STUDIES ON THE ORIGIN, DISTRIBUTION AND MOBILITY OF CADMIUM IN PASTORAL SOILS

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Soil Science at Massey University

JULIE MARIA ZANDERS

1998

ABSTRACT

Cadmium (Cd) is a toxic heavy metal with no known biological function. Exposure of the human population to Cd is predominantly through cigarette smoke and Cd–containing foodstuffs. Many phosphatic fertilizers contain Cd and their application to land used for food production results in increased concentrations of Cd in the soil. The fate of this Cd in soils is poorly understood. In this study, factors influencing the concentration and residence time of Cd in pastoral soils were investigated.

Total Cd concentrations in topsoil samples (0 - 7.5 cm) from a regularly fertilized farm were found to range between 0.07 and 0.91 mg Cd kg^{-1} (arithmetic mean of 0.36 mg Cd kg^{-1}). The top soil Cd concentration was unrelated to soil type or parent material but correlated well with total phosphorus and total carbon. In a study of the distribution of total Cd throughout the profiles of 17 soil types on the farm, Cd concentrations generally decreased with depth and soil parent material contributed little to topsoil Cd loads.

A comparison of pedologically matched fertilized and unfertilized soils on the same farm confirmed that phosphatic fertilizer was the dominant source of Cd. Fertilized sites showed a 3- to 20-fold increase in soil Cd loading. Increased Cd concentrations were detectable to 15 cm. These increased Cd loads were easily accounted for by an estimated phosphatic fertilizer input of 6 g Cd ha^{-1} yr^{-1} over 7 decades.

Soil Cd concentrations were also influenced by stock camping behaviour, although the magnitude of this effect was much less than that due to fertilizer.

To investigate conditions under which Cd may move deeper in the soil profile, laboratory-based leaching studies on repacked soil columns using various electrolyte leaching solutions were conducted. Columns leached with 2.5 mM $CaCl_2$, $CaSO_4$ and $Ca(NO_3)_2$ showed some limited movement of Cd, but columns leached with 2.5 to 7.5 mM KCl showed no significant redistribution of the added Cd. Under the soil conditions studied (pH$_{H2O}$ 5.45), cation exchange appeared the predominant driving force behind Cd mobility, not anion complexation. On the same soil, Cd mobility increased linearly

as leachate $CaCl_2$ concentration increased. By 50 mM $CaCl_2$ most Cd was leached from the column. In view of the dominance of Cl^- in coastal soil solutions, this mobility under the influence of $CaCl_2$ may be important.

In a further experiment, four soils differing in physical and chemical properties were leached with 2.5 mM $CaCl_2$. The wide range of Cd mobility seen, could be explained by differences in soil pH (pH_{H2O} 4.95 - 6.02). The movement observed in these columns was adequately modelled using a simple convection-dispersion equation and adsorption isotherms. The movement of Cd observed and modelled in these laboratory studies suggests that leaching is likely to be a much more important mechanism of Cd loss from the soil profile than removal of animal products. This work was supported by findings from a field-based mass balance study of Cd inputs and accumulation in soil developed under pasture on a Wharekohe podzol. Despite clear accumulation of fertilizer-derived Cd in the surface of these pastoral soils, up to 44% of the applied Cd remained unaccounted for. The most likely reason for this was leaching.

Accurate modelling of the residence time and plant availability of Cd in soils will rely on a quantitative understanding of the factors influencing Cd mobility in soils. This is an area requiring further research.

ACKNOWLEDGMENTS

And finally, a grateful thank you to all my friends and colleagues who kept me going during the times when finishing this thesis began to look like an impossibility.

Special thanks also goes to the C Alma Baker Trust for financial support of the project.

Since writing the above, I have additional thanks to make to the wonderful staff of the Palmerston North Hospital. I am especially thankful to the doctors and nurses of Ward 24 who cared for me and maintained my spirits during the several weeks I spent there recuperating. I also wish to thank my friends who came to visit during that time for their cheer and laughter.

To all of the above mentioned persons:

This is the thesis that WOULD be completed ... eventually!

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF MAPS

Maps enclosed in back pocket

Map 1   Reconnaissance soil map of Limestone Downs showing the positions of soil profiles.

Soil profiles studied in Chapter 4, section 4.3.2, are shown by white labels. Detailed soil profile descriptions are given in Appendix 2.

Soil profiles studied in Chapter 5, section 5.2, are shown by pink labels. Detailed soil profile descriptions are given in Appendix 3.

LIST OF SYMBOLS

(Chapter 7)

C $\quad$ = solute concentration $(M\,L^{-3})$

C_{tot} $\quad$ = total concentration of solute in unit soil volume $(M\,L^{-3})$

D $\quad$ = dispersion coefficient $(L^{2}\,T^{-1})$

D_{s} $\quad$ = molecular diffusion coefficient in soil $(L^{2}\,T^{-1})$

K_{d} $\quad$ = distribution coefficient $(L^{3}\,M^{-1})$

q_{s} $\quad$ = solute flux density $(M\,L^{-2}\,T^{-1})$

q_{w} $\quad$ = Darcy flux density $(L\,T^{-1})$

R $\quad$ = retardation coefficient (dimensionless)

S $\quad$ = amount of solute adsorbed by the soil matrix $(M\,M^{-1})$

t $\quad$ = time (T)

V $\quad$ = average pore water velocity $(L\,T^{-1})$

z $\quad$ = diffusion distance (L)

θ $\quad$ = volumetric water content $(L^{3}\,L^{-3})$

λ $\quad$ = dispersivity (L)

ρ_{b} $\quad$ = soil bulk density $(M\,L^{-3})$

CHAPTER 1
INTRODUCTION AND STRUCTURE OF STUDY

1.1 INTRODUCTION

New Zealand gains the majority of its overseas revenue from primary industry – agriculture, horticulture and forestry. However, the success of these activities depends significantly on the quality of our greatest asset, our soil. Sustainable production relies on protection of the soil quality. In agriculture and horticulture this is achieved by the application of fertilizers and soil amendments to replace lost nutrients and also maintain the physical condition of the soil.

