2} \text{M}$ $\text{CuCl}_2$ $\mu\text{mol g}^{-1}$	Desorbed by $\text{Ca} + \text{Cu}$ $\mu\text{mol g}^{-1}$	Not Desorbed by $\text{Ca} + \text{Cu}$ $\mu\text{mol g}^{-1}$	Desorbed by $\text{Ca} + \text{Cu}$ as a percentage of amount adsorbed %
23	0.70	1.00	0.32	76
23	1.17	1.64	0.45	78
23	1.41	2.01	0.58	78
25	2.08	3.05	0.79	80
28	2.81	4.22	0.78	84
31	3.93	6.17	1.12	85
34	5.89	9.82	1.87	84
37	8.41	14.84	2.52	85
40	10.07	18.33	2.49	88
42	12.07	24.03	4.68	84
43	13.94	29.18	6.45	82

of adsorbed Zn is retained by the surfaces against desorption by Ca + Cu. Kalbasi et al. (1978) reported that only a proportion of adsorbed Zn was desorbed by Ba, Mg and Ca ions from Fe oxide, however Cu ions were not used in their study. The amounts of Zn desorbed by Ba, Mg and Ca ions were found to decrease with increasing pH and also with increasing amounts of Zn initially adsorbed on the surface. They concluded that Zn desorbed by Ba corresponded to amounts adsorbed by one mechanism and the remainder represented Zn adsorbed by a second mechanism.

The possibility that non-desorbable Zn may result from absorption is investigated in Chapter 6.

#### 5.4 General Discussion

##### 5.4.1 Summary of evidence for the existence of two mechanisms for adsorption of Zn and Cd by Fe gel

The evidence obtained in this chapter strongly suggests the existence of two different mechanisms for the adsorption of Zn and Cd by Fe gel, and hence possibly by soils, since Fe gel may well serve as a model for soils (on the basis of the similarity of adsorption parameters for soils and Fe gel found in Chapter 4). Previous workers (Quirk and Posner, 1975; Kalbasi et al., 1978) have similarly pointed to the existence of two mechanisms for Zn adsorption. Few, however, have compared Zn and Cd in the same study.

The experimental finding that following desorption by Ca 60-77% (Table 5.6) of the Zn still remained adsorbed on the gel surface (Section 5.3.4) suggests that surface Zn is adsorbed in at least two different forms or by two different mechanisms. This finding of differential desorbability of adsorbed Zn is in agreement with the work

of Kalbasi et al. (1978). The fact that not all of the Zn and Cd adsorbed by Fe gel was isotopically exchangeable (Section 5.3.3) is further confirmation for the occurrence of at least two different bonding mechanisms. The isotopic exchangeability data shows that the proportion of Zn not exchangeable after 1 hr, ranges from 40-70% (Table 5.5) while that for Cd ranges from 20-40% (Table 5.5). The non-exchangeable Zn and Cd is assumed to represent more-tightly held forms of Zn and Cd and the significance of the differences in the proportions of more-tightly held Zn as compared with Cd will be discussed in Section 5.4.2.

Although the Langmuir treatment of adsorption data (Chapter 4) suggested the existence of two populations of adsorption sites, the predicted distribution of Zn between these 'regions' using calculated Langmuir parameters is not the same as that found using desorption and isotopic exchangeability data (Table 5.7). At low surface coverages of Zn and high surface coverage of Cd there is reasonable agreement on the proportions of Zn or Cd found in the more tightly held 'regions'. However, at high surface coverages of Zn and low surface coverages of Cd, good agreement was not found between the Langmuir data and the proportions of more-tightly bound Zn or Cd (non-exchangeable forms). The data in Table 5.7 casts doubt on the validity of calculating adsorption maxima and binding energy constants for Zn and Cd, especially for region II, from Langmuir-type treatments of adsorption data on Fe gel systems.

Further evidence for two mechanisms of adsorption of Zn and Cd by Fe gels is found in the proton release data in Section 5.3.2. The non-integer values found for the number of protons released per Zn and Cd adsorbed can be explained by postulating two different mechanisms with

Table 5.7 Proportion of more tightly held Zn and Cd, expressed as a percentage of total adsorption, as given by desorption, isotopic exchange and Langmuir adsorption data

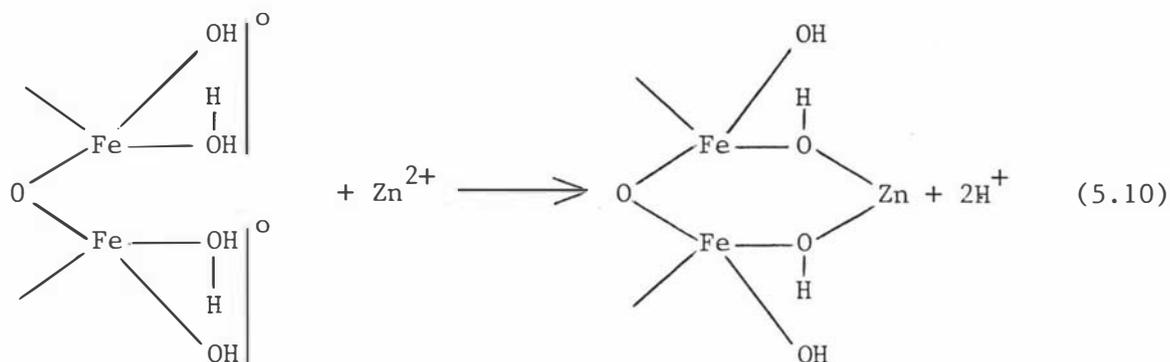
Initial addition $\mu\text{mol g}^{-1}$	Proportion of more tightly held Zn or Cd		
	Desorption data %	Isotopic exchange data %	Langmuir data for Region I %
<u>Zinc</u>			
3.06	77	64	74
30.60	60	66	28
<u>Cadmium</u>			
1.78	-	40	59
17.80	-	15	12

different proton release characteristics. Such a postulate would require that one mechanism release a single proton per Zn and Cd adsorbed, whereas the second mechanism release two protons (although Cd does not always release even one proton).

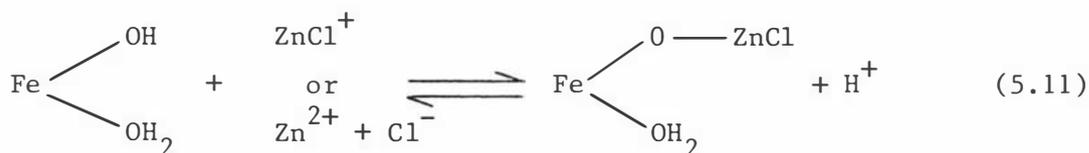
Thus, from this study it would appear that Zn and Cd adsorbed on Fe gel surfaces may be held by at least two mechanisms, the nature of which are discussed below.

#### 5.4.2 Mechanisms proposed for Zn and Cd adsorption by Fe gel

Experimental evidence obtained from proton release, desorption and isotopic exchange studies in this study is consistent with the suggestion that Zn adsorption on Fe gel occurs by two mechanisms involving monodentate and bidentate bonding. It is suggested that Zn bound through a bidentate linkage as indicated below, would result in the release of two protons per Zn adsorbed. Of the two mechanisms, this form of adsorbed Zn would be relatively more difficult to displace by competing cations.



Zn bound by a monodentate mechanism involves release of one proton for every Zn adsorbed. Such Zn would be expected to be more easily displaced by competing cations. Monodentate bonding of Zn could involve the adsorption of a complex ion such as  $\text{ZnCl}^+$ , e.g.,



The results already presented in this study are essentially in agreement with the mechanisms shown above (Equations (5.10) and (5.11)) as put forward by Quirk and Posner (1975) and Kalbasi et al. (1978). The model for cation adsorption proposed by Bowden et al. (1973) while only requiring one adsorption maximum (as opposed to two adsorption maxima found in the present study), is based on the postulate that Zn is adsorbed as  $Zn^{2+}$  and  $Zn(OH)^+$  by hydrous Fe oxide which again suggests that Zn adsorption involves two different mechanisms.

Adsorption of Cd can also be attributed to the same two mechanisms as proposed for Zn. However, in the case of Cd the relative importance of the two differs with a much larger proportion being held by the weaker (monodentate) bond. Evidence for this can be found not only from proton release data which give ratios much closer to unity (i.e., 0.8 to 1.4) for Cd, but also from the much higher percentage of isotopically exchangeable Cd (60 to 83%) at both low and high surface coverages, compared to Zn.

If the hypothesis of Kalbasi et al. (1978), that the weaker type of Zn adsorption involves a species of the type  $ZnCl^+$ , is correct then a greater proportion of this type of adsorption would indeed be expected in the case of Cd as this type of chloro-complex is much more stable for Cd than for Zn (Cotton and Wilkinson, 1966) and would be present in much greater concentrations in solution. This was verified using stability constants derived by Kivalo and Luoto (1957) (as quoted in Sillen and Martell, 1964). Calculations using these stability constants indicated that in the  $3 \times 10^{-2} M$  chloride solutions used in this study, the ratio  $\frac{CdCl^+}{Cd^{2+}}$  would be 100 times greater than the corresponding ratio for  $\frac{ZnCl^+}{Zn^{2+}}$ .

Although a bidentate-type bond has been proposed as the mechanism by which more-tightly held Zn and Cd is adsorbed, no direct evidence was obtained in the present study, or by Quirk and Posner (1975) or Kalbasi et al. (1978) for the existence of a bidentate-type bond. Furthermore, the fact that in the present study, only a proportion of the more-tightly held Zn, i.e., that Zn not displaced by Ca, could be subsequently displaced by Cu may even (Section 5.3.4) suggest a further possible subdivision within the more-tightly held Zn form. As discussed in Section 5.3.3 the finding that not all the Zn removed from solution was isotopically exchangeable, and that the isotopic exchangeability of Zn did not increase with increasing equilibration time, would suggest that some portion of the adsorbed Zn may be in an adsorbed or occluded state. This possibility is investigated in Chapter 6.

CHAPTER SIX

TIME-DEPENDENT ADSORPTION OF Zn AND Cd  
BY HYDROUS FERRIC OXIDES

6.1 Introduction

Zn and Cd adsorption by soils and soil components can be extremely rapid (Shah Singh, 1979) due to rapid adsorption of Zn or Cd on accessible surfaces of soil and soil components (although this has not been well-established). After the initial rapid uptake, adsorption of Zn and Cd continues slowly, with equilibrium being attained after long equilibration periods.

In Chapter 5, it was shown that with synthetic Fe gel a proportion (12-24%) of adsorbed Zn was not desorbed by other competing cations (Ca and Cu), under the experimental conditions used for the study. This finding could indicate that a certain fraction of Zn previously assumed to be tightly adsorbed may, in fact, be "occluded" (absorbed) within the hydrous oxide structure. The process of absorption could equally well be regarded as adsorption onto internal surfaces. This chapter reports an investigation into the possibility of "occlusion" by comparing adsorption of Zn and Cd over time using synthetic Fe gel, synthetic goethite, and ground natural goethite.

These hydrous ferric oxides differ in degree of crystallinity. Whereas Fe gel is exclusively short-range order in character, synthetic goethite contains little or no short-range order material and is mostly crystalline. Ground natural goethite, however, contains some short-range order material, developed during grinding. The concept of "occlusion" often implies a diffusion process which would be expected

to occur more readily in materials with short-range order character. If diffusion of adsorbed Zn and Cd does occur, then the adsorbents containing short-range order material would be expected to show time-dependent adsorption. The crystalline synthetic goethite on the other hand would not show time-dependent adsorption as the continual removal of Zn or Cd from solution should not occur once the accessible surface sites are occupied.

## 6.2 Materials

The preparation of synthetic Fe gel has been described previously in Chapter 2, and the same procedure was used for this experiment.

Synthetic goethite was prepared by incubating synthetic Fe gel for 65 days at pH 12.0, in a water bath at 60°C. The goethite was then washed by suspending in deionised water, and centrifuged (10 min at 2000 r.p.m.), and the supernatant solution discarded. The goethite was washed several times to remove excess NaOH, and finally 0.1M HCl was added dropwise to lower the pH to 3.5 and prevent flocculation. The 0.02 - 0.2 µm fraction was separated by the method of Jackson (1956) using differential centrifugation and used for the adsorption studies.

Natural goethite (Biwabik, Minnesota), obtained from Ward's Natural Science Establishment, was ground for 10 min in a ring grinder (Rocklabs, Auckland, N.Z.). The resultant powder was then washed by suspending in deionised water. The pH was adjusted to pH 8.5, with 0.1M NaOH, to prevent flocculation. The 0.02 - 0.2 µm fraction (Jackson, 1956) was separated by centrifugation and used for the adsorption experiments. Grinding treatment was used to induce formation of an outer "crust" of short-range order material on the crystalline natural goethite and to either accentuate or initiate defects in the crystalline

structure of the natural goethite (Ryden et al., 1977a).

The three hydrous oxides were dialysed against  $3 \times 10^{-2}$  M NaCl for five days in order to bring the pH of the oxide suspensions to within 0.1 pH units of each other.

The synthetic and natural goethite materials gave identical X-ray diffraction patterns, both showing a dominant peak of  $4.18\text{\AA}$ , and a smaller secondary peak of  $4.94\text{\AA}$  typical for goethite (Brown, 1961). An example is given in Fig. 6.1.

### 6.3 Methods

The time-dependent adsorption of Zn and Cd by the various hydrous oxides, was determined at one level of Zn or Cd addition. Adsorption was followed by monitoring solution concentrations at time periods ranging from 0.5 to 192 hr after addition. To obtain similar final solution Zn or Cd concentrations for each oxide system at the end of the 192-hr equilibration, different amounts of Zn and Cd were added to each adsorbent. The actual additions of Zn used were  $26.6 \mu\text{mol Zn g}^{-1}$  for Fe gel,  $22.2 \mu\text{mol Zn g}^{-1}$  for natural goethite and  $17.4 \mu\text{mol Zn g}^{-1}$  for synthetic goethite. The corresponding Cd additions were  $8.80 \mu\text{mol Cd g}^{-1}$  for Fe gel,  $6.46 \mu\text{mol Cd g}^{-1}$  for natural goethite, and  $5.62 \mu\text{mol Cd g}^{-1}$  for synthetic goethite.