During the last few decades, an awareness has developed that in applying these fertilizers and soil amendments, we may also be compromising the soil quality by coincidentally adding undesirable elements (Bøckman *et al*., 1990). In addition to the valuable nutrients, impurities, for example Cd (cadmium), As (arsenic), Cr (chromium), Pb (lead), Hg (mercury), Ni (nickel) and V (vanadium), are also present in the phosphate rock used to manufacture phosphatic fertilizer, and in sewage sludges (Mortvedt, 1996; McLaughlin *et al*. 1996). These heavy metals have a residence time in soils in the order of several thousands of years (Witter 1996), and are therefore likely to accumulate.

Cadmium has claimed much attention in the literature due to its possible adverse effect on human health from both acute and chronic exposure (Herber, 1994). Soil has comparatively low concentrations of Cd, but it is present in considerably higher concentrations in some phosphatic fertilizers and sewage sludges. Once in the soil, Cd is relatively immobile and, as a surface derived contaminant, it accumulates in the surface layer. Here it poses the greatest risk to the ecosystem. As plant Cd concentrations have been found to increase with increases in soil Cd concentrations, this accumulation of Cd may, over time, increase the flow of Cd through the food chain.

Even though animals such as livestock and humans tend to retain only a small proportion of their ingested Cd, the Cd that is retained is concentrated mainly in the kidneys and liver. In these tissues, Cd usually accumulates with age. If sufficiently high concentrations are attained, organ dysfunction may occur.

Concern from our Northern Hemisphere trading partners over heavy metal accumulation has prompted research work in New Zealand to understand better the behaviour of Cd in our own soils and environment. As a result of studies which showed low concentrations of Cd in native soils compared with soils exposed to superphosphate additions, the predominant soil Cd source in New Zealand agriculture has been identified as phosphatic fertilizer (Bramley, 1990; Roberts *et al.* 1994).

The Cd issue affects only a small portion of New Zealand's meat export revenue – the sale of kidneys from ruminants (Smith, 1993). In response to anxiety about Cd toxicity, New Zealand has established a stringent, self-imposed maximum residue limit (MRL) of 1 mg Cd kg^{-1} fresh weight Cd (compared to 2.5 mg Cd kg^{-1} set by Australia) for such meat products. However, this MRL threatens to become a trade barrier (Smith, 1993). Importers of New Zealand animal products now hold New Zealand to this limit and reject product which exceeds it.

Though difficult to screen for, compliance with the 1 mg Cd kg^{-1} criterion is effectively achieved by exporting only offal from young animals. Although this meets our trade requirements, any perception of New Zealand having a 'heavy metal' problem tarnishes our image of a 'safe' and 'environmentally friendly' food producer. To preserve this image, we are therefore obliged to follow other countries as they tighten controls on heavy metal contamination of soils.

Though a policy of zero Cd application through low Cd fertilizers may appear the answer, the solution is not that simple. Phosphate fertilizer is a necessary input to the farming system, and removal of the Cd impurity with current technology is difficult and expensive (Mortvedt 1996). Furthermore, fertilizer is not the only source for soil Cd. Other sources, notably soil parent material and atmospheric deposition from air pollution, have been found to make significant contributions to European soil Cd loads. The chance that reducing fertilizer Cd content will only partially address Cd concerns led Furness (1994) to conclude: "If the health concerns expressed in New Zealand in relation to cadmium are of genuine concern, then all sources of cadmium should be evaluated".

The Cd accumulation rate in surface soil also depends on the rate of loss – through animal product and crop removal, and possibly by leaching to depth (Rothbaum *et al.* 1986, Loganathan *et al.* 1997). However, although data are available on the first two means of Cd loss, little work has been done on Cd leaching in New Zealand soils. This mechanism needs to be investigated specifically for New Zealand soils and conditions (Roberts *et al.* 1994).

With a firm understanding of the sources, and behaviour, of Cd in New Zealand soils, constructive and informed decisions on ways to minimize the risk this element poses can then be made.

1.2 STRUCTURE OF THE STUDY

In view of the issues and background discussed above, the present study was designed to investigate the major sources of Cd to pastoral agriculture in New Zealand and evaluate its potential for leaching.

Chapter 2 presents a literature review on Cd and discusses the routes of exposure and risks that this element poses to the general human population, including its transfer to the human food chain from soils via uptake by plants and animals. The various sources of Cd that have been identified are reviewed, and current Cd concentrations and accumulation rates in New Zealand pastoral soils are examined in terms of international trends. Finally, aspects of managing Cd in the pastoral system are discussed with an emphasis on ways of limiting its entry into the human food chain.

From the literature review, soil Cd concentrations are seen to be central to the Cd issue. However, it was necessary to establish an appropriate methodology for determining these Cd concentrations. Basic considerations involved in trace metal analysis and the extraction methodologies developed for subsequent studies are described in Chapter 3.

Cadmium concentrations in soil are known to vary across the landscape. Unless the underlying factors causing this variation are understood, successful management of Cd within the pastoral farming system is difficult. In a country essentially free from

atmospheric pollution, this variability generally evolves from a complex interaction between soil type, parent material, farm-specific fertilizer management and animal transfer. But, by confining studies to within the boundaries of a single pastoral farm, one source of variation, the effect of fertilizer management, can be minimized. Cadmium variation can then be evaluated in terms of parent material, soil type and animal transfer. The results from a study which does this are presented in Chapter 4.

Examination of the data collected in Chapter 4 indicated, however, that the above-mentioned factors generally could not explain the observed variation in Cd concentrations. Instead, evidence was found which suggested a major influence from exposure to phosphatic fertilizer. This aspect was investigated in a subsequent study comparing the Cd status of soils on adjacent fertilized and unfertilized sites. These results are presented and discussed in Chapter 5.

The information presented in both Chapters 4 and 5, showed that the majority of soil Cd was derived from surface applied phosphatic fertilizer. The appearance of Cd at depth in some soils, therefore introduced the possibility of Cd redistribution down the soil profile. While extensive downwards movement of Cd could provide an important means for slowing Cd accumulation in the topsoil, even limited redistribution of Cd within the active rooting zone may impact significantly on Cd availability to plants because of changes in soil properties such as soil pH and organic matter content.