The initial additions of Zn and Cd were added to bulk suspensions ( $1.20\text{g l}^{-1}$ ) of the hydrous ferric oxides in a matrix of  $3 \times 10^{-2}$  M NaCl at pH 7.0. The bulk suspensions were shaken on an end-over-end shaker (40 r.p.m.) at  $23 \pm 2^\circ\text{C}$  for 192 hr. In order to follow adsorption, 10-ml subsamples were withdrawn from the vigorously stirred bulk suspensions at various times after initial Zn and Cd addition. These

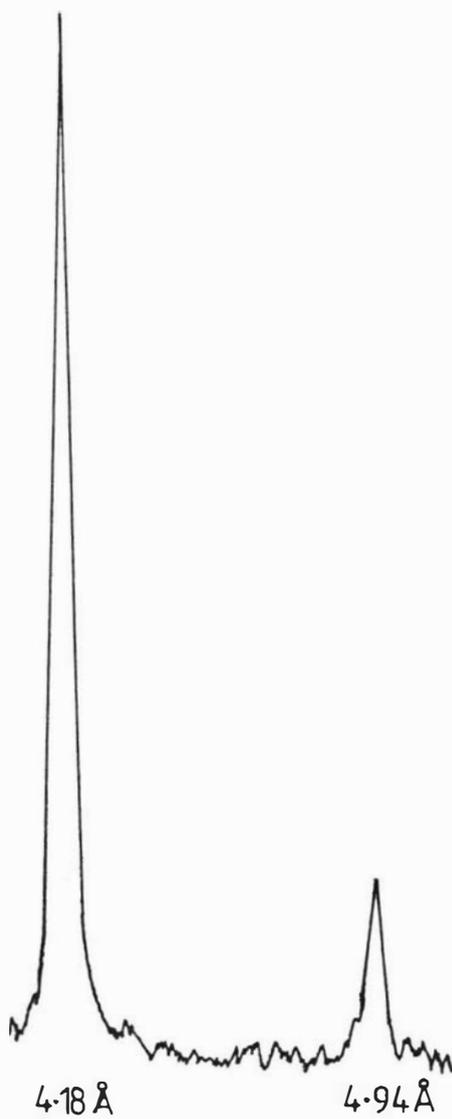


Figure 6.1 X-ray diffraction peaks for a natural goethite sample from Biwabik, Minnesota.

were centrifuged at  $23 \pm 2^{\circ}\text{C}$  for 5 min at 15,000 r.p.m. on a Sorvall Super-Centrifuge (RC-5), and the supernatants filtered through Millipore filters ( $< 0.45 \mu\text{m}$ ) and then analysed for Zn and Cd.

Desorption of Zn and Cd from Fe gel, natural and synthetic goethite was carried out after the adsorption studies by resuspending the hydrous oxides in 10 ml of  $1 \times 10^{-2}\text{M}$   $\text{CaCl}_2$  and shaking for 1 hr on an end-over-end shaker (40 r.p.m.) at  $23 \pm 2^{\circ}\text{C}$ . The suspensions were then centrifuged at  $23 \pm 2^{\circ}\text{C}$  for 5 min at 15,000 r.p.m. and filtered through Millipore filters ( $< 0.45 \mu\text{m}$ ). The supernatant solutions were analysed to give a measure of Ca-extractable Zn or Cd. The hydrous oxides were then resuspended in 10 ml of  $1 \times 10^{-2}\text{M}$   $\text{CuCl}_2$  and the process repeated as for  $\text{CaCl}_2$ , to obtain the Cu-extractable Zn or Cd.

#### 6.4 Results and Discussion

##### 6.4.1 Adsorption of Zn and Cd by hydrous ferric oxides

Evidence was found for a rapid initial uptake of Zn and Cd by all three hydrous ferric oxides. Loss of Zn and Cd from the solution phase was taken to indicate adsorption by the appropriate oxide surface, as it was earlier shown that 50-ml polycarbonate centrifuge tubes did not remove Zn or Cd from an NaCl matrix (Chapter 4) to any significant extent. A slow continuing uptake of Zn and Cd occurred between 24 to 192 hr with natural goethite, and to a very much lesser extent with synthetic goethite and Fe gel (Figs. 6.2 and 6.3).

For both Zn and Cd similar patterns for removal from solution, as shown in Figs. 6.2 and 6.3, were apparent for the three adsorbents. For example, whereas Fe gel and synthetic goethite both tended towards a constant solution concentration within 2 hr after addition of both Zn and Cd, ground natural goethite did not attain a constant solution

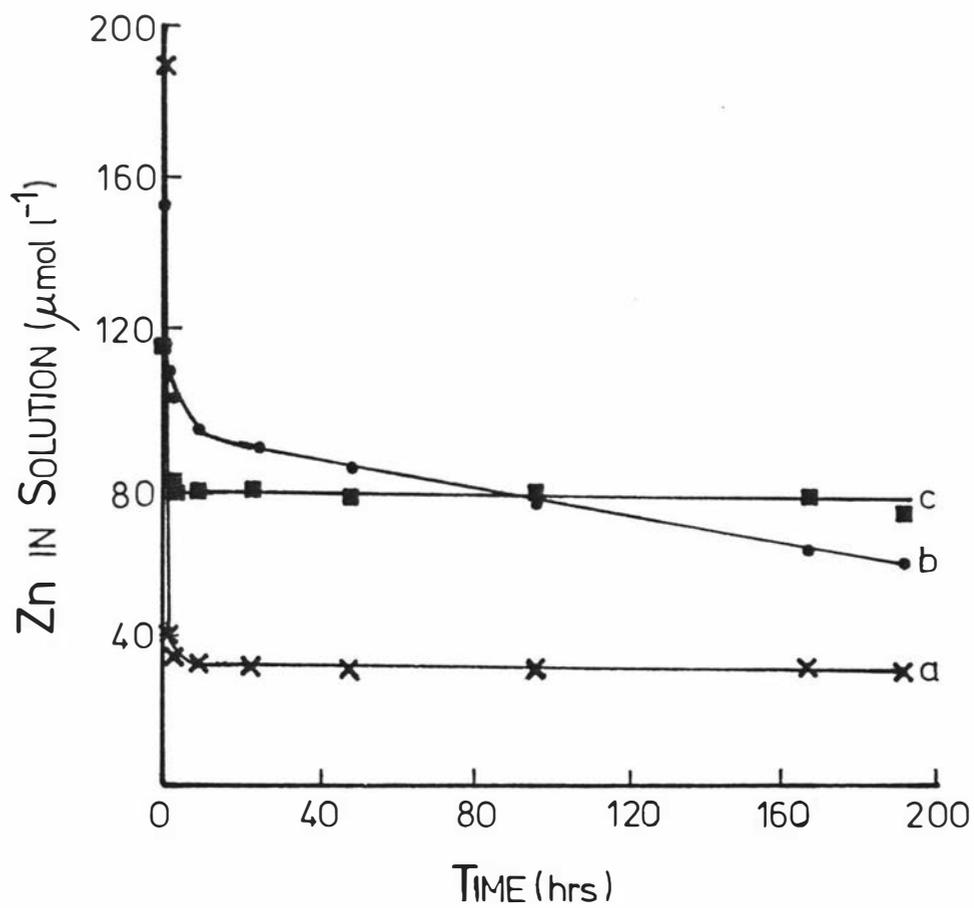


Figure 6.2 Time-dependent adsorption of Zn by Fe gel (a), natural goethite (b) and synthetic goethite (c).

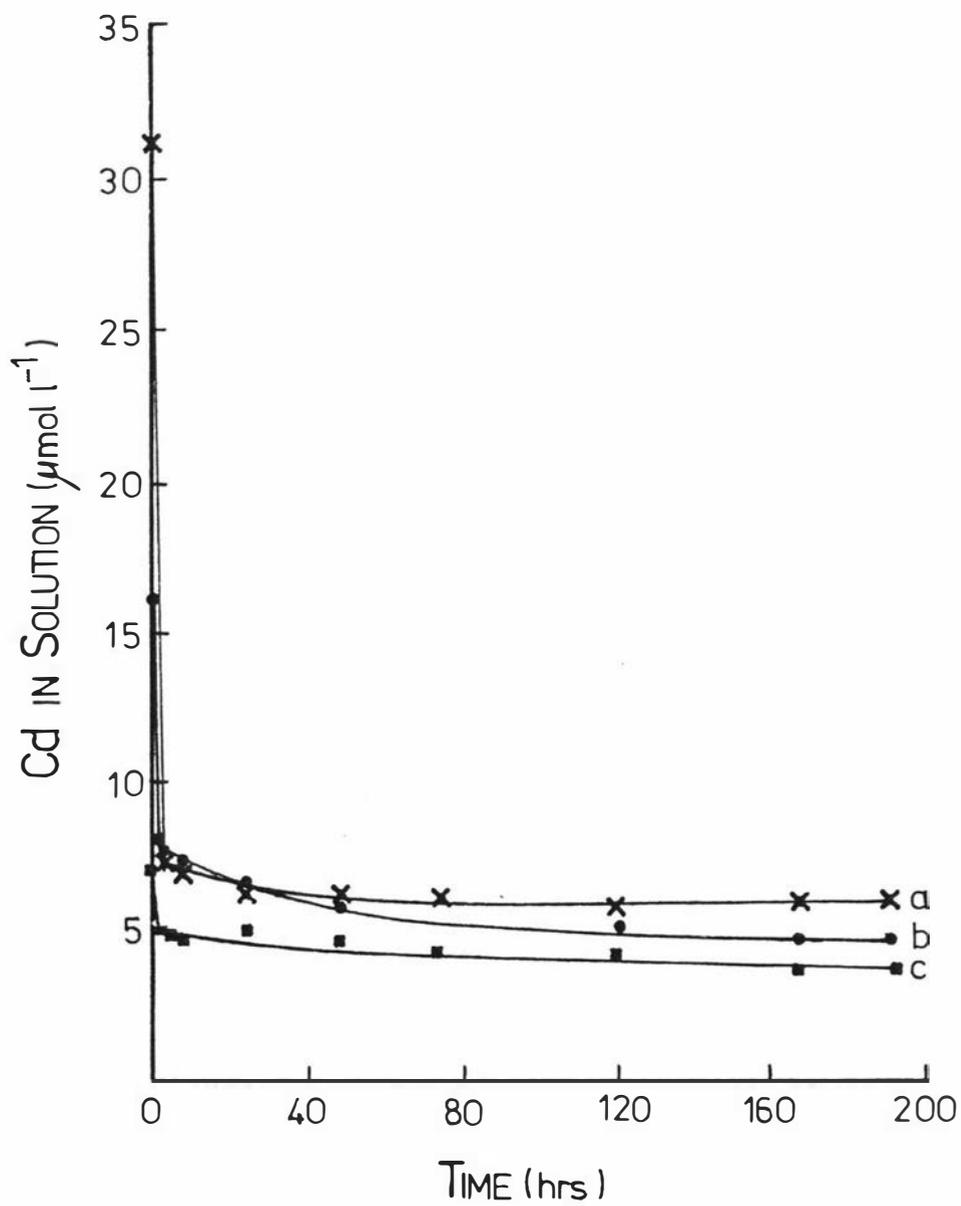


Figure 6.3 Time-dependent adsorption of Cd by Fe gel (a), natural goethite (b) and synthetic goethite (c).

concentration even at 192 hr.

For both Zn and Cd adsorption by the three hydrous ferric oxides an Index of Completion was calculated as follows:

$$\text{Index of Completion} = \frac{x_i - x_n}{x_i - x_{192}} \quad (6.1)$$

where  $x_i$  = Initial Zn or Cd solution concentration in  $\mu\text{mol l}^{-1}$

$x_n$  = Zn or Cd solution concentration at time, n, in  $\mu\text{mol l}^{-1}$

and  $x_{192}$  = Zn or Cd solution concentration at 192 hr in  $\mu\text{mol l}^{-1}$ .

The results (Tables 6.1 and 6.2) show that after 24 hr, the adsorption of Zn and Cd was virtually complete for the synthetic Fe gel and goethite, whilst for ground natural goethite the approach to equilibrium continued up until the time the experiment was terminated.

These results obtained for Zn and Cd are in marked contrast to those previously reported for the reactions of P with Fe gel, synthetic goethite, ground natural goethite and some soils (Ryden et al., 1977a). For P, it was found that, with the exception of synthetic goethite, the other adsorbents exhibited a continuing sorption which was attributed to a shift of initially sorbed P to chemisorbed (or absorbed) P. The cause of this contrasting behaviour for the different hydrous oxides of Fe was thought to be due to the presence of short-range order material. Synthetic goethite contained little or no short-range order material, and did not show time-dependent adsorption (Ryden et al., 1977a).

As indicated in Chapter 5, Zn and Cd adsorption involves bonding to  $-\text{OH}_2$  and  $-\text{OH}$  groups at hydrous oxide surfaces. The large initial decrease in solution Zn and Cd concentrations noted at short equilibrium times (less than 2 hr) probably involves adsorption at outer accessible sites on the oxides. For Fe gel and synthetic goethite the solution

Table 6.1 Solution Zn concentrations and index of completion of adsorption, at various times following Zn additions to Fe gel, natural goethite and synthetic goethite

Time (hrs)	Fe Gel		Natural Goethite		Synthetic Goethite	
	Solution Zn ( $\mu\text{mol l}^{-1}$ )	Index of completion	Solution Zn ( $\mu\text{mol l}^{-1}$ )	Index of completion	Solution Zn ( $\mu\text{mol l}^{-1}$ )	Index of completion
0	191	-	153	-	115	-
0.5	41	0.94	110	0.45	80	0.81
2.0	35	0.98	103	0.53	79	0.84
8.0	33	0.99	95	0.61	79	0.84
24.0	31	1.00	88	0.68	79	0.84
48.0	30	1.01	83	0.74	76	0.91
96.0	31	1.00	74	0.83	77	0.88
168.0	31	1.00	63	0.95	76	0.91
192.0	31	1.00	58	1.00	72	1.00

Table 6.2 Solution Cd concentrations and index of completion of adsorption, at various times following Cd additions to Fe gel, natural goethite and synthetic goethite

Time (hrs)	Fe Gel		Natural Goethite		Synthetic Goethite	
	Solution Cd ( $\mu\text{mol l}^{-1}$ )	Index of completion	Solution Cd ( $\mu\text{mol l}^{-1}$ )	Index of completion	Solution Cd ( $\mu\text{mol l}^{-1}$ )	Index of completion
0	31	-	16	-	16	-
0.5	7.1	0.96	7.9	0.72	5.1	0.89
2.0	7.2	0.95	7.7	0.74	5.0	0.89
8.0	7.1	0.96	7.1	0.80	4.8	0.91
24.0	6.4	0.98	6.6	0.84	5.0	0.89
48.0	6.3	0.99	6.0	0.89	4.6	0.93
74.0	6.1	1.00	-	-	4.3	0.95
120.0	5.9	1.00	5.1	0.97	4.2	0.96
168.0	6.0	1.00	4.7	1.01	3.9	0.98
192.0	6.0	1.00	4.8	1.00	3.7	1.00

concentrations of Zn and Cd quickly come to equilibrium (Figs. 6.2, 6.3 and Tables 6.1, 6.2) and no evidence was found for any "occlusion" resulting from diffusive penetration into either the short-range order material of Fe gel or the crystalline synthetic goethite at least at the concentrations of Zn and Cd used in this study. Ground natural goethite, however, displayed pronounced time-dependent adsorption of both Zn and Cd as shown in Figs. 6.2 and 6.3, and by the indices in Tables 6.1 and 6.2. Such a continuing and slow decrease of solution Zn and Cd, with time, could not readily be attributed to diffusion of Zn or Cd into short-range order material, because no such trend was noted for the synthetic gel. It is possible that this continuing adsorption of Zn and Cd by ground natural goethite is due to either: (a) slow diffusion of Zn and Cd into defects in the natural goethite crystals, either developed or accentuated during the grinding procedure or: (b) the occurrence and participation in the adsorption process of other unidentified contaminants camouflaged within the natural goethite towards Zn and Cd either by offering a different surface onto which adsorption can take place or by modifying the reaction mechanism of the goethite.

Hence, unlike the situation found for P, no evidence was obtained in this study to indicate the presence of any significant time-dependent diffusive penetration of Zn and Cd, into Fe gel or synthetic goethite. However, for natural goethite, some diffusion of Zn and Cd may occur into defects in the goethite structure. In this respect, this study does highlight the fact that it may be misleading to infer cation adsorption behaviour based on results obtained for anion studies using the same or similar adsorbents.

#### 6.4.2 Desorption of Zn and Cd from hydrous ferric oxides

The desorption of previously adsorbed Zn and Cd, using  $1 \times 10^{-2} \text{M}$   $\text{CaCl}_2$  and  $1 \times 10^{-2} \text{M}$   $\text{CuCl}_2$  (Figs. 6.4 and 6.5) showed, as expected, that  $1 \times 10^{-2} \text{M}$   $\text{CuCl}_2$  desorbed more Zn and Cd, from all adsorbents, than did  $1 \times 10^{-2} \text{M}$   $\text{CaCl}_2$ . A similar result was found for Zn desorption from Fe gel (Chapter 5). The percentage of Zn and Cd desorbed from both Fe gel and synthetic goethite by  $\text{CaCl}_2$  and  $\text{CuCl}_2$  solutions (Tables 6.3 and 6.4) showed little change after 24 hr of adsorption. For ground natural goethite, however, a decrease in the amount of Zn and Cd that could be desorbed occurred right up to 192 hr. Such a decrease may be further evidence for time-dependent adsorption. This situation occurred only for natural goethite for the reasons outlined above.

From the evidence regarding the absence of time-dependent adsorption of Zn and Cd by the short-range order Fe gel and the totally crystalline synthetic goethite, coupled with the constant desorbability of Zn and Cd from these two adsorbents, it was concluded that the sorption process for both Zn and Cd appears to involve adsorption onto accessible sites with little or no subsequent absorption. Where crystalline hydrous oxides may contain crystal structure defects (e.g., represented by ground natural goethite in this study) some slow diffusion of Zn and Cd may occur into internal and relatively inaccessible sites.

Thus, as the sorption reactions for Zn and Cd appear to be dominated by adsorption with little or no evidence for absorption (diffusive penetration) as noted for Fe gel, it appears that Zn and Cd could remain relatively more accessible for desorption or dissolution into the matrix solution, than is the situation encountered for anions, such as P, which show a marked time-dependent sorption behaviour.

Table 6.3 Amounts and percentages of Zn desorbed by  $1 \times 10^{-2}M$   $CaCl_2$  and  $1 \times 10^{-2}M$   $CuCl_2$  from hydrous ferric oxides

Time (hrs)	Amount Zn adsorbed on surface $\mu\text{mol g}^{-1}$	Amount Zn desorbed by $1 \times 10^{-2}M$ $CaCl_2$		Amount Zn desorbed by $1 \times 10^{-2}M$ $CuCl_2$	
		$\mu\text{mol g}^{-1}$	%	$\mu\text{mol g}^{-1}$	%
<u>Synthetic Fe Gel</u>					
2	22.61	2.76	12.2	5.37	23.8
8	22.95	2.47	10.8	5.23	21.2
24	23.20	2.32	10.0	5.08	21.9
48	23.39	2.18	9.3	4.65	19.9
96	23.31	2.18	9.4	4.79	20.6
168	23.22	2.18	9.4	4.50	19.4
192	23.31	2.03	8.7	4.36	18.7
<u>Ground Natural Goethite</u>					
2	8.31	1.27	15.3	1.90	22.9
8	9.55	1.22	12.8	2.11	22.1
24	10.75	1.29	12.0	2.29	21.3
48	11.49	1.50	13.1	2.41	21.0
96	13.09	1.37	10.5	2.57	19.6
168	14.76	1.30	8.8	3.00	20.3
192	15.71	1.37	8.7	3.10	19.7
<u>Synthetic Goethite</u>					
2	6.26	1.18	18.9	1.58	25.1
8	6.18	1.05	17.0	1.60	25.9
24	6.28	0.98	15.6	1.46	23.3
48	6.85	1.23	18.0	1.86	27.2
96	6.90	1.33	19.9	2.03	29.4
168	6.87	1.02	15.0	1.98	28.9
192	7.20	1.07	14.3	2.14	29.7

Table 6.4 Amounts and percentages of Cd desorbed by  $1 \times 10^{-2}M$   $CaCl_2$  and  $1 \times 10^{-2}M$   $CuCl_2$  from hydrous ferric oxides

Time (hrs)	Amount Cd adsorbed on surface $\mu\text{mol g}^{-1}$	Amount Cd desorbed by $1 \times 10^{-2}M$ $CaCl_2$		Amount Cd desorbed by $1 \times 10^{-2}M$ $CuCl_2$	
		$\mu\text{mol g}^{-1}$	%	$\mu\text{mol g}^{-1}$	%
<u>Synthetic Fe Gel</u>					
2	3.48	0.48	13.8	0.78	22.5
8	3.49	0.48	13.7	0.76	21.6
24	3.59	0.45	12.5	0.78	21.8
48	3.61	0.49	13.7	0.77	21.3
74	3.63	0.48	13.2	0.78	21.6
120	3.66	0.41	11.1	0.71	19.5
168	3.65	0.47	12.7	0.74	20.3
192	3.65	0.48	13.1	0.76	20.7
<u>Ground Natural Goethite</u>					
2	2.15	0.31	14.6	0.43	20.0
8	2.25	0.35	15.4	0.46	20.5
24	2.34	0.33	14.2	0.43	18.3
48	2.43	0.31	12.9	0.45	18.4
74	-	-	-	-	-
120	2.59	0.30	11.5	0.41	16.0
168	2.65	0.26	10.0	0.36	13.7
192	2.51	0.26	10.5	0.33	13.2
<u>Synthetic Goethite</u>					
2	1.85	0.30	16.1	0.42	22.8
8	1.89	0.30	15.8	0.40	21.3
24	1.86	0.30	16.0	0.40	21.7
48	1.92	0.30	15.5	0.40	21.0
74	1.98	0.30	15.1	0.40	20.4
120	1.99	0.30	15.0	0.40	20.3
168	2.04	0.32	15.5	0.40	19.8
192	2.09	0.33	15.9	0.44	21.0

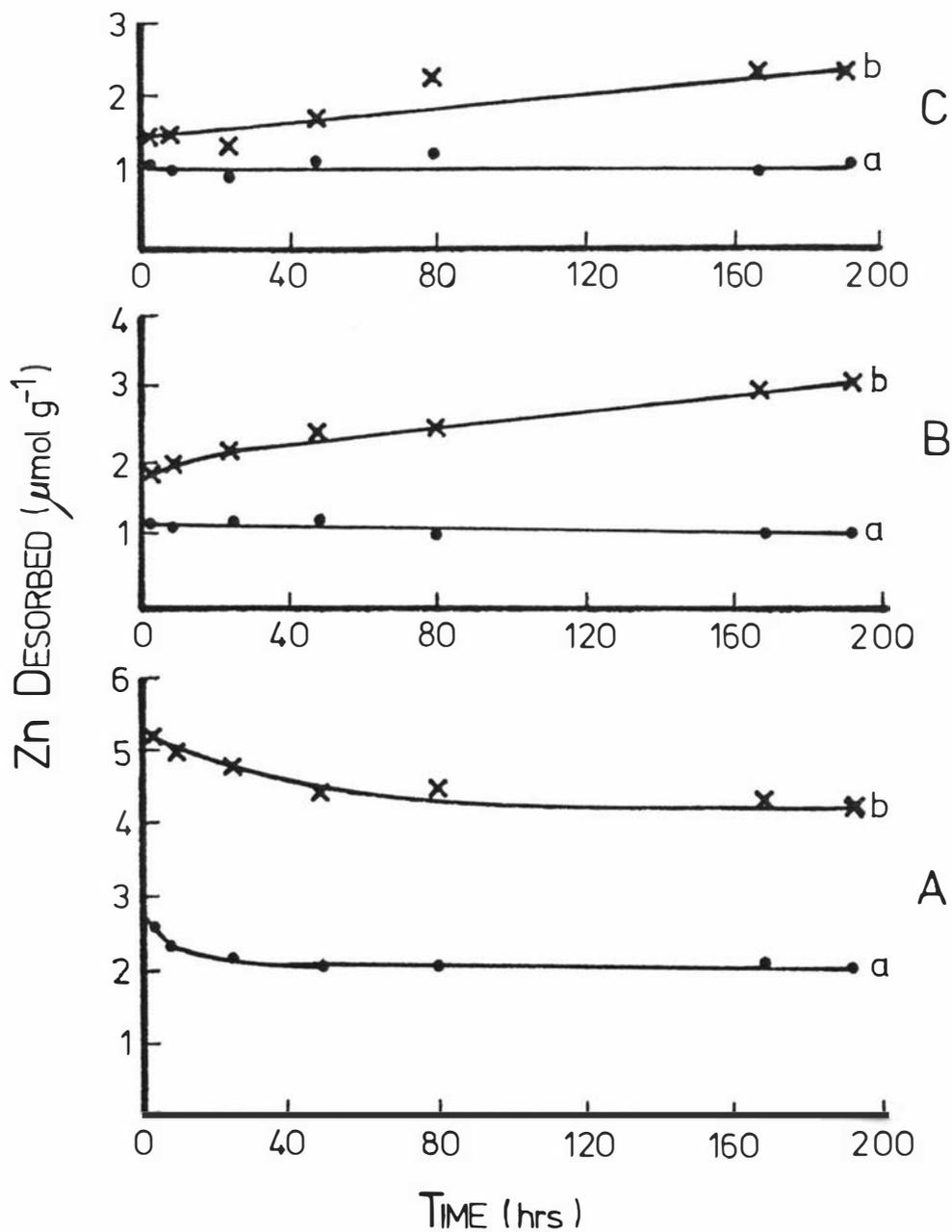


Figure 6.4 Desorption of Zn from hydrous ferric oxides  
 A: desorption of Zn from iron gel by  $1 \times 10^{-2}\text{M CaCl}_2$ (a), and  $1 \times 10^{-2}\text{M CuCl}_2$ (b)  
 B: desorption of Zn from natural goethite by  $1 \times 10^{-2}\text{M CaCl}_2$ (a), and  $1 \times 10^{-2}\text{M CuCl}_2$ (b)  
 C: desorption of Zn from synthetic goethite by  $1 \times 10^{-2}\text{M CaCl}_2$ (a), and  $1 \times 10^{-2}\text{M CuCl}_2$ (b).

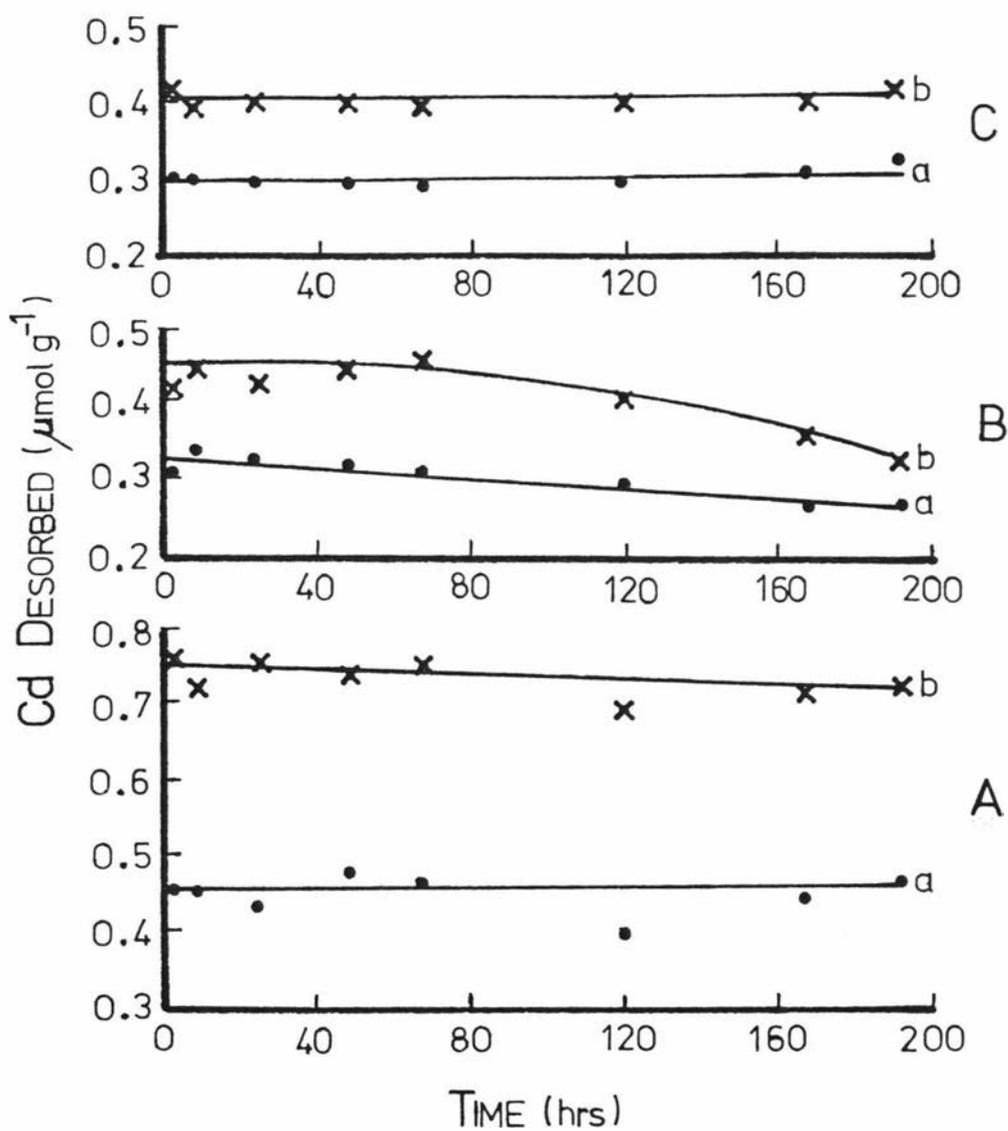


Figure 6.5 Desorption of Cd from hydrous ferric oxides

A: desorption of Cd from iron gel by  $1 \times 10^{-2}\text{M}$  CaCl<sub>2</sub> (a), and  $1 \times 10^{-2}\text{M}$  CuCl<sub>2</sub> (b)

B: desorption of Cd from natural goethite by  $1 \times 10^{-2}\text{M}$  CaCl<sub>2</sub> (a) and  $1 \times 10^{-2}\text{M}$  CuCl<sub>2</sub> (b)

C: desorption of Cd from synthetic goethite by  $1 \times 10^{-2}\text{M}$  CaCl<sub>2</sub> (a) and  $1 \times 10^{-2}\text{M}$  CuCl<sub>2</sub> (b).