Given the depth to which surface-derived Cd was observed in the profiles discussed in Chapters 4 and 5, it appeared that leaching was most likely responsible for this redistribution. Conditions known to influence Cd mobility are reviewed and discussed at the beginning of Chapter 6. Following this review a study is presented in which the potential for Cd movement by leaching in several New Zealand soils was investigated.

The results given in Chapter 6 are, however, difficult to transfer to the field situation because they are constrained to the parameters of the experimental set-up (effluent volumes, flow rates and Cd concentrations). A more practical approach is to use numerical simulation models which allow solute transport to be predicted under a wider range of soil and environmental conditions. Accordingly, numerical leaching models

were developed to describe Cd movement in four different soils using simple chemical equilibria and soil-water physics (Chapter 7). Of greatest interest was the ability of these simple models to predict the Cd movement found in the soil columns studied in Chapter 6. This being satisfactorily demonstrated, the models were then used to investigate the potential for Cd loss from the active rooting zone of several New Zealand soils.

The results of studies discussed in Chapters 4 to 7 provide substantial information on Cd concentrations, source, variation and behaviour in a selection of New Zealand soils. In the final section of this work (Chapter 8), this knowledge and understanding has been integrated to explain and predict the fate of Cd in a pasture soil for which a pasture development chronosequence exists.

Final conclusions and recommendations are presented in Chapter 9.

6

CHAPTER 2

A GENERAL REVIEW OF LITERATURE ON CADMIUM IN THE ENVIRONMENT

2.1 INTRODUCTION

Of the heavy metals that we are releasing into our environment, Cd poses a major concern due to its toxic effect on human health, and its ease of entry into the food-chain through plant uptake (Mortvedt, 1996).

Several texts are devoted to the subject of Cd in the environment (Webb, 1979; Nriagu, 1980c; Mislin and Ravera, 1986; Simpson and Cumow, 1988; Stoeppler and Piscator, 1988; McLaughlin and Singh, 1997), while other texts cover trace metals in general (Adriano, 1986; Vernet, 1991; Adriano, 1992; Kabata-Pendias and Pendias, 1992; Seiler *et al.*, 1994; Ross, 1994d; Alloway, 1995b). Review articles on Cd that relate to agriculture have also been published (Chaney and Hornick, 1977; Bramley, 1990; McLaughlin *et al.*, 1996).

This literature review covers some background chemistry of Cd; its entry into, and effect on sectors of the biosphere related to agricultural-based food production; the sources that contribute Cd to agricultural and horticultural soils on a world-wide scale and typical Cd concentrations in the surface of these soils; and management policies relevant to minimising the impact of Cd on the human food-chain.

2.2 CADMIUM CHEMISTRY AND INDUSTRIAL USE

Cadmium for industrial use is obtained solely as a by-product of Zn and Pb production (Nriagu, 1980a). Its identification as a new, and previously unknown, element in 1817 by F. Strohmeyer (Germany) came about by the unusual yellowing of a zinc carbonate sample when heated. The name cadmium is derived from the Greek name for zinc carbonate (also known as calamine), *cadmia* (Nriagu, 1980a).

Cadmium has the atomic number 48, an atomic mass of 112.411, and sits in Group IIb of the periodic table, below Zn and above Hg – the last of the d-block transition

elements. The metal has a melting point of 321.07 $^{\circ}$C and a boiling point of 767 $^{\circ}$C (CRC Handbook of Chemistry and Physics, p 4-6) and it exists mainly in the Cd^{2+} oxidation state. Of the eight stable isotopes, ^{112}Cd (24.13 %) and ^{114}Cd (28.73 %) are the most abundant (Thornton, 1986; CRC Handbook of Chemistry and Physics, p 11-74). With a density greater than water, Cd fits into the group of elements often referred to as 'heavy metals'. Although the term 'heavy metal' has been criticised as misleading for its lack of distinction between essential biological elements and the non-essential biological elements such as Cd and Hg, it remains in use (Tiller, 1989).

Of the stable compounds formed by Cd, the fluoride, chloride, bromide, iodide, nitrate and sulphate forms are water soluble and the sulphide, carbonate, oxide and hydroxide are insoluble (Förstner, 1980). Cadmium is soluble in acids, especially nitric acid, but not in alkalis (Nriagu, 1980a). This characteristic of high solubility under acidic conditions and virtual insolubility above neutral pH has been found to hold in the soil environment. As a result, one means of limiting plant available Cd in surface soils, and therefore plant uptake, is to raise soil pH by the application of lime. Other variables also affect Cd solubility and mobility in soils. These are discussed in greater detail in Chapter 6.

The chemistry of Cd is closely related to that of Zn and many Zn ore deposits contain Cd impurities (Ross, 1994a). Cadmium is strongly chalcophilic (has an affinity for sulphur) and forms CdS under natural conditions, usually as a coating on the weathered Zn sulphide mineral sphalerite (Thornton, 1986). Prior to the 1940's a considerable portion of the Cd in superphosphate fertilizer originated from Zn sulphide used to make the sulphuric acid component of the fertilizer (Walkley, 1940; Peterson and Alloway, 1979). The similar ionic radii of Cd (0.97 Å) and Ca^{2+} (0.99 Å) may allow substitution of Cd for Ca in Ca-containing minerals, for example calcite and hydroxy-apatite – the latter causing problems in production of high quality phosphatic fertilizer (Pierce *et al.*, 1982; Thornton, 1986; McBride, 1994; Ghosheh *et al.*, 1996). Isomorphous substitution of Cd for Cu, Zn, Hg and Pb in sulphides similarly occurs (Sposito, 1983). Cadmium-compounds are also isotypic with the corresponding compounds of Mg^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} (Brehler, 1972).

Commercial uses of Cd include: pigments for plastics, ceramics, paints, coated fabrics, textiles, rubber, glass, enamels and printing inks (ranging from primrose yellow to maroon); batteries (e.g. nickel-cadmium alkaline batteries); plastic stabilizers (polyvinylchloride); electroplating of steel, iron, copper, brass etc. – the Cd confers resistance to corrosion; alloy manufacture; and other minor uses (Nriagu, 1980a; Förstner, 1980).