CHAPTER SEVEN

THE EFFECT OF PHOSPHATE FERTILISER  
ADDITIONS ON Zn AND Cd CONTENTS OF SOILS

7.1 Introduction

Superphosphate fertiliser, normally used as a P and S supplement to soils, can also contribute to the content of plant available Zn (Ozanne et al., 1965; Williams and David, 1976) and Cd (Schroeder and Balassa, 1963; Schroeder et al., 1967; Williams and David, 1973). This is because superphosphate fertilisers may contain from 0.765 to 26.652  $\mu\text{mol Zn g}^{-1}$  and 0.080 to 1.513  $\mu\text{mol Cd g}^{-1}$  (Walkley, 1940; Brown et al., 1954; Clark and Hill, 1958; Bingham, 1959; Schroeder and Balassa, 1963; Williams, 1974) and in most agricultural and horticultural practice superphosphate fertilisers become distributed within the root zone of plants. In one study soil Cd levels were found to increase from 0.021 to 0.047  $\mu\text{mol Cd g}^{-1}$  per 1000 kg ha<sup>-1</sup> of superphosphate applied (Williams and David, 1973). Two-fold increases in tissue levels of Zn and up to ten-fold increases in Cd were found in cereal crops and pasture plants grown on soils to which at least a total of 2,500 kg ha<sup>-1</sup> superphosphate had been added (Williams and David, 1973).

For this present investigation, use was made of three soils drawn from long-term experiments in which superphosphate fertiliser had been added for periods of between 15 and 30 years. Details of the three soils are as follows:

- (a) Papateotoe silt loam - located at the New Zealand Fertiliser Manufacturers' Research Association (N.Z.F.M.R.A.) Otara, Auckland.

The treated soil had received regular annual superphosphate top-dressings at a rate of  $36 \text{ kg P ha}^{-1}$  for a period of 30 years.

The fertilised soils, together with an adjacent, unfertilised control area were sampled at two depths, 0-5 cm, 5-10 cm. The Zn and Cd content of the superphosphate fertiliser used was not known.

- (b) Lismore silt loam - the fertilised soil from Winchmore Research Station, Ashburton, had received regular superphosphate fertiliser additions at two rates, namely  $189 \text{ kg ha}^{-1}$  and  $375 \text{ kg ha}^{-1}$  annually for a period of 15 years. These soils, together with adjacent unfertilised controls were sampled at 0-7.5 cm depth. Information on the Zn and Cd content of the fertiliser was again not available.
- (c) Whatatiri clay loam - was sampled from a market garden property near Pukekohe, Auckland. The fertilised soil had received  $1300 \text{ kg ha}^{-1}$  superphosphate annually for 15 years. The fertilised soil, along with unfertilised soil of the same type was sampled at 0-20 cm depth.

Amounts of  $\text{H}_2\text{O}$ -,  $\text{CaCl}_2$ -, and  $\text{CuCl}_2$ -extractable Zn and Cd and total Zn and Cd contents were measured for both unfertilised (control) and fertilised soils from each site using the method described below.

## 7.2 Methods for Determining Extractable and Total

### Soil Zn and Cd Contents

#### 7.2.1 Extractable Zn and Cd

A 5-g sample of soil was shaken with either 40 ml of deionised water,  $1 \times 10^{-2} \text{ M}$  calcium chloride or  $1 \times 10^{-2} \text{ M}$  copper chloride solution, in 50-ml polycarbonate centrifuge tubes. The extractions were carried out at

$23 \pm 2^{\circ}\text{C}$ , on an end-over-end shaker (40 r.p.m.) for 16 hr. The suspensions were centrifuged at 15,000 r.p.m. at  $23 \pm 2^{\circ}\text{C}$  in a Sorvall refrigerated supercentrifuge (Model RC2B) and the supernatants filtered through  $0.45 \mu\text{m}$  Millipore filters.

For those extractants that removed only small amounts of Zn and Cd, (viz.,  $\text{H}_2\text{O}$ -extractable and  $\text{CaCl}_2$ -extractable Zn, and  $\text{CuCl}_2$ -extractable Cd) the extracts were analysed for Zn and Cd content following concentration using the dithizone method described in Chapter 3.

Ca ions were used to extract Zn and Cd because, in addition to being a common soil cation, Ca ions are of the same charge as Zn and Cd ions, similar ionic radii, (i.e.,  $0.99\text{\AA}$  for Ca,  $0.74\text{\AA}$  for Zn, and  $0.97\text{\AA}$  for Cd) and show little tendency to form co-ordinate bonds (Cotton and Wilkinson, 1966). Therefore, if present in excess, the Ca ions would be expected to displace Zn and Cd ions that are non-specifically held by electrostatic attraction on soil surfaces. Cu ions, on the other hand, are known to form large numbers of complexes with ligands co-ordinated through oxygen atoms (Cotton and Wilkinson, 1966). If present in excess, Cu ions should displace Zn and Cd held by co-ordinate bonding. Thus, using these extractants, it should be possible then to determine whether fertilised soils showed any build-up of readily or potentially available Zn and Cd compared to respective control situations.

### 7.2.2 Total soil Zn and Cd contents

Total Zn and Cd contents of the three soils were determined using a modified lithium tetraborate fusion (Norrish and Hutton, 1969).

A 0.1-g sample of < 60 mesh soil was mixed with 0.71 g flux (60 parts  $\text{Li}_2\text{B}_4\text{O}_7$ , 10 parts  $\text{Li}_2\text{CO}_3$  and 1 part RbI). The mixture was fused in a platinum crucible, by heating, over an air/propane flame. The

fusion was continued until no black minerals remained visible in the melt. The crucible was then cooled, by removing from the flame, and gently agitated so as to form the contents into a bead as the mixture coalesced on cooling. Finally, the bead was dissolved in 50 ml of 1M HCl and made up to a final volume of 100 ml with deionised water. The total Zn and Cd contents were determined by A.A.S., preconcentrating where necessary.

### 7.3 Results and Discussion

The amounts of Zn and Cd, extracted by water,  $\text{CaCl}_2$ , and  $\text{CuCl}_2$ , and total amounts of Zn and Cd in the respective unfertilised and fertilised soils are shown in Tables 7.1 and 7.2.

For Papatotetoe silt loam a minor increase in total Zn content of the fertilised soil was noted (Table 7.1). However, no increases in  $\text{H}_2\text{O}$ -,  $\text{CaCl}_2$ - or  $\text{CuCl}_2$ -extractable Zn could be demonstrated. Small increases in  $\text{CuCl}_2$ -extractable Cd were measured, as was an increase in total Cd content (Table 7.2). The increases in measured Zn and Cd contents of soil fertilised with superphosphate compared to the control soil (unfertilised) may be attributed to the application of superphosphate containing Zn and Cd. The ratio of Zn:Cd was 578:1 for the unfertilised soil, and to 526:1 for the fertilised soil.

No significant increase in total or extractable Zn content was found for the Lismore silt loam samples at either fertiliser rate. Total Cd increased at both rates of fertiliser addition and as Cd increased between control and fertilised soils and Zn did not markedly increase, the Zn:Cd ratios decreased from 160:1 for the control to 70:1 for the soil fertilised at the lower rate and 80:1 at the higher rate of addition.

Application of  $1300 \text{ kg ha}^{-1}$  superphosphate fertiliser for 15 years

Table 7.1 H<sub>2</sub>O-extractable, CaCl<sub>2</sub>-extractable, CuCl<sub>2</sub>-extractable and total Zn contents of soils treated with long-term superphosphate additions

Soil	Depth (cm)	Total Superphosphate Applied (kg ha <sup>-1</sup> )	H <sub>2</sub> O- Extractable (μmol 100g <sup>-1</sup> )	Ca- Extractable (μmol 100g <sup>-1</sup> )	Cu- Extractable (μmol 100g <sup>-1</sup> )	Total (μmol 100g <sup>-1</sup> )
Papatoetoe silt loam						
Control	0-10	-	0.51	0.58	8.3	214
Fertilised	0-10	12,000	0.45	0.59	8.2	242
Whatatiri clay loam						
Control	0-20	-	0.09	0.31	8.4	219
Fertilised	0-20	19,500	0.09	0.18	7.4	225
Lismore silt loam						
Control	0-7.5	-	N.D.	0.13	3.0	122
Fertilised	0-7.5	2,835	0.04	0.09	3.0	124
Control	0-7.5	-	0.07	0.53	7.1	116
Fertilised	0.7.5	5,625	0.11	0.36	4.6	119

N.D. = not detectable. Average variation in replicates for total Zn measurements:  $\pm 1.8 \mu\text{mol Zn } 100\text{g}^{-1}$

Table 7.2 H<sub>2</sub>O-extractable, CaCl<sub>2</sub>-extractable, CuCl<sub>2</sub>-extractable and total Cd contents of soils treated with long-term superphosphate additions

Soil	Depth (cm)	Total Superphosphate Applied (kg ha <sup>-1</sup> )	H <sub>2</sub> O-Extractable (μmol 100g <sup>-1</sup> )	Ca-Extractable (μmol 100g <sup>-1</sup> )	Cu-Extractable (μmol 100g <sup>-1</sup> )	Total (μmol 100g <sup>-1</sup> )
Papatoetoe silt loam						
Control	0-10	-	N.D.	N.D.	0.20	0.37
Fertilised	0-10	12,000	N.D.	N.D.	0.27	0.46
Whatatiri clay loam						
Control	0-20	-	N.D.	N.D.	0.12	0.76
Fertilised	0-20	19,500	N.D.	N.D.	0.18	1.64
Lismore silt loam						
Control	0-7.5	-	N.D.	N.D.	0.11	0.74
Fertilised	0-7.5	2,835	N.D.	N.D.	0.17	1.78
Control	0-7.5	-	N.D.	N.D.	0.14	0.74
Fertilised	0-7.5	5,625	N.D.	N.D.	0.17	1.49

N.D. = not detectable. Average variation in replicates for total Cd measurements:  $\pm 0.15 \mu\text{mol Cd } 100\text{g}^{-1}$ .

to Whatatiri clay loam produced no major change in total Zn content, and no detectable increases in  $H_2O$ -,  $CaCl_2$ - or  $CuCl_2$ -extractable Zn.

However,  $CuCl_2$ -extractable Cd and total Cd contents increased in the fertilised soils, and because of this the Zn:Cd ratio narrowed from 304:1 for unfertilised soil to 137:1 for the fertilised soil.

The narrowing of the Zn:Cd ratios noted for all the fertilised soils is presumably attributable to the "enrichment" of soil Cd by the long-term addition of superphosphate fertiliser which often contains Zn:Cd ratios of around 11:1 (Swaine, 1962).

### 7.3.1 Measured and predicted increases in soil Zn and Cd, from superphosphate fertiliser addition

Increases in total soil Zn and Cd contents can be predicted for the particular fertiliser programmes operating at each of the sites used, if values for the Zn and Cd contents of superphosphate are assumed. The calculated total soil Zn and Cd contents are shown, together with the actual increases found for each soil, in Table 7.3. Assumed bulk densities of the soils were  $1000 \text{ kg m}^{-3}$  for Papatoetoe silt loam and Whatatiri clay loam and  $1200 \text{ kg m}^{-3}$  for Lismore silt loam.

Predictions were made to cover the range of Zn and Cd concentrations reported for superphosphate fertiliser made from Nauru Island rock phosphate, viz.,  $4.13\text{--}11.47 \mu\text{mol Zn g}^{-1}$  and  $0.18\text{--}1.46 \mu\text{mol Cd g}^{-1}$  (Swaine, 1962). This source was used in the calculations because, historically, most of the rock phosphate used for superphosphate manufacture in New Zealand came from Nauru Island.

For all three experimental sites, the measured increases in total Zn content of the fertilised soils were within the ranges predicted (Table 7.3). Thus the measured increases in total soil Zn contents could be adequately accounted for by the additions from superphosphate fertiliser.

Table 7.3 Comparison of measured and predicted increases in total Zn and Cd contents of soils due to long-term superphosphate fertiliser additions

Soil	Predicted increases in total Zn ( $\mu\text{mol Zn } 100\text{g}^{-1}$ )	Measured increase in total Zn ( $\mu\text{mol Zn } 100\text{g}^{-1}$ )	Predicted increases in total Cd ( $\mu\text{mol Cd } 100\text{g}^{-1}$ )	Measured increase in total Cd ( $\mu\text{mol Cd } 100\text{g}^{-1}$ )
Papatoetoe silt loam				
0-10 cm	9.9 - 27.5	28.0	0.43 - 1.12	0.09
Whatatiri clay loam				
0-20 cm	4.1 - 11.2	6.0	0.17 - 0.45	0.90
Lismore silt loam				
0-7.5 cm	1.3 - 3.6	2.0	0.06 - 0.15	1.04
	2.6 - 7.2	3.0	0.11 - 0.29	0.75

N.B. Predicted increases calculated for the depth to which each soil was sampled.

However, the predicted and measured increases in total soil Cd (Table 7.3) were not in such good agreement. For Whatatiri clay loam and for Lismore silt loam, the increases measured were greater than those predicted; a situation that could result from either (a) the use of superphosphate with a higher Cd content than allowed for in the calculations, (b) the use of higher actual rates of superphosphate than those specified or (c) the addition of Cd to the soil from sources other than superphosphate fertiliser. However, for Papatoetoe silt loam, increases in total Cd measured were less than those predicted. The most likely causes of this result would be either (a) the use of fertiliser with a lower Cd content than used in the calculations (b) the use of lower actual rates than specified or (c) the loss of Cd from the soil by plant uptake or leaching.

Previous workers (Schroeder and Balassa, 1963; Ozanne et al., 1965; Schroeder et al., 1967; Williams and David, 1973; Williams and David, 1976, Williams and David, 1976a) have measured increased soil Zn and Cd following superphosphate addition. Zn added to soil through superphosphate fertiliser can result in pasture growth responses (Ozanne et al., 1965) and in New Zealand, During (1972) suggests that such Zn may have prevented and even corrected incipient deficiencies in plants and animals, in recent times.

Since superphosphate fertilisers used in New Zealand probably contain similar amounts of Zn and Cd to the materials used by overseas workers (Walkley, 1940; Bingham, 1959; Swaine, 1962; Barrows, 1966), e.g., 0.77-21.87  $\mu\text{mol Zn g}^{-1}$  and 0.45-1.51  $\mu\text{mol Cd g}^{-1}$  (Swaine, 1962) they contribute some Zn and Cd to soils. The somewhat inconclusive results found in this study, particularly with respect to soil Cd, which contrast with overseas studies (Schroeder and Balassa, 1963; Schroeder

et al., 1967; Williams and David, 1973; Williams and David, 1976a) are probably explainable on the basis of higher levels of Cd in our control soils.

The reasons why our control soils have higher Cd levels are not readily apparent and this finding renders the detection of small increases in soil Cd more difficult than in situations of lower initial Cd contents. For example, in an Australian study, soils which had received from between 1000 and 4500 kg ha<sup>-1</sup> total superphosphate over a number of years showed 2 to 5-fold increases in HCl-extractable soil Cd (Williams and David, 1973). However, both the unfertilised and fertilised Australian soils had lower HCl-extractable soil Cd levels, than the total soil Cd levels measured in the unfertilised soils of the present study (HCl-extractable Cd was claimed to be almost equivalent to total Cd by Williams and David (1973)). In the present study, only 2-fold increases in total soil Cd were measured for fertilised soils.

The higher levels of Cd found in unfertilised soils in this study, coupled with the removals of Zn and Cd that occur in plant and animal products make for difficulty in the detection of small increases in soil Zn and Cd resulting from fertiliser use. It has been reported that Zn and Cd added to soils by superphosphate application appears to remain largely plant available (Ozanne et al., 1965; Williams and David, 1976; Williams and David, 1976a) and thus results in elevated plant concentrations of these cations (Schroeder and Balassa, 1963; Ozanne et al., 1965; Williams and David, 1973; Williams and David, 1976; Williams and David, 1976a).

The results of this study indicate that superphosphate additions could in effect offset any decline in soil Zn levels that accompany

intensive land-use practices. The situation with respect to Cd appears to be that accumulation, if occurring at all, is difficult to detect in fertilised New Zealand soils. At common rates of superphosphate used in this country, the accumulation of Cd is not readily measurable, at least under the conditions occurring at the three experimental sites used in this study. Longer term use of higher rates of fertiliser may increase the rate of accumulation of Zn and Cd, as would a change to fertiliser materials containing higher Zn and Cd contents.

## SUMMARY

The work presented in this thesis may be summarised as follows:

1. Literature relating to the biochemical significance of Zn and Cd, natural background levels of Zn and Cd in rocks and soils, and additions of Zn and Cd to soils from external sources was reviewed. The surface chemistry of soil components believed to be important in cation adsorption was examined and the adsorption of Zn and Cd by soils and soil components was considered in detail.
2. A technique involving dithizone/carbon tetrachloride for extracting and concentrating low amounts of Zn and Cd from solution was developed and evaluated for use in Zn and Cd adsorption studies and for determining extractable and total Zn and Cd levels in soils.
3. Certain soil properties of four New Zealand soils were determined in an attempt to relate their importance to Zn and Cd adsorption by the soils. There was no obvious relationships between the measured soil properties and adsorption of Zn and Cd by these soils.
4. Evaluation of the kinetics of Zn and Cd adsorption by soils indicated that the initial removal of Zn and Cd from solution was extremely rapid. At low levels of addition, removal of both Zn and Cd from solution was virtually complete within the first 12 hr of equilibration, but at high levels of addition the initial rapid removal was followed by a gradual, continuing removal from solution. Estimates of equilibrium Zn and Cd concentrations, obtained by extrapolation of reciprocal time plots for the relationship between solution concentrations of Zn and Cd to the value of  $\frac{1}{t} = 0$ , i.e.,  $t = \alpha$  were found to be unreliable.

5. In a time study of adsorption, 40-hr isotherms carried out in a matrix of  $3 \times 10^{-2}$  M NaCl over the concentration range 0-300  $\mu\text{mol Zn or Cd l}^{-1}$  for Makerua topsoil and Okaihau subsoil could be described by two Langmuir isotherms, as could the isotherms at 120, 144, and 192 hr. As the Langmuir constants obtained at each time were essentially the same, 40-hr isotherms were subsequently used in the study to approximate the equilibrium condition.

6. Isotherms (40 hr) for the adsorption of Zn and Cd by both topsoils and subsoils of Makerua, Egmont and Tokomaru soils were used to describe adsorption and obtain the appropriate Langmuir parameters. The isotherms were carried out over the concentration ranges of 0 - 800  $\mu\text{mol Zn l}^{-1}$  and 0 - 400  $\mu\text{mol Cd l}^{-1}$  in a matrix of  $3 \times 10^{-2}$  M NaCl. For all soils, adsorption was described by two Langmuir isotherms for both Zn and Cd. Determination of Langmuir constants for each region of adsorption showed that adsorption maxima within each region varied between soils, and adsorption maxima for Zn were generally higher than Cd for all soils in both regions. The free energies of adsorption of both Zn and Cd were higher for region I than region II, suggesting that Zn and Cd adsorbed in region I is more tightly held than in region II, and thus by different mechanisms. The mean free energies of Zn and Cd adsorption, however, were not significantly different within region I nor within region II for all soils, suggesting that Zn and Cd may be held by two similar mechanisms.

7. Isotherms (40 hr) for the adsorption of Zn and Cd by synthetic Fe gel and allophane could also be described by two distinct Langmuir equations. For Fe gel the free energies of adsorption for each adsorption region were very similar to those obtained for soils. Hence,

it was concluded that Fe gel may be a suitable model for Zn and Cd adsorption by soils. Although Zn and Cd adsorption by allophane was described by two Langmuir equations, the Langmuir constants were not the same as those obtained for soils.

8. Isotherms (40 hr) for Zn and Cd adsorption by Fe gel carried out at different pH values showed that although the actual amounts of Zn and Cd adsorbed increased with increasing pH, the free energies of adsorption were similar at all pH values. It was concluded that pH affected the amount of Zn and Cd adsorbed but not the mechanisms of bonding.

9. Adsorption of Zn and Cd by Fe gel was found to increase as pH increased from pH 5.0 to 7.0, presumably due to increasing negative charge on the surface, with a similar pH response for adsorption of Zn and Cd at both low and high equilibrium concentrations. However, the  $pH_{50}$  values (the pH at which 50% adsorption of initial amounts occur) were higher for Cd than those for Zn. As Zn has a higher electronegativity than Cd, the  $pH_{50}$  values for Zn might be expected to occur at a lower value than that for Cd.

10. The indication that two mechanisms operated for both Zn and Cd adsorption (Langmuir adsorption isotherm studies) was further investigated using proton release, isotopic exchangeability and desorption studies.

The number of protons released for each Zn ion adsorbed (mole ratio) for Zn ranged between 1.31 and 1.67 with no obvious trend noted with either increasing amounts of Zn adsorbed ( $2.1$  to  $55.3 \mu\text{mol g}^{-1}$ ) or increasing pH (pH 6.4 to pH 6.8). By contrast, for Cd the mole ratio

increased (0.80 to 1.12) with increasing amounts of Cd adsorbed (0.80 to 1.12) with increasing amounts of Cd adsorbed (0.8 to 17.6  $\mu\text{mol Cd g}^{-1}$ ) and with pH, i.e., 0.80 to 1.12 (pH 6.4) and 1.05 to 1.43 (pH 6.8). These mole ratios were determined using a pH-stat and auto-titrator.

The exchangeability of Zn was similar at all levels of Zn adsorbed, but did decrease from 58% down to 27% as pH increased from pH 5.85 to 6.65, indicating an increased proportion of Zn which is more tightly bound. Although cadmium was less exchangeable at low levels of adsorbed Cd (55 - 76%) than at higher levels (80 - 85%), this cation was more exchangeable than Zn at equivalent pH values even though Cd was present at much lower surface coverages. This indicated that a greater proportion of adsorbed Cd was less tightly held than was the case for Zn.

Detailed investigations showed that after desorption of Zn with calcium and copper ions, a proportion of Zn (12 - 24%) was retained by the surfaces. This is further evidence for the presence of at least two adsorption mechanisms for Zn. Exchange and desorption data suggested that less Zn was adsorbed in region II than was estimated using the Langmuir equation. This was especially true at the higher loadings of Zn.

11. Based on the results of Langmuir isotherm and proton release data, as well as isotopic exchangeability and desorption studies, a two-region model for Zn and Cd adsorption was proposed. Adsorption in region I was considered to involve exchange of Zn and Cd ions for protons with the aquo-,  $-\text{OH}_2^+$ , or hydroxyl,  $-\text{OH}$ , group on the Fe gel surface resulting in the formation of a bidentate complex and release of two protons. Adsorption in region II probably involves the adsorption of monovalent complex ions of Zn and Cd, e.g.,  $\text{ZnCl}^+$  or  $\text{CdCl}^+$ , forming a monodentate

complex on the gel surface and release of one proton. No explanation has been forwarded for mole ratios of less than unity found for Cd. The greater exchangeability and fewer protons released per mole of Cd adsorbed compared to Zn can be explained by a larger proportion of Cd being held by the weaker monodentate bonds, especially as monovalent  $\text{CdCl}^+$  is relatively more stable than  $\text{ZnCl}^+$ , and constitutes a greater fraction of the total soluble species.

12. The uptake of Zn and Cd added to Fe gel, synthetic goethite, and ground natural goethite was initially rapid, followed by a slow continuing uptake of Zn and Cd from 24 to 192 hr by natural goethite and to a very much lesser extent by synthetic goethite and Fe gel. Fe gel and synthetic goethite both tended towards an equilibrium solution concentration within 2 hr of equilibration with added Zn and Cd, whereas ground natural goethite had not attained equilibrium even after 192 hr. Amounts of Zn and Cd desorbed from Fe gel and synthetic goethite by  $\text{CaCl}_2$  and  $\text{CuCl}_2$  solutions showed little change after 24 hr, but for ground natural goethite, a decrease in the extent of Zn and Cd desorption occurred up to 192 hr.

13. Time-dependent adsorption of Zn and Cd and the decrease in the extent of Zn and Cd desorption with time was evident with ground natural goethite but not with Fe gel or synthetic goethite. This time-dependent adsorption by ground goethite is thought to be due to a slow diffusion of Zn and Cd into defects in the crystalline structure of natural goethite developed or accentuated during grinding. Hence, 'occlusion' or absorption of Zn and Cd does not appear to be a significant sorption process for hydrous ferric oxides.

14. For three soils which had received relatively high annual additions

of superphosphate fertiliser for periods ranging from 15 to 30 years, increases in extractable and total Zn and Cd were barely detectable. Increases in total Zn measured, agreed with predicted increases in Zn calculated on the basis of the known fertiliser history for each soil. Measured increases in total Cd did not agree well with the predicted increases.

## BIBLIOGRAPHY

## BIBLIOGRAPHY

- Allaway, W.H. 1968. Agronomic controls over the environmental cycling of trace elements. *Advances in Agronomy* 20: 235-274.
- Aveyard, R.; Haydon, D.A. 1973. An introduction to the principles of surface chemistry. Cambridge University Press, London. 232 p.
- Barnard, A.K. 1965. Theoretical basis of inorganic chemistry. McGraw-Hill, London. 372 p.
- Barrow, N.J. 1978. The description of phosphate adsorption curves. *Journal of Soil Science* 29: 447-462.
- Barrows, H.L. 1966. Soil pollution and its influence on plant quality. *Journal of Soil and Water Conservation* 21: 211-216.
- Barshad, I. 1955. Chemistry of soil development, p.1-70. In Bear, F.E. (Ed) *Chemistry of the Soil*. Reinhold, New York.
- Bar-Yosef, B.; Posner, A.M.; Quirk, J.P. 1975. Zinc adsorption and diffusion in goethite pastes. *Journal of Soil Science* 26: 1-21.
- Bear, F.E. (Ed). 1964. *Chemistry of the soil*. 2nd edition. American Chemical Society Monograph, Reinhold Publishing Corporation, Holland. 515 p.
- Beavington, F. 1973. Contamination of soil with zinc, copper, lead and cadmium in the Wollongong city area. *Australian Journal of Soil Research* 11: 27-31.
- Beavington, F. 1975. Some aspects of contamination of herbage with copper, zinc and iron. *Environmental Pollution* 8: 65-71.
- Berrow, M.L.; Webber, J. 1972. Trace elements in sewage sludges. *Journal of the Science of Food and Agriculture* 23: 93-100.
- Bingham, F.T. 1959. Micronutrient content of phosphorus fertilisers. *Soil Science* 88: 7-10.
- Bingham, F.T.; Page, A.L.; Sims, J.R. 1964. Retention of copper and zinc by H-montmorillonite. *Soil Science Society of America Proceedings* 28: 351-354.
- Biswas, T.D.; Gawande, S.P. 1964. Relation of manganese in genesis of catenary soils. *Indian Society of Soil Science Journal* 12: 261-267.
- Bolland, M.D.A.; Posner, A.M.; Quirk, J.P. 1977. Zinc adsorption by goethite in the absence and presence of phosphate. *Australian Journal of Soil Research* 15: 279-286.