Although recovery of Cd during Zn and Pb production prevents dispersion of the element into the environment from raw ore processing, Nriagu (1980a) suggests that "the current uses of Cd are almost completely dissipative; less than 5% of the metal consumed is now recovered". Thus, this element ultimately ends up dispersed in the environment. The percentage recovery may have increased over the last decade – Kross *et al.* (1995) cite a dissipation value of about 67%, presumably referring to the situation in the USA. However, it may also be dependent on countries having legislation requiring recycling of Cd-containing by-products and obsolete end products (e.g. Ni-Cd batteries). Förstner (1980), for example, reports that up to 20% of the total processed Cd in the Federal Republic of Germany in 1975 came from recycled material.

2.3 CADMIUM IN THE BIOSPHERE

The greatest concern regarding Cd comes from its entry into the human food-chain. Therefore an understanding of the relationship between Cd concentrations at each trophic level is necessary to assess both the threat this element presents, and factors that determine the best means of protection.

2.3.1 Pasture plants and horticultural crops

Cadmium has no known essential biological function, but it is readily taken up by plants. However, it is not sufficiently phytotoxic to protect the human food chain from significant, long-term Cd exposure (Chaney and Hornick, 1977; Kross *et al.*, 1995). Therefore, Cd-induced plant growth inhibition or plant death can not be relied on to prevent hazardous dietary intakes of the element.

Root absorption provides the major pathway for Cd uptake with the extent of absorption dependent on many factors, in particular soil pH and soil Cd concentrations (Van Bruwaene *et al.*, 1986; Hornburg and Brümmer, 1990). Some studies show increased plant uptake of Cd with increasing soil Cd concentrations (Williams and David, 1973 and 1976; Mulla *et al.*, 1980; Kabata-Pendias and Pendias, 1992; Bramley and Barrow, 1994; Loganathan *et al.*, 1997), while others, particularly those on the edible portions of crops, do not (Yost, 1979; Mulla *et al.*, 1980; Smilde and van Luit, 1983, as cited in Mortvedt, 1996; Mortvedt, 1987; He and Singh, 1993a).

Plant uptake of heavy metals varies both between and within plant species, and also between the parts of each plant (Van Bruwaene *et al.*, 1986; He and Singh, 1993a; Mullins and Mitchell, 1995). Highest Cd concentrations are generally found in the roots, followed by the foliage and then seed (Van Bruwaene *et al.*, 1986; Kabata-Pendias and Pendias, 1992). Bramley and Barrow (1994), for example, found several Australian pasture species retained more than 60% of the total plant Cd in their roots. In contrast, Capeweed – considered a Cd accumulator because of its greater Cd herbage concentrations compared with other plant species – translocated about 80% of its Cd into its foliage.

For many plants grown in contaminated soil, Cd concentrations in the plant are generally the same order of magnitude as Cd concentrations in the substrate (Förstner, 1980). For example, Roberts *et al.* (1994) present data from a New Zealand field survey in which pastoral soils averaging 0.4 mg Cd kg^{-1} produced Cd concentrations in grasses and legumes averaging 0.10 mg Cd kg^{-1} DM and 0.07 mg Cd kg^{-1} DM respectively. Bramley and Barrow (1994) found common Australian pasture species to vary between about 0.5 to 2 mg Cd kg^{-1} dry matter (DM) when grown on a soil containing 0.2 mg Cd kg^{-1} – a soil Cd concentration typical in both Australia and New Zealand (section 2.6.2).

Plant uptake of Cd is strongly dependent on the soil Cd pool which is available to the plant (Van Bruwaene *et al.*, 1986; He and Singh, 1993a; Mullins and Mitchell, 1995). This may be very small when compared to the total soil Cd store. In agreement with the findings of Williams and David (1973) for horticultural plants, Loganathan and Hedley (1997) calculated that only 1.5 – 4.5% of the Cd applied via phosphatic fertilizer could

be accounted for in the pasture plants over 10 years. These percentages contrast with those for macro-nutrients such as phosphorus, and subsequently influence Cd loss rates (see section 2.7) caused by plant uptake and removal.

2.3.2 Farm animals

The predominant focus with regard to Cd entering the biosphere in New Zealand is its accumulation in the tissue of livestock produced for human consumption. A strong similarity in chemistry between Cd and Zn, an essential trace element (Barak and Helmke, 1993), allows Cd to enter metabolic pathways for which Zn is needed (Kross *et al.*, 1995).

The majority of an animal's Cd burden is stored in the kidneys and liver (Fitzgerald *et al.*, 1985; Van Bruwaene *et al.*, 1986). Lee *et al.* (1996) estimated that the kidneys and liver combined accounted for between 50 and 67% of total body Cd in sheep. A further 6 to 26% of the body Cd was associated with muscle, which had one of the lowest Cd concentrations (≤ 0.004 mg Cd kg^{-1} fresh weight), and 16 to 25% with the digestive tract. Similar distributions could be expected in other livestock such as beef cattle and dairy cows (Fitzgerald *et al.*, 1985; Van Bruwaene *et al.*, 1986).

Cadmium concentrations in milk appear, like muscle, to be very low. A survey of whole milk on sale in New Zealand produced an average concentration of 0.33 μg Cd L^{-1}. This is somewhat lower than that found in dairy products from Queensland, Australia, where homogenized market milk contained on average 6 μg Cd L^{-1} (Mitchell, 1981). Sharma *et al.* (1982) reported that whole milk Cd concentrations from cows (20 μg Cd L^{-1}) were unaffected by Cd intake. However, more recently Rounce *et al.* (1997) found Cd in sheep milk and pasture Cd to be significantly related at much lower milk concentrations (0.039 - 0.06 μg Cd L^{-1}, assuming 15% milk solids).

Cadmium burdens in livestock originate from the animal's diet after birth, as the foetus is generally found to be virtually free of Cd (Koh, 1988; WHO 1992a; Rounce *et al.*, 1995). Increases in soil Cd concentrations therefore impact significantly on the animal Cd burden, in particular the liver and kidneys, through both direct soil ingestion and increased plant uptake (Lee *et al.*, 1996).