- Bowden, J.W.; Bolland, M.D.A.; Posner, A.M.; Quirk, J.P. 1973. Generalised model for anion and cation adsorption at oxide surfaces. *Nature (Physical Science)* 245: 81-83.
- Bowden, J.W. 1974. Models for ion adsorption on mineral surfaces. Ph.D. Thesis, University of Western Australia. As cited in Bar-Yosef B.; Posner, A.M.; Quirk, J.P. 1975. *Journal of Soil Science* 26: 1-21.
- Bowden, J.W., Posner, A.M.; Quirk, J.P. 1974. A model for ion adsorption on variable charge surfaces. *Transactions of the 10th International Congress of Soil Science, Moscow II*: 29-30.
- Bowden, J.W.; Posner, A.M.; Quirk, J.P. 1977. Ionic adsorption on variable charge mineral surfaces. Theoretical charge development and titration curves. *Australian Journal of Soil Research* 15: 121-136.
- Bower, C.A.; Truog, E. 1941. Base exchange capacity determination as influenced by nature of cation employed and formation of basic exchange salts. *Soil Science Society of America Proceedings* 5: 86-89.
- Bradford, G.R.; Page, A.L.; Lund, L.J.; Olmstead, W. 1975. Trace element concentration of sewage treatment plant effluents and sludges; their interactions with soils and uptake by plants. *Journal of Environmental Quality* 4: 123-127.
- Broadbent, F.E. p.1398-1400. In Black, C.A. (Ed). 1965. *Methods of soil analysis, Part 2. Agronomy* 9: 1572 p.
- Brown, L.C.; Viets, F.G.; Crawford, C.L. 1954. Effect of phosphate fertiliser on zinc nutrition of field beans. *Soil Science* 78: 1-7.
- Brooks, R.R.; Ahrens, L.H.; Taylor, S.R. 1960. The determination of trace elements in silicate rocks by a combined spectrochemical-anion exchange technique. *Geochimica et Cosmochimica Acta* 18: 162.
- Brooks, R.R.; Presley, B.J.; Kaplan, I.R. 1967. APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic absorption spectrophotometry. *Talanta* 14: 809-816.
- Brown, G. (Ed). 1961. *The X-ray diffraction and crystal structures of clay minerals. Mineralogical Society (London)*. 544 p.
- Brunauer, S.; Copeland, L.E.; Kantro, D.L. 1967. The Langmuir and B.E.T. theories. In *The gas-solid interface, Vol. 1*, E.A. Flood (Ed): 77-85. Marcel Dekker, New York.
- Carroll, D. 1958. Role of clay minerals in the transportation of iron. *Geochimica et Cosmochimica Acta* 14: 1-28.
- Cartwright, B.; Merry, R.H.; Tiller, K.G. 1977. Heavy metal contamination of soils around a lead smelter at Port Pirie, South Australia. *Australian Journal of Soil Research* 15: 69-81.
- Chapman, D.L. 1913. A contribution to the theory of electrocapillarity. *Philosophical Magazine* 25: 475-481.

- Chatterjee, R.K. 1974. Effect of zinc treatment of ammonia adsorption capacity and adsorption properties in binary mixtures of colloidal clays. Transactions of the 10th International Congress of Soil Science, Moscow II: 365-371.
- Clark, F.W.; Washington, H.S. 1974. The composition of the earth's crust. United States Geological Survey Professional Paper 127: 112 p.
- Clark, L.J.; Hill, W.L. 1958. Occurrence of manganese, copper, zinc, molybdenum and cobalt in phosphate fertilisers and sewage sludges. Journal of the Association of Official Analytical Chemists 41: 631-637.
- Cotton, F.A.; Wilkinson, G. 1966. Advanced inorganic chemistry. 2nd edition. John Wiley and Sons, London. 1136 p.
- Cotzias, G.C.; Borg, D.C.; Selleck, B. 1961. Virtual absence of turnover in cadmium metabolism:  $Cd^{109}$  studies in the mouse. American Journal of Physiology 201: 927-930.
- Daniels, R.B.; Brasfield, J.F.; Riecken, F.F. 1962. Distribution of sodium hydrosulphite extractable manganese in some Iowa soil profiles. Soil Science Society of America Proceedings 26: 75-78.
- Day, F.H. 1963. The chemical elements in nature. G.G. Harrap and Co. Ltd., London. 372 p.
- Day, P.R. p.552-562. In Black, C.A. (Ed). 1965. Methods of soil analysis, Part 1. Agronomy 9: 770 p.
- De Haan, F.A.M.; Zwerman, P.J. 1976. Pollution of soil, p.192-264. In Bolt, G.H.; Bruggenwert, M.G.M. (Eds). Soil Chemistry. Elsevier Scientific Publishing Company, Amsterdam.
- DeMumbrum, L.E., Jackson, M.L. 1956. Infra-red absorption evidence on exchange reaction mechanism of copper and zinc ions with layer silicate clays and peat. Soil Science Society of America Proceedings 20: 334-338.
- de Vries, M.P.C.; Tiller, K.G.; Beckwith, R.S. 1975. Sources of error in the determination of cadmium and lead in plant material by atomic absorption. Communications in Soil Science and Plant Analysis 6: 629-640.
- During, C. 1972. Fertilisers and soils in New Zealand farming. 2nd edition. N.Z. Department of Agriculture Bulletin No.409. 312 p.
- Elgabaly, M.M. 1950. Mechanism of zinc fixation by colloidal clays and related minerals. Soil Science 69: 167-174.
- Elgabaly, M.M.; Jenny, H. 1943. Cation and anion interchange with zinc montmorillonite clays. Journal of Physical Chemistry 47: 399-408.

- Ellis, B.G.; Knezek, B.D. 1972. Adsorption reactions of micronutrients in soils, p.59-78. In Mortvedt, J.J., Giordano, P.M., Lindsay, W.L. (Eds), *Micronutrients in Agriculture*. Soil Science Society of America Incorporated, Madison, Wisconsin, U.S.A. 66 p.
- Fieldes, M.; Swindale, L.D. 1954. Chemical weathering of silicates in soil formation. *N.Z. Journal of Science and Technology* 50: 140-154.
- Fleischer, M.; Sarofim, A.F.; Fassett, D.W.; Hammond, P.; Shacklette, H.T.; Nisbet, I.C.T.; Espstein, S. 1974. Environmental impact of cadmium: A review by panel on hazardous trace substances. *Environmental Health Perspective* 7: 253-323.
- Forbes, E.A.; Posner, A.M.; Quirk, J.P. 1976. The specific adsorption of divalent cadmium, cobalt, copper, lead and zinc on goethite. *Journal of Soil Science* 27: 154-166.
- Freundlich, H. 1926. *Colloid and capillary chemistry*. Translated from the 3rd German edition by H. Stafford Hatfield, Methuen and Co. Ltd., London.
- Furr, A.K.; Lawrence, A.W.; Tong, S.C.S.; Grandolfo, M.C.; Hofstader, R.A.; Bache, C.A.; Gutenmann, W.H.; Lisk, D.J. 1976. Multi-element and chlorinated hydrocarbon analyses of municipal sewage sludges of American cities. *Environmental Science and Technology* 10: 683-687.
- Gadde, R.R.; Laitinen, H.A. 1974. Studies of heavy metal adsorption by hydrous iron and manganese oxides. *Analytical Chemistry* 46: 2022-2026.
- Gajan, R.J.; Gould, J.H.; Watts, J.O.; Fiorino, J.A. 1973. Collaborative study of a method for atomic absorption spectrophotometric and polarographic determination of cadmium in food. *Journal of the Association of Official Analytical Chemists* 56: 876-881.
- Garcia-Miragaya, J.; Page, A.L. 1976. Influence of ionic strength and inorganic complex formation on sorption of trace amounts of cadmium by montmorillonite. *Soil Science Society of America Journal* 40: 658-663.
- Giles, C.J.; MacEwan, T.H.; Nakhwa, S.N.; Smith, D. 1960. Studies in Adsorption, Part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurements of specific surface areas of solids. *Journal of the Chemical Society* 3: 3973-3993.
- Gilkes, R.J.; Young, R.C.; Quirk, J.P. 1975. Leaching of copper and zinc from trace element superphosphate. *Australian Journal of Soil Research* 13: 33-41.
- Giordano, P.M.; Mortvedt, J.J.; Mays, D.A. 1975. Effect of municipal wastes on crop yields and uptake of heavy metals. *Journal of Soil Research* 13: 33-41.
- Goldschmidt, V.M. 1958. Group IIB: Zinc, p. 260-267. In *Geochemistry*. Oxford University Press, London.

- Goldschmidt, V.M. 1958. Group IIB: Cadmium, p.268-273. In Geochemistry. Oxford University Press, London.
- Gouy, G. 1910. Sur la constitution de la charge electrique a la surface d'un electrolyte. Annales Physique (Paris) Serie 4, 9: 457-468.
- Grace, N.D. 1972. Observations on plasma zinc levels in sheep grazing New Zealand pastures. N.Z. Journal of Agricultural Research 15: 284-288.
- Graham, D. 1953. The characterisation of physical adsorption systems I. The equilibrium function and standard free energy of sorption. Journal of Physical Chemistry 57: 665-669.
- Grahame, D.C. 1947. The electrical double layer and the theory of electrocapillarity. Chemical Reviews 41: 441-501.
- Hahne, H.C.H.; Krootje, W. 1973. Significance of pH and chloride concentration on behaviour of heavy metal pollutants; Mercury (II), cadmium (II), zinc (II) and lead (II). Journal of Environmental Quality 2: 444-450.
- Helmholtz, 1897 as cited in Bear, F.E. (Ed). Chemistry of the soil. Reinhold Publishing Corporation, New York. 515 p.
- Hibbard, P.L. 1940. A soil zinc survey in California. Soil Science 49: 63-72.
- Hibbard, P.L. 1940a. The chemical status of zinc in the soil with methods of analysis. Hilgardia 13: 1-29.
- Hinesly, T.D.; Jones, R.L.; Ziegler, E.L.; Tyler, J.J. 1977. Effects of annual and accumulative applications of sewage sludges on assimilation of zinc and cadmium by corn (Zea mays). Environmental Science and Technology 11: 182-188.
- Hingston, F.J. 1970. Specific adsorption of anions on goethite and gibbsite. Ph.D. thesis, University of Western Australia. As cited in Bowden, J.W.; Bolland, M.D.A.; Posner, A.M.; Quirk, J.P. 1973. Nature (Physical Science) 245: 81-83.
- Hingston, F.J.; Posner, A.M.; Quirk, J.P. 1967. Specific adsorption of anions. Nature (London) 215: 1459-1461.
- Hope, G.D. 1977. Interaction of molybdate and phosphate with soils. Ph.D. Thesis, Massey University. 258 p.
- Horne, R.A.; Holm, R.H.; Meyers, M.D. 1957. The adsorption of zinc (II) on anion-exchange resins, II. Stoichiometry, thermodynamics, loading studies, Dowex-2 absorption and factors influencing the rate of the adsorption process. Journal of Physical Chemistry 61: 1655-1661.
- Huang, C.P. 1975. Adsorption of phosphate at the hydrous  $Al_2O_3$ -electrolyte interface. Journal of Colloid Interface Science 53: 178-186.

- Hunter, R.J.; Wright, H.J.L. 1971. The dependence of electrokinetic potential on concentration of the electrolyte. *Journal of Colloid Interface Science* 37: 564-580.
- Irish, D.E.; McCarroll, B.; Young, T.F. 1963. Raman study of zinc chloride solutions. *Journal of Chemical Physics* 39: 3436-3444.
- Jackson, M.L. 1956. *Soil chemical analysis - Advanced course*. 5th Printing. Published by Author, Department of Soil Science, University of Wisconsin, Madison, U.S.A.
- James, R.D.; Healy, T.W. 1972. Adsorption of hydrolysable metal ions at the oxide-water interface, III. A thermodynamic model of adsorption. *Journal of Colloid Interface Science* 40: 65-81.
- Jenne, E.A. 1968. Controls on manganese, iron, cobalt, nickel, copper and zinc concentrations in soils and waters: The significant role of manganese and iron oxides, p. 337-387. In *Trace inorganics in water*. Advances in Chemistry Series 1 No. 73, American Chemical Society, Washington D.C., U.S.A. 396 p.
- Jensen, H.L.; Lamm, C.G. 1959. On the zinc content of Danish soils. *Acta Agriculturae Scandinavica* 11: 63-81.
- John, M.K. 1971. Influence of soil characteristics on adsorption and desorption of cadmium. *Environmental Letters* 2: 173-179.
- John, M.K. 1972. Uptake of soil applied cadmium and its distribution in radishes. *Canadian Journal of Plant Science* 52: 715-719.
- Jones, R.L.; Hinesly, Y.D.; Ziegler, E.L. 1973. Cadmium content of soybeans grown in sewage sludge amended soil. *Journal of Environmental Quality* 2: 351-353.
- Kalbasi, M.; Racz, G.J.; Loewen-Rudgers, L.A. 1978. Mechanisms of adsorption by iron and aluminium oxides. *Soil Science* 125: 146-150.
- Keilin, D.; Mann, T. 1940. Carbonic anhydrase purification and nature of enzyme. *Biochemical Journal* 34: 1163.
- Kelly, J.B.; Midgeley, A.R. 1943. Phosphate fixation - an exchange of phosphate and hydroxyl ions. *Soil Science* 55: 167-176.
- Kinniburgh, D.G.; Syers, J.K.; Jackson, M.L. 1975. Specific adsorption of trace amounts of calcium and strontium by hydrous oxides of iron and aluminium. *Soil Science Society of America Proceedings* 39: 464-470.
- Kinniburgh, D.G.; Jackson, M.L.; Syers, J.K. 1976. Adsorption of alkaline earth, transition and heavy metal cations by hydrous oxide gels of iron and aluminium. *Soil Science Society of America Journal* 40: 796-799.
- Kipling, J.J. 1965. *Adsorption from solutions of non-electrolytes*. Academic Press, London. 328 p.

- Kivalo, P.; Luoto, R. 1957. p.163. As cited in Sillen, L.G.; Martell, A.E. 1964. Stability constants of metal ion complexes. Special Publication No. 17. The Chemical Society, London. 754 p.
- Krauskopf, K.B. 1956. Factors controlling the concentrations of thirteen rare metals in sea-water. *Geochimica et Cosmochimica Acta* 9: 1-26.
- Krauskopf, K.B. 1972. VII: Zinc, p.31-33. In Mortvedt, J.J.; Giordano, P.M.; Lindsay, W.L. (Eds), *Micronutrients in Agriculture*. Soil Science Society of America Incorporated, Madison, Wisconsin, U.S.A. 666 p.
- Lagerwerff, J.V. 1967. Heavy metal contamination of soils. P.343-353. In Brady, N.C. (Ed), *Agriculture and the quality of our environment*. American Association for the Advance of Science, Publication No. 85. 460 p.
- Lagerwerff, J.V. 1971. Uptake of cadmium, lead and zinc by radish from soil and air. *Soil Science* 111: 129-132.
- Lagerwerff, J.V. 1972. IV: Cadmium, p.619-639. In Mortvedt, J.J.; Giordano, P.M.; Lindsay, W.L. (Eds), *Micronutrients in Agriculture*. Soil Science Society of America Incorporated, Madison, Wisconsin, U.S.A. 666 p.
- Lagerwerff, J.V.; Specht, A.W. 1970. Contamination of roadside soil and vegetation with cadmium, nickel, lead and zinc. *Environmental Science and Technology* 4: 583-585.
- Langmuir, I. 1918. The adsorption of gases on plain surfaces of glass, mica and platinum. *Journal of the American Chemical Society* 40: 1361-1403.
- Levi-Minzi, R.; Soldatini, G.F.; Riffaldi, R. 1976. Cadmium adsorption by soils. *Journal of Soil Science* 27: 10-15.
- Levine, S.; Smith, A.L. 1971. Theory of the differential capacity of the oxide/aqueous interface. *Discussions of the Faraday Society* 52: 290-301.
- Lindsay, W.L. 1972. Zinc in soils and plant nutrition. *Advances in Agronomy* 24: 147-186.
- Lindsay, W.L. 1972a. Inorganic phase equilibria of micronutrients in soils. p.41-58. In Mortvedt, J.J.; Giordano, P.M.; Lindsay, W.L. (Eds), *Micronutrients in Agriculture*. Soil Science Society of America Incorporated, Madison, Wisconsin, U.S.A. 666 p.
- Loganathan, P.; Burau, R.G.; Fuerstenau, D.W. 1977. Influence of pH on the sorption of cobalt (II), zinc (II) and calcium (II) by a hydrous manganese oxide. *Soil Science Society of America Journal* 41: 57-62.

- Lundegårdh, P.H. 1947. Some aspects to the determination and distribution of zinc. *Lantbrukshögskolans Annaler* 15: 1-36.  
As cited in Whitton, J.S.; Wells, N. 1974. A pedochemical survey, 2. Zinc. *N.Z. Journal of Science* 17: 351-356.
- McLaughlin, J.R.; Ryden, J.C.; Syers, J.K. 1977. Development and evaluation of a kinetic model to describe phosphate sorption by hydrous ferric oxide gel. *Geoderma* 18: 295-307.
- Maes, A.; Cremers, A. 1975. Cation exchange hysteresis in montmorillonite. A pH-dependent effect. *Soil Science* 119: 198-202.
- Malin, H.M. 1971. Metal focus shifts to cadmium. *Environmental Science and Technology* 5: 754-755.
- Mann, P.J.G.; Quastel, J.A. 1946. Manganese metabolism in soils. *Nature (London)* 158: 154-156.
- Marcias, F.D. 1973. Copper and zinc status in pasture soils of Salamanca, Spain. *Soil Science* 115: 276-283.
- Mason, B. 1966. Principles of geochemistry. 3rd edition. J. Wiley and Sons Incorporated, New York. 310 p.
- Masui, J.; Shoji, S.; Minami, K. 1972. Copper and zinc in volcanic ash soils. *Soil Science and Plant Nutrition* 18: 31-37.
- Mattingly, G.E.G. 1975. Labile phosphate in soils. *Soil Science* 119: 369-375.
- Mattson, S.; Alvsaker, E.; Koulter-Andersson, E.; Barkoff, E.; Vahtras, K. 1950. Phosphate relationships of soil and plant, VI. The salt effect on phosphate solubility in pedalfer soils. *Lantbrukshögskolans Annaler* 17: 141-160.
- Mays, D.A.; Terman, G.L.; Duggan, J.C. 1973. Municipal compost: Effects on crop yields and soil properties. *Journal of Environmental Quality* 2: 89-92.
- Melsted, S.W. 1973. Proceedings of the joint conference on recycling municipal sludges and effluents on land. Nature Association of the State University and Land-Grant College, Washington D.C. p. 121-128. As cited in Hinesly, T.D.; Jones, R.L.; Ziegler, E.L.; Tyler, J.J. 1977. *Environmental Science and Technology* 11: 182-188.
- Metson, A.J. 1956. Methods of chemical analysis for soil survey samples. *N.Z. Soil Bureau Bulletin* 12: 104-105.
- Mitchell, B.D.; Farmer, V.C.; McHardy, W.J. 1964. Amorphous inorganic materials in soils. *Advances in Agronomy* 16: 327-383.
- Moore, W.J. 1962. Physical Chemistry. 4th edition. Longmans Green and Co. Ltd., London. 844 p.
- Morrison, G.H.; Freisher, H. 1957. Solvent extraction in analytical chemistry. John Wiley and Sons, New York. 269 p.

- Mortvedt, J.J.; Giordano, P.M. 1975. Response of corn to zinc and chromium in municipal wastes applied to soils. *Journal of Environmental Quality* 4: 170-173.
- Mulford, C.E. 1966. Solvent extraction techniques for atomic absorption spectroscopy. *Atomic Absorption Newsletter* 5: 88-89.
- Munro, D.C. 1968. Effects of acidity and extraction ratio in a solvent extraction procedure for atomic absorption flame spectroscopy 22: 199-200.
- Navrot, J.; Singer, A.; Banin, A. 1978. Adsorption of cadmium and its exchange characteristics in some Israeli soils. *Journal of Soil Science* 29: 501-511.
- Nelson, J.L.; Melsted, S.W. 1955. The chemistry of zinc added to soils and clays. *Soil Science Society of America Proceedings* 19: 439-443.
- New Zealand Soil Bureau. 1954. General Survey of the Soils of the North Island, New Zealand. *N.Z. Soil Bureau Bulletin* 5: 140-141.
- New Zealand Soil Bureau. 1968. Soils of New Zealand, Part 3. *N.Z. Soil Bureau Bulletin* 26: 82-83, 106-107.
- New Zealand Soil Bureau. 1973. Maps of parent rocks of New Zealand soils 1:1,000,000. *N.Z. Soil Survey, Report* 5.
- Norrish, K.; Hutton, J.T. 1969. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochimica et Cosmochimica Acta* 33: 431-453.
- Oertel, A.C.; Stace, H.C.T. 1947. A spectrochemical survey of some phosphate rocks and superphosphates :1. Qualitative. *Journal for the Commonwealth Scientific and Industrial Research Organisation, Australia* 20: 110-203.
- Øien, A.; Gjerdingen, K. 1977. Determination of cadmium and lead in soils by means of solvent extraction and atomic absorption. *Acta Agriculturae Scandinavica* 27: 67-70.
- Onoda, G.Y.; de Bruyn, P.L. 1966. Proton adsorption at the ferric oxide-aqueous solution interface. I. A kinetic study of adsorption. *Surface Science* 4: 48-63.
- Ozanne, P.G.; Shaw, T.C.; Kirton, D.J. 1965. Pasture response to traces of zinc in phosphate fertilisers. *Australian Journal of Experimental Agriculture and Animal Husbandry* 5: 29-33.
- Page, A.L.; Bingham, F.T.; Nelson, C. 1972. Cadmium adsorption and growth of various plant species as influenced by solution cadmium concentration. *Journal of Environmental Quality* 1: 288-291.
- Parfitt, R.L.; Farmer, V.C.; Russell, J.D. 1977. Adsorption on hydrous oxides I. Oxalate and benzoate on goethite. *Journal of Soil Science* 28: 24-39.

- Parfitt, R.L.; Frazer, A.R.; Russell, J.D.; Farmer, V.C. 1977a. Adsorption on hydrous oxides II. Oxalate, benzoate and phosphate on gibbsite. *Journal of Soil Science* 28: 40-47.
- Parfitt, R.L.; Russell, J.D. 1977. Adsorption on hydrous oxides IV. Mechanisms of adsorption of various ions on goethite. *Journal of Soil Science*. 28: 297-305.
- Parisi, A.F.; Vallee, B.T. 1969. Zinc metalloenzymes: Characteristics and significance in biology and medicine. *American Journal of Clinical Nutrition* 22: 1222-1239.
- Parks, G.A. 1965. The isoelectric points of solid oxides, solid hydroxides and aqueous hydroxo-complex systems. *Chemical Reviews* 65: 177-198.
- Parks, G.A. 1967. Aqueous surface chemistry of oxides and complex minerals. *Advances in Chemistry Series* 67: 121.
- Parks, G.A.; de Bruyn, P.L. 1962. The zero point of charge of oxides. *Journal of Physical Chemistry* 66: 967-973.
- Pollok, J.A. 1975. A comparative study of certain New Zealand and German soils formed from loess. Ph.D. Thesis, University of Bonn. 312 p.
- Price, C.A.; Clark, H.E.; Funkhouser, E.A. 1972. Functions of micro-nutrients in plants. p. 231-242. In Mortvedt, J.J.; Giordano, P.M.; Lindsay, W.L. (Eds), *Micronutrients in Agriculture*. Soil Science Society of America Incorporated, Madison, Wisconsin, U.S.A. 666 p.
- Purves, D. 1972. Consequences of trace element contamination of soils. *Environmental Pollution* 3: 17-24.
- Quin, B.F.; Syers, J.K. 1978. Surface irrigation of pasture treated with sewage effluent, III. Heavy metal content of sewage effluent, sludge, soil and pasture. *N.Z. Journal of Agricultural Research* 21: 435-442.
- Quirk, J.P.; Posner, A.M. 1975. Trace element adsorption by soil minerals. p.95-107. In Nicholas, D.J.D.; Egan, A.R. (Eds), *Trace elements in Soil-Plant-Animal Systems*. Academic Press, New York. 417 p.
- Raulin, J. 1869. *Études cliniques sur la végétation*. *Annales Scientifique Natural Botanique Biologic Végétale* 11: 93. As cited in Parisi, A.F.; Vallee, B.L. 1969. *American Journal of Clinical Nutrition* 22: 1222-1239.
- Reddy, M.R.; Perkins, H.F. 1974. Fixation of zinc by clay minerals. *Soil Science Society of America Proceedings* 38: 229-231.
- Russell, E.W. 1973. *Soil conditions and plant growth*. 10th edition. Longmans Green and Co. Ltd., London. 849 p.

- Ryden, J.C. 1975. The reactions and mechanisms of inorganic phosphate sorption by soils. Ph.D. Thesis, Massey University. 171 p.
- Ryden, J.C.; McLaughlin, J.R.; Syers, J.K. 1977. Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel. *Journal of Soil Science* 28: 72-92.
- Ryden, J.C.; McLaughlin, J.R.; Syers, J.K. 1977a. Time-dependent sorption of phosphate by soils and hydrous ferric oxides. *Journal of Soil Science* 28: 585-595.
- Ryden, J.C.; Syers, J.K. 1975. Rationalisation of ionic strength and cation effects on phosphate sorption by soils. *Journal of Soil Science* 26: 395-406.
- Sachdev, S.L.; West, P.W. 1970. Concentration of trace metals by solvent extraction and their determination by atomic absorption spectrophotometry. *Environmental Science and Technology* 4: 749-751.
- Saeed, M.; Fox, R.L. 1978. Influence of residual phosphate fertiliser on labile and extractable zinc in Hawaiian soils. *Communications in Soil and Plant Analysis* 9: 685-698.
- Sandell, E.B. 1959. *Colorimetric determination of traces of metals*. Interscience Publishers, New York. 1032p.
- Sandell, E.B.; Goldich, S.S. 1943. The rare metallic constituents of some American igneous rocks. *Journal of Geology* 51: 99-115, 167-189.
- Scott, M.L. 1972. Trace elements in animal nutrition. p.555-591. In Mortvedt, J.J.; Giordano, P.M.; Lindsay, W.L. (Eds). *Micro-nutrients in Agriculture*. Soil Science Society of America Incorporated, Madison, Wisconsin, U.S.A. 666 p.
- Schroeder, H.A.; Balassa, J.J. 1961. Abnormal trace metals in man : Cadmium. *Journal of Chronic Diseases* 14: 236.
- Schroeder, H.A.; Balassa, J.J. 1963. Cadmium : Uptake by vegetables from superphosphate in soil. *Science* 140: 819-820.
- Schroeder, H.A.; Nason, A.P.; Tipton, I.H.; Balassa, J.J. 1967. Essential trace metals in man : Zinc in relation to environmental cadmium. *Journal of Chronic Diseases* 20: 179-210.
- Shah Singh S. 1979. Sorption and release of cadmium in some Canadian soils. *Canadian Journal of Soil Science* 59: 119-130.
- Shukla, U.C.; Mittal, S.B. 1979. Characterisation of zinc adsorption in some soils of India. *Soil Science Society of America Journal* 43: 905-908.
- Shuman, L.M. 1975. Effect of soil properties on zinc adsorption by soils. *Soil Science Society of America Proceedings* 39: 454-458.