Although animals generally retain less than 1% of their ingested Cd (Van Bruwaene *et al.*, 1986; Lee *et al.,* 1994; Lee *et al.*, 1996), the dependence of accumulated Cd levels on age can lead to older animals, e.g. ewes over 3-5 years, having Cd concentrations in their kidneys which exceed the 1 mg Cd kg^{-1} FW maximum residue limit which is monitored by New Zealand's Ministry of Agriculture and Fisheries (MAF) (Lee *et al.*, 1996). For example, a survey of kidneys from New Zealand livestock found 22% of ewes, 25% of dairy cows and 32% of beef cows under 5 years of age exceeded this value (B. Marshall, unpublished data).

The focus of Cd accumulation in livestock destined for human consumption can overshadow the fact that Cd is also present in the broader ecosystem. Populations of feral deer and sheep, isolated from major anthropogenic Cd inputs, have likewise been found to show accumulated Cd in the kidneys (Roberts *et al.*, 1994). Therefore reductions in animal product Cd concentrations can only proceed until a minimum, environment-specific level is reached.

Despite the problems that Cd accumulation in the kidney and liver presents for offal sale and consumption, the efficiency with which these organs sequester Cd minimizes Cd concentrations in muscle and milk. In this respect, the animal becomes an important barrier against entry of Cd into the human diet – with the exception of offal consumption (Lee *et al.*, 1996; Van Bruwaene *et al.*, 1986).

2.3.3 Humans

Diet and cigarette smoke are major sources of Cd to the human population with the latter possibly equalling or exceeding that from food (Ryan *et al.*, 1982; Black, 1988; WHO 1992a; Herber, 1994).

Although some of the highest Cd concentrations can be found in leafy and root vegetables such as lettuce, spinach, carrot, parsnip; cereals/grains; shellfish and animal offal (Sherlock, 1986), most Cd in the adult human diet comes generally from grains and cereal products and potatoes – by virtue of their large consumption volume (Chaney and Hornick, 1977; Marro, 1996). From a total diet survey conducted in New Zealand it was found that potatoes and related products contributed 22% of the dietary

Cd, oysters provided 17% and breads 11% for young males between 19 and 24 years of age (Vannoort *et al.*, 1995).

Despite the concern over Cd accumulating in livestock, products from animals contribute only a small proportion of Cd to the diet – 3% from offal in the case of an average Australian diet (Marro, 1996) and 6% from lamb liver in the case of New Zealand (Vannoort *et al.*, 1995). Hence, in spite of the large Cd concentrations found in lamb liver from the New Zealand study (255 μg Cd kg^{-1}), its low consumption compared to potatoes and bread – whose Cd concentrations Vannoort *et al.* (1995) report as 9 - 71 μg Cd kg^{-1} and 11.8 μg Cd kg^{-1} respectively – reduces the impact that offal consumption has on Cd intakes. The other single dominant dietary source of Cd for New Zealand consumers comes from oysters (392 μg Cd kg^{-1}). However Vannoort *et al.* (1995) suggest that this food is likely to be only a minor component of the diet for most people.

Absorption of ingested Cd has been estimated as 5% while adsorption of Cd from inhaled air, including cigarette smoke, is greater and ranges from 10 - 50% (Herber, 1994). The estimated total daily Cd intake for the non-smoking population in a non-polluted area is 10 - 40 μg day^{-1} (where water and air contribute insignificant amounts). When stated in terms of body absorption, this equates to 0.5 - 1.3 μg day^{-1}, though the presence of antagonistic elements such as Ca, Zn and Se modify Cd absorption, accumulation and toxic effects (Crounse *et al.*, 1983; WHO, 1992a). An estimated additional 1 - 2 μg day^{-1} would also be absorbed by smoking 20 cigarettes per day (WHO, 1992a).

Acute Cd poisoning, now rare, can occur through ingestion of acidic food or beverage which has been held in Cd-containing or -coated vessels, or through inhalation of Cd fumes, in particular CdO (Yasumura *et al.*, 1980; Bernard and Lauwerys, 1986; Herber, 1994). But, it is the possible threat of chronic Cd poisoning in the wider population that is driving current research on Cd entry into the food-chain.

As for other animals, Cd in the human body is stored in the kidneys and liver in association with metallothionein – these organs account for over 50% of the body's Cd

burden (Yasumura *et al.*, 1980; Kross *et al.*, 1995). Its half-life in the human body is estimated between 20 and 30 years(Kross *et al.*, 1995). Figures from the US indicate that, although a small proportion of the human population (probably about 0.6%) exceed 100 mg Cd kg^{-1} wet weight of kidney cortex, the mean Cd concentration is likely to be between 20 and 35 mg Cd kg^{-1} wet weight (Ryan *et al.*, 1982).

As a result of the elevated Cd concentrations in the kidney, this organ exhibits the earliest signs of Cd toxicity. Accordingly, in order to protect against the onset of disease through accumulated Cd, the threshold for onset of kidney damage (estimated as 200 mg Cd kg^{-1} wet weight of kidney cortex) is used to establish a maximum acceptable Cd dietary intake level (WHO, 1992a). The resulting provisional tolerable weekly intake (PTWI) of 400 - 500 µg Cd (non-smoking adult) (WHO, 1992a) has been adopted by New Zealand as 7µg Cd week^{-1} kg^{-1} body weight (Dr. Bill Jolly, pers. comm.). Current information indicates that Cd dietary intakes for the general New Zealand population is about half this recommended maximum (Vannoort *et al.*, 1995). Even so, considerable biological variation occurs within the human population and Roels *et al.* (1981) calculate that critical kidney Cd concentrations for individuals range from 160 to 285 mg Cd kg^{-1} wet weight of kidney cortex.

Besides the adverse effects of Cd on the kidneys (renal dysfunction), long-term exposure to Cd is also suspected to cause emphysema, chronic obstructive pulmonary disease, osteomalacia, anaemia, anosmia and perhaps cancer (Cd may be a carcinogen) (Mennear, 1979; Yasumura *et al.*, 1980; Ryan *et al.*, 1982; Bernard and Lauwerys, 1986; WHO, 1992a; Herber, 1994; Kross *et al.*, 1995). Cadmium is also implicated in adverse effects on the nervous system and immune system (Chang, 1992, and Murray and Thomas, 1992 – as cited by Kross *et al.*, 1995).

2.4 SOURCES OF CADMIUM TO AGRICULTURAL SOIL

In general, metal concentrations in the soil are determined by parent material composition and soil forming factors (Peterson and Alloway, 1979; Thornton, 1986; Kabata-Pendias and Pendias, 1992; Blaser and Zimmermann, 1993). Exogenous

contributions are then superimposed on the natural variation of soil Cd concentrations (Merry and Tiller, 1991).

Cadmium additions to agricultural land on a global scale typically come from the deliberate use of sewage sludges and phosphatic fertilizers as soil amendments, and deposition of atmospheric Cd derived from industrial emissions (particularly from the non-ferrous metal industry, steel and iron manufacturing), coal, oil and wood combustion and refuse incineration (Pacyna *et al.*, 1991) (Table 2.1). However, not all exogenous sources of Cd are of anthropogenic origin. Natural sources also contribute to surface soil Cd concentrations via wind-blown dusts, forest fires, volcanic emissions, vegetation and sea salt sprays – though these are exceeded globally almost 10 fold by anthropogenic sources (Table 2.1).

2.4.1 Soil parent material

The considerable influence that soil parent material has on native soil Cd levels has been illustrated and discussed by various authors (Lund *et al.*, 1981; Pierce *et al.*, 1982;

Table 2.1 Estimated annual atmospheric emissions of Cd world-wide.

Source		Cd emission ($\times 10^3$ kg yr^{-1})
Natural Sources [†‡]	Volcanic	520 (40 - 7800)
	Vegetation	210 (50 - 2700)
	Wind-blown dusts	100 (50 - 850)
	Forest fires	12 (10 - 1500)
	Sea salt sprays	1.0 (1 - 400)
	Total	**843**
Anthropogenic sources [†]	Mining, non-ferrous metals	2.8
(during 1975 - 1976)	Production, non-ferrous metals	5316
	Production, iron and steel	72
	Industrial applications	53
	Coal combustion	62
	Oil and petrol combustion	2.8
	Wood combustion	200
	Waste incineration	1350
	Rubber tyre wear	10
	Phosphatic fertilizers	118
	Total	**7186**

[†] Source: Nriagu (1980b)
[‡] Values given in parentheses are ranges given by Pacyna (1986)

Chen *et al.*, 1991; Holmgren *et al.*, 1993). In the Santa Monica Mountains of Los Angeles and Ventura Counties (California) for instance, the average surface soil Cd concentrations can be directly related back to their original bedrock parent material (Lund *et al.*, 1981). While shale rock in this region contains 8 mg Cd kg^{-1}, the basalt rock is much lower (0.01 mg Cd kg^{-1}) and this difference is reflected by the overlying soil.

The parent material influence is reduced in more weathered and older soils because of mobilization and redistribution of elements within the soil profile and between neighbouring soils during pedogenic processes (Thornton, 1983; Adriano, 1986).

Table 2.2 Cadmium concentrations in some common crustal rocks.

Rock	Range			Mean	(mg Cd kg^{-1} rock)
Igneous					
Granodiorite	0.016	-	0.10	0.07	
Gabbro	0.08	-	0.20	0.11	
Granite	0.001	-	0.60	0.12	
Syenite	0.04	-	0.32	0.16	
Pitchstone	0.05	-	0.34	0.17	
Basalt	0.006	-	0.60	0.22	
Obsidian	0.22	-	0.29	0.25	
Metamorphic					
Ecologite	0.04	-	0.26	0.11	
Gneiss	0.12	-	0.16	0.14	
Garnet schist				1.0	
Sedimentary					
Sandstone				0.01	
Limestone, dolomites				0.035	
Shale				0.3	
Bituminous shale	0.3	-	11	0.8	
Bentonite	0.3	-	11	1.4	
Marl	0.4	-	10	2.6	

Source: Bewers *et al.* (1987), as cited by Cook and Freney (1988) and Kabata-Pendias and Pendias (1992).

Holmgren *et al.* (1993) commented on this in their study of trace elements in USA agricultural soils. These workers found that Cd concentrations were lowest in the strongly weathered Alfisols and Ultisols, and highest in Aridisols which had experienced little weathering. But, where the overlying soil has not resulted from *in situ* weathering, the influence of the underlying bed rock may be completely masked (Thornton, 1983).

In general, crustal rocks have been reported to range between 0.01 and 2.6 mg Cd kg^{-1}, but mean levels are generally below 0.25 mg Cd kg^{-1} (Table 2.2) (Bewers *et al.*, 1987, as cited in Cook and Freney, 1988). Some sedimentary rocks, e.g. shale, marl and bentonite, can have much higher Cd concentrations and soil developed from them can show Cd levels sufficiently high to constitute natural pollution. Although some high Cd rocks have been found in New Zealand, up to 2.5 mg Cd kg^{-1} for one shale, the major rock types generally average below 0.2 mg Cd kg^{-1} (J. S. Whitton, pers. comm.).

The relationship between elemental concentrations in parent material and those in the soil developed from it (*in situ*) therefore provides information on the source of a soil's heavy metal content. With inorganic elements that occur naturally in the environment, assessment of anthropogenic pollution cannot be done solely on the basis of top-soil samples and requires instead a knowledge of the concentrations from the entire profile (Blaser and Zimmermann, 1993) (see section 2.5). Comparison of topsoil with either subsoil or soil parent material has been used in several instances to separate the effects of anthropogenic inputs and natural heavy metal (including Cd) soil concentrations (Schmidt and Walter, 1988; Merry and Tiller, 1991; Blaser and Zimmermann, 1993; Holmgren *et al.*, 1993). This distinction appears important in light of evidence indicating that Cd from anthropogenic origins has greater plant availability than that of lithogenic origins (Grupe and Kuntze, 1988; Filipinski and Kuntze, 1990) (see section 2.6). Anthropogenic Cd would therefore represent a greater risk to the food chain.

2.4.2 Soil amendments

Application of chemical fertilizers such as superphosphate, diammonium phosphates and lime are regarded as normal agricultural practices needed to maintain soil productivity for sustained cropping or grazing (Holmgren *et al.*, 1993). However, the

18

use of sewage sludge, a common soil amendment overseas and frequently the subject of scientific studies into heavy metal contamination, is not widespread in commercial New Zealand agriculture.