- Shuman, L.M. 1976. Zinc adsorption isotherms for soil clays with and without iron oxides removed. *Soil Science Society of America Journal* 40: 349-352.
- Sillen, L.G.; Martell, A.E. 1964. Stability constants of metal ion complexes. Special Publication No. 17, The Chemical Society, London. 754 p.
- Sidhu, A.S.; Randhawa, N.S.; Sinha, M.K. 1977. Adsorption and desorption of zinc in different soils. *Soil Science* 124: 211-218.
- Singh, B.; Sekhon, G.S. 1977. The effect of soil properties on adsorption and desorption of zinc by alkaline soils. *Soil Science* 124: 366-369.
- Singh, B.; Sekhon, G.S. 1977a. Adsorption, desorption and solubility relationships of lead and cadmium in some alkaline soils. *Journal of Soil Science* 28: 271-275.
- Smythe, L.E.; Gatehouse, B.M. 1955. Polarographic determination of traces of copper, nickel, cobalt, zinc, and cadmium in rocks, using rubeanic acid and 1-nitroso-2 naphalene. *Analytical Chemistry* 27: 901.
- Stanton, D.A. 1964. Studies on zinc in selected Orange Free State soils. Ph.D. thesis, University of Orange Free State, Bloemfontein. 209 p.
- Stanton, D.A.; Burger, R. DuT. 1966. Studies on zinc in selected Orange Free State soils, 2. Distribution of zinc in selected soil profiles and in particle-size fractions. *South African Journal of Agricultural Science* 9: 809-821.
- Stanton, D.A.; Burger, R. duT. 1967. Availability to plants of zinc sorbed by soil and hydrous iron oxides. *Geoderma* 1: 13-17.
- Stanton, D.A.; Burger, R. duT. 1970. Studies on zinc in selected Orange Free State soils: V. Mechanisms for the reaction of zinc with iron and aluminium oxides. *Agrochemophysica* 2: 65-76.
- Stern, O. 1924. The theory of the electrolyte double layer. *Zeitschrift Elektrochemie* 30: 508-516.
- Stuanes, A. 1976. Adsorption of manganese (II), zinc (II), cadmium (II) and mercury (II) from binary solutions by mineral material. *Acta Agriculturae Scandinavica* 26: 243-250.
- Stumm, W.; Morgan, J.J. 1970. *Aquatic chemistry*. Wiley-Interscience, New York. 583 p.
- Swaine, D.J. 1955. Cadmium. Commonwealth Agricultural Bureau of Soil Science Technical Communication 48: 20.
- Swaine, D.J. 1955a. Zinc. Commonwealth Agricultural Bureau of Soil Science Technical Communication 48: 122-130.

- Swaine, D.J. 1962. Cadmium. Commonwealth Agricultural Bureau of Soil Science Technical Communication 52: 52-54.
- Swaine, D.J. 1962a. Zinc. Commonwealth Agricultural Bureau of Soil Science Technical Communication 52: 265-282.
- Syers, J.K.; Browman, M.G.; Smillie, G.W.; Coley, R.B. 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. Soil Science Society of America Proceedings 37: 358-363.
- Tiller, K.G. 1967. Silicic acid and the reaction of zinc with clays. Nature (London) 214: 852.
- Tiller, K.G. 1968. Stability of hectorite in weakly acidic solutions, III. Adsorption of heavy metal cations and hectorite solubility. Clay Minerals 7: 409-419.
- Tiller, K.G. 1968a. The interaction of some heavy metal cations and silicic acid at low concentrations in the presence of clays. Transactions of the 9th International Congress on Soil Science, Adelaide 2: 567-575.
- Tiller, K.G.; Hodgeson, J.F. 1962. The specific sorption of cobalt and zinc by layer silicates. Clays and Clay Minerals 9: 393-403.
- Tiller, K.G.; Nayyar, V.K.; Clayton, P.M. 1979. Specific and non-specific sorption of cadmium by soil clays as influenced by zinc and cadmium. Australian Journal of Soil Research 17: 17-28.
- Tisdale, S.L.; Nelson, W.L. 1970. Soil fertility and fertilisers. 2nd edition. Macmillan, New York. 694 p.
- Thorn, G.A.; Ludwig, R.A. 1962. The dithiocarbamates and related compounds. Elsevier Publishing Company, Amsterdam. 298 p.
- Thorne, D.W.; Laws, W.D.; Wallace, A. 1942. Zinc relationships of some Utah soils. Soil Science 54: 463-468.
- Thorne, W. 1957. Zinc deficiency and its control. Advances in Agronomy 9: 31-65.
- Toth, S.J. 1964. The physical chemistry of soils, p. 142-162. In Bear, F.E. (Ed). Chemistry of soil. Reinhold Publishing Corporation, New York. 515 p.
- Tremaine, J.H.; Willison, R.S. 1962. A methiolate-induced precipitation in gelfusion tests with plant sap. Phytopathology 52: 179-180.
- Underwood, E.J. 1977. Trace elements in human and animal nutrition. 4th edition. Academic Press, New York. 545 p.
- Ure, A.M.; Mitchell, M.C. 1976. The determination of cadmium in plant material and soil extracts by solvent extraction and atomic absorption with carbon-rod atomiser. Analytica Chimica Acta 87: 283-290.

- Udo, E.J.; Bohn, H.L.; Tucker, T.C. 1970. Zinc adsorption by calcareous soils. *Soil Science Society of America Proceedings* 34: 405-407.
- Vallee, B.L. 1959. Biochemistry, physiology and pathology of zinc. *Physiological Reviews* 39: 443-490.
- Vallee, B.L. 1971. Spectral characteristics of metals in metalloenzymes, p. 33-50. In Mertz, W.; Cornatzer, W.E. (Eds). *Newer trace elements in nutrition*. Marcell Dekker, New York. 438 p.
- Vallee, B.L. 1976. Zinc biochemistry: A perspective. *Trends in Biochemical Science* 1: 88-91.
- Vallee, B.L.; Neurath, H. 1954. Carboxypeptidase - a zinc metalloprotein *Journal of the American Chemical Society* 76: 5006.
- Vallee, B.L.; Wacker, W.E.C. 1970. Metalloproteins. In Neurath, H. (Ed). *The Proteins Vol. 5*. 2nd edition. New York Academic Press. 192 p.
- van Olphen, H. 1963. *An introduction to clay colloid chemistry*. Interscience, New York. 301 p.
- van Reeuwijk, L.P.; de Villiers, J.M. 1968. Potassium fixation by amorphous alumino-silica gels. *Soil Science Society of America Proceedings* 32: 238-240.
- Veith, J.A.; Sposito, G. 1977. On the use of the Langmuir equation in the interpretation of 'adsorption' phenomena. *Soil Science Society of America Journal* 41: 697-702.
- Vesély, V.; Pekárek, V. 1972. Synthetic inorganic ion-exchangers, I. Hydrous oxides and acidic salts of multivalent metals. *Talanta* 19: 219-262.
- Vinogradov, A.P. 1959. *The geochemistry of rare and dispersed chemical elements in soils*. Translation by Consultants Bureau, New York. 210 p.
- Vlaslov, K.A. (Ed). 1966. *Geochemistry of rare elements. Vol. I*. Academy of Sciences of U.S.S.R., Israel Program for Scientific Translations, Jerusalem. 688 p.
- Walkley, A. 1940. The zinc content of some Australian fertilisers. *Journal for the Commonwealth Scientific and Industrial Research Organisation, Australia*. 13: 255-260.
- Webb, M. 1975. Cadmium. *British Medical Bulletin* 31: 246-250.
- Wedepohl, K.H. 1953. Untersuchungen zur Geochemie des Zinks. *Geochimica et Cosmochimica Acta* 3: 93-143. As cited in Mortvedt, J.J.; Giordano, P.M.; Lindsay, W.L. (Eds). *Micronutrients in Agriculture*. Soil Science Society of America Incorporated, Madison, Wisconsin, U.S.A. 666 p.

- Wedepohl, K.H. 1970. Cadmium section 40-B to 40-0. In Handbook of Geochemistry. Vol. 11/2. Springer-Verlag, Berlin.
- Wedepohl, K.H. 1972. Zinc section 30-A to 30-0. In Handbook of Geochemistry. Vol. 11/2. Springer-Verlag, Berlin.
- Wells, N. 1960. Total elements in topsoils from igneous rocks: An extension of geochemistry. *Journal of Soil Science* 11: 409-424.
- Wells, N.; Teoh, T.S. 1975. The utilisation of sewage sludge in Singapore. 3rd Asean Soil Conference, Kuala Lumpur.
- Wells, N.; Whitton, J.S. 1976. Influence of dried digested sewage sludge on yield and element composition of lucerne. *N.Z. Journal of Agricultural Research*. 19: 331-341.
- Wells, N.; Whitton, J.S. 1979. The element content of Auckland sewage sludge and its influence on soil and plant composition. Proceedings of the Australia New Zealand Association for the Advancement of Science Conference, Auckland, N.Z.
- Westöö, G. 1963. A dithizone method for determining zinc in organic material. *Analyst* 88: 287-291.
- White, M.L. 1957. The occurrence of zinc in the soil. *Economic Geology* 52: 645-651.
- Whitton, J.S.; Wells, N. 1974. A pedochemical survey, 2. Zinc. *N.Z. Journal of Science* 17: 351-367.
- Wild, A. 1950. The retention of phosphate by soil. A review. *Journal of Soil Science* 1: 221-238.
- Williams, C.H. 1974. Heavy metals and other elements in fertilisers. Environmental considerations, p. 123-129. In Leece, D.R. (Ed). *Fertilisers and the Environment*. Australian Institute for Agricultural Science (N.S.W. Branch), Sydney. 132 p.
- Williams, C.H.; David, D.J. 1973. The effect of superphosphate on the cadmium content of soils and plants. *Australian Journal of Soil Research* 11: 43-56.
- Williams, C.H.; David, D.J. 1976. Effects of pasture improvement with Subterranean clover and superphosphate on the availability of trace metals to plants. *Australian Journal of Soil Research* 14: 85-93.
- Williams, C.H. David, D.J. 1976a. The accumulation in soil of cadmium residues from fertilisers and their effect on the cadmium content of plants. *Soil Science* 121: 86-93.
- Williams, C.H.; David, D.J.; Iismaa, O. 1972. The determination of cadmium in soils, plants and fertilisers by dithizone extraction and atomic absorption spectroscopy. *Communications in Soil Science and Plant Analysis* 3: 399-407.

- Wright, H.J.L.; Hunter, R.J. 1973. Adsorption at solid-liquid interfaces, II. Models of the electrical double layer at the oxide-solution interface. *Australian Journal of Chemistry* 26: 1191-1206.
- Wright, J.R.; Levick, R.; Atkinson, H.J. 1955. Trace element distribution in virgin profiles representing four great soil groups. *Soil Science Society of America Proceedings* 19: 340-344.
- Yaalon, D.H. 1959. Weathering reactions. *Journal of Chemical Education* 36: 73-76.
- Yamamoto, Y.; Kumamaru, K.; Hayashi, Y.; Kanke, M. 1972. Effect of solvent extraction on the atomic absorption spectrophotometry in determination of ppm. levels of cadmium with dithizone. *Talanta* 19: 953-959.

APPENDICES

APPENDIX 1

Amounts of Zn and Cd Remaining in Polycarbonate

Centrifuge Tubes After Shaking for 40 hr.

Initial Zn Concentration $\mu\text{mol l}^{-1}$	Final Zn Concentration $\mu\text{mol l}^{-1}$	Initial Cd Concentration $\mu\text{mol l}^{-1}$	Final Cd Concentration $\mu\text{mol l}^{-1}$
0.153	0.153	0.089	0.089
0.153	0.168	0.089	0.089
0.153	0.153	0.089	0.080

## APPENDIX 2

### Method of Successive Approximations for Evaluating Adsorption Isotherm Data by the Langmuir Equation.

Adsorption data for Zn and Cd on soil samples and Fe gels were treated according to the method of Ryden et al. (1977) for P adsorption whereby successive approximations are used to obtain the Langmuir constants in systems where 2 or more adsorption 'regions' are operating.

A reciprocal plot ( $\frac{1}{x}$  against  $\frac{1}{c}$ ) is made of the experimental data for the amounts of Zn or Cd adsorbed ( $x$ ) over a range of Zn or Cd solution concentrations ( $c$ ). A linear relationship can then be found for the low final solution concentrations (i.e., high  $\frac{1}{c}$  values). From the slope and intercept of this linear relationship, a first approximation of the Langmuir constant values  $k$  (related to binding energy) and  $b$  (the adsorption maximum) is obtained. These constants are referred to as  $k_I$  and  $b_I$  values since they relate to the first linear region. These  $k_I$  and  $b_I$  constants are then used to calculate the amounts of Zn or Cd adsorbed at higher final  $c$  values (corresponding to low  $\frac{1}{c}$  values). Next, these  $X_I$  values are subtracted from the total amount of Zn or Cd adsorbed to give the amounts adsorbed on the second population of sites,  $X_{II}$ . The  $X_{II}$  values are again plotted as reciprocals,  $\frac{1}{X_{II}}$  against  $\frac{1}{c}$ , and from the slope and intercept of this line  $k_{II}$  and  $b_{II}$  values are calculated. The  $k_{II}$  and  $b_{II}$  constants are then used to calculate  $X_{II}$  values for low final  $c$  values (high  $\frac{1}{c}$  values). These are then subtracted from the total amounts of adsorbed Zn or Cd at each  $c$  value used, to obtain  $X_I'$  values. The new  $X_I'$  values are then used to recalculate new constants  $k_I'$  and  $b_I'$  for adsorption of Zn and Cd on the

first population of sites. The  $k'_I$  and  $b'_I$  constants are better estimates of the adsorption in the first region, since they have been 'corrected' for adsorption occurring in the second population of sites. This reiterative process continues until the difference between successive approximations of  $k$  is less than 5%.

OUTLINE OF THE METHOD OF SUCCESSIVE APPROXIMATIONS USED TO  
 TEST THE FIT OF EXPERIMENTAL DATA TO THE LANGMUIR EQUATION,  
 BASED ON THE METHOD DESCRIBED BY RYDEN ET AL. (1977).

STEP	PLOT	DETERMINE
1.	$\frac{1}{X}$ vs $\frac{1}{c}$	$k_I, b_I$
2.		$X_I$
3.		$X_{II} = X - X_I$
4.	$\frac{1}{X_{II}}$ vs $\frac{1}{c}$	$k_{II}, b_{II}$
5.		$X_{II}^*$
6.		$X'_I = X - X_{II}$
7.	$\frac{1}{X'_I}$ vs $\frac{1}{c}$	$k'_I, b'_I$
8.		$X'_I^*$
9.		$X'_{II} = X - X'_I$

Repeat steps 4-9 until difference between successive approximations of k is < 5%.

X = Zn or Cd adsorbed (added Zn/Cd adsorbed + native Zn/Cd).

c = final Zn/Cd concentrations

k: related to bonding energy of adsorbed ions.

b: related to the adsorption maxima of adsorbed ions

\* from preceding k and b values for all values of c.