Liming material

Limestones and dolomites generally have only low Cd concentrations – on average 0.035 mg Cd kg^{-1} (Table 2.2) – but information on this amendment as a Cd source to agricultural soils is not commonly available. Contents of trace elements in limestone formations can vary due to small veins and inclusions of other minerals and, as a result, soils amended repeatedly with trace metal-rich limestone could show increased trace metal concentrations (Mattigod and Page, 1983; Hansen and Schaeffer, 1995).

Phosphatic fertilizers

Cadmium contamination in New Zealand agricultural soils is widely believed to arise from the use of phosphatic fertilizer (Bramley, 1990; Roberts *et al.*, 1994; Taylor and Percival, 1992; Loganathan *et al.*, 1995 and 1997). Single superphosphate (SSP) describes phosphate containing material (e.g. bones, phosphate rock) which has been acidulated with sulphuric acid to produce a more soluble, faster release phosphate component. In New Zealand, it is manufactured from natural mineral calcium phosphate rock which, besides the predominant calcium- and phosphate- containing apatite minerals, also contains trace elements and impurities such as Mn, Co, Cu, Zn and Cd, As and uranium (U) in the mg kg^{-1} concentration range (Williams, 1977; Syers *et al.*, 1986). It is of concern that Cd present in this product has a high plant availability – similar to Cd from $CdCl_2$ (Williams and David, 1973).

During the manufacture of SSP very little of the original phosphate rock impurities are lost and instead they tend to remain in the final product in similar ratios to P as those in the raw material (Williams and David, 1973; Rothbaum *et al.*, 1986). The preservation of the P/Cd ratio during processing allows the Cd concentration in the fertilizer to be estimated where Cd concentrations have not regularly been determined. With the Cd issue being of only recent interest, this is often the case.

In contrast to the P concentration in phosphate rock, the Cd concentration can vary widely (e.g. 2 to 134 mg Cd kg^{-1} of rock; Syers *et al.*, 1986; Pulsford, 1989; Bramley, 1990). Rock used by the New Zealand fertilizer industry generally lies at the higher end of the Cd range (Table 2.3), and thereby present a substantial threat of Cd accumulation in New Zealand soils (Bramley, 1990). However, phosphorite sources for New Zealand manufactured fertilizer have changed over the last three decades and, as a consequence, so too has the Cd content of the final fertilizer product.

Prior to 1970, fertilizer production relied on the high P, high Cd guano-derived deposits of Ocean Island and Nauru Island (Table 2.3). But, post-1970 these earlier sources began to be blended with the lower P, lower Cd containing rock of Christmas Island (Williams, 1985). Although both Ocean Island and Christmas Island are now closed (in

Table 2.3 Cadmium and phosphorus contents of phosphate rock used in New Zealand to manufacture superphosphate. [†]

Phosphate Rock	Cd content (mg/kg rock)	P content (%)	P/Cd ratio in rock (mg P/mg Cd)
Ocean Island	**134** [a]	**-**	**1269**
	-	**17** [f]	
	99 [g]	-	
Nauru Island	**88** [a]	**-**	**1818**
	-	**16 (to 17)** [f]	
	100 [b]	15.6 [b]	1560
	71 [c]	15.9 [c]	2239
	75 - 110 [d]	16.8 [d]	2240 - 1527
Christmas Island	**38** [a]	**-**	**4316**
	-	**16.4** [e]	
	30 - 50 [d]	15.2 [d]	5067 - 3040
North Carolina	**40** [d]	**13.4** [d]	**3350**
	54 [a]	-	-
	39 [c]	11.9 [c]	3051
Jordon	4 - 8 [d]	14.8 [d]	
Sechura	11 - 12 [a, b]	13.1 [b]	

† Values in bold relate to the concentrations of Cd and P used to construct the Cd mass balances discussed in Chapter 8.

[a] Bramley (1990)
[b] Syers *et al.* (1986)
[c] Loganathan and Hedley (1993)
[d] Pulsford (1989)
[e] Bolan *et al.* (1993)
[f] During (1984)
[g] Williams (1974)

1979 and 1988 respectively [Williams, 1985]), Nauru rock continues to be used in conjunction with rock from North Carolina (USA), Jordan and/or Khouribga (Morocco) (M J Hedley, pers. comm.). Because the Cd contents of these new rocks are generally much lower than those of the South Pacific Islands (Table 2.3), their use has reduced substantially the Cd content of New Zealand produced SSP fertilizers.

Although the current focus for Cd contamination of SSP centres on the Cd content of the raw phosphorite, SSP produced earlier this century may have also gained Cd from the sulphuric acid used in the acidulation process. Sulphuric acid derived as a by-product of ZnS ore production often had a considerable Cd content itself and this was added to the final fertilizer product (Walkley, 1940; Peterson and Alloway, 1979). In contrast, phosphatic fertilizer prepared with phosphoric acid contains less than 70% of the original rock Cd as a result of partitioning between the fertilizer and a by-product, phosphogypsum (Mortvedt, 1996).

The rate of Cd addition from phosphatic fertilizer depends on both the final fertilizer Cd content and the fertilizer application rate – which is based on P fertility requirements. Given a fertilizer rate of 33 kg P ha^{-1} yr^{-1}, Rothbaum et $al.$ (1986) estimated that 5 g Cd ha^{-1} was added annually to grassland experiments in England, but 20 g Cd ha^{-1} yr^{-1} accompanied the application of 37 kg P ha^{-1} yr^{-1} to a New Zealand soil. The difference in these addition rates was attributed to the higher Cd content of phosphate rock used in the manufacture of New Zealand SSP from 1954. In more recent studies, however, Cd application rates are lower (9.7 - 14 g Cd ha^{-1} yr^{-1} for a P rate of 30 - 38 kg P ha^{-1} yr^{-1}) and reflect the dilution of the Nauru rock with rocks lower in Cd such as Christmas Island and North Carolina (Loganathan et $al.$, 1995, 1997).

A unique feature of phosphatic fertilizers is the strong relationship between their P content and their Cd and Zn contents (Williams and David, 1973). This strong P-Cd relationship in the fertilizer translates into a significant correlation between P and Cd in the surface layer of SSP fertilized soils and thereby indicates a strong link between Cd accumulation and phosphatic fertilizer application (Williams and David, 1973; Mulla et $al.$, 1980; Hilliard et $al.$, 1988; Roberts et $al.$, 1994; Loganathan et $al.$, 1995). It appears, however, that this correlation does not extend to the soil solution (Mulla et $al.$, 1980).

Zinc and Cd are closely associated in the natural environment (section 2.2) and this includes an association in phosphate rock which persists in the final P fertilizer (Williams and David, 1973). However, the Zn to Cd ratio in phosphatic fertilizers (10:1) is much smaller than that found in either: non-agricultural soils (180:1 to 1120:1; Roberts *et al.*, 1994); or terrestrial rock (approximately 250:1; Adriano, 1986). Hence, the application of phosphatic fertilizer to soil decreases this ratio. Therefore the lower soil Zn/Cd ratios in agricultural soils, compared to matched natural soils, provides another means of confirming phosphatic fertilizer as a major source of Cd (Holmgren *et al.*, 1993; Roberts *et al.*, 1994; Loganathan *et al.*, 1995).

2.4.3 Atmospheric cadmium of anthropogenic origins

Industrialized regions throughout Europe and the United Kingdom experience significant Cd inputs from atmospheric pollution (Jones *et al.*, 1987; Jackson and Alloway, 1992; Kabata-Pendias and Pendias, 1992; Tjell and Christensen, 1992; Mortvedt, 1996). Similarly, a regional budget calculated by Merry and Tiller (1991) for South Australia had Cd inputs almost equally divided between phosphate fertilizers and atmospheric deposition (3.3 and 3.0 g Cd ha^{-1} yr^{-1} respectively). However, a study in Christchurch (New Zealand) showed that, while Cd deposition close to the city (< 20 km) could average over 2 g Cd ha^{-1} yr^{-1}, at distances above 36 km, this reduced to < 0.1 g Cd ha^{-1} yr^{-1} (Fergusson and Stewart, 1992). These values suggest that Cd deposition from atmospheric pollution is of less concern in New Zealand than other countries.

Land surrounding a major atmospheric point source commonly shows a halo of soil pollution in the down-wind direction. Metal concentrations can be elevated for up to 20 km, or sometimes more (Chaney and Hornick, 1977; Tiller, 1988; Tiller, 1989). Roadside soils also commonly show Cd pollution derived from tyre wear and exhaust emissions. This pollution is, however, limited to comparatively short distances (Williams and Harrison, 1986).

2.4.4 Atmospheric cadmium of natural origins

Cadmium deposition from the natural sources given in Table 2.1 are more difficult to quantify due to a paucity of measurements on emission or mobilization rates from these sources (Hutton, 1982).

Information on additions of Cd to coastal soils from sea salt spray is sparse and seldom considered in metal input budgets. An idea of the relative importance of this as a Cd source can be obtained, however, from a comparison of the Cd content of ice sampled from the Antarctic and Artic Oceans (0.3 pg Cd g^{-1} and 5 pg Cd g^{-1} respectively) (Wolff and Peel, 1985). Assuming that seawater in the Antarctic Ocean contains only naturally-occurring Cd while seawater in the Artic Ocean has been influenced by atmospheric pollution, it can be seen that the Cd contribution possible from sea spray is likely to be much less than that from atmospheric deposition.

Wind blown dusts are also seldom considered to be of major importance when constructing Cd budgets for atmospheric deposition (Hutton, 1982; Merry and Tiller, 1991). Given the predominance of vegetative ground cover in New Zealand this is probably the case here also. At the remote site studied by Fergusson and Stewart (1992), soil-derived atmospheric deposition of Cd was estimated to be only 0.02 g ha^{-1} yr^{-1}. This is insignificant compared with the possible addition rate to New Zealand soils from phosphatic fertilizers (10+ g Cd ha^{-1} yr^{-1}) (section 2.4.2).

In contrast to the above Cd sources, volcanic activity has the potential to contribute significantly to atmospheric Cd loads (Hutton, 1982). A study by Buat-Ménard and Arnold (1978) indicates that, compared to background levels (0.01 - 0.04 ng m^{-3}), airborne Cd concentrations around volcanoes may be significantly elevated (about 90 ng m^{-3}). The central North Island of New Zealand has an extensive history of volcanic activity. However, analysis of ash from the Mount Ruapehu eruptions of October 1995 showed low concentrations of Cd (< 0.11 mg Cd kg^{-1} dry ash) with water-soluble Cd concentrations less than 0.0054 mg Cd kg^{-1} dry ash (S. J. Cronin, pers. comm.). These values are well below the Cd concentrations present in New Zealand SSP (32 mg Cd kg^{-1} Cd and 29 mg Cd kg^{-1} for total water-soluble Cd respectively) (Loganathan and Hedley, 1997). The indication is, therefore, that volcanic emissions may not always constitute a significant source of atmospheric Cd.

2.5   CADMIUM DISTRIBUTIONS DOWN THE SOIL PROFILE

Comparison of Cd concentrations in the surface soil with those from depth provides a

means of differentiating between anthropogenic Cd and Cd derived from *in situ* weathering of the parent bedrock material. Thus, the Cd distribution pattern within the soil profile as a whole, provides greater information on the probable sources of Cd than would be possible if only topsoil Cd concentrations were considered (Filipinski and Grupe, 1990; Haygarth and Jones, 1992; Blaser and Zimmermann, 1993). Holmgren *et al.* (1993) suggest a ratio of more than one for the surface soil Cd concentration/subsoil Cd concentration as a means of identifying soils with anthropogenic contamination.

While providing evidence for the source of soil Cd, the distribution of Cd within a soil profile is also important because of its effect on plant uptake. For example, increased uptake may occur where high Cd concentrations coincide with zones of intense root activity. This may be enhanced by the presence of other soil constituents, such as phosphorus, that stimulate root development (Williams and David, 1977). In addition, Cd at different depths in the soil may have different plant availability because of changes in the chemical and physical properties of the soil, particularly soil pH and soil organic matter (Loganathan and Hedley, 1997; see also section 6.2).

2.6 CADMIUM CONCENTRATIONS IN SURFACE SOILS

Entry of soil Cd into the food-chain comes predominantly from stores in the surface soil. A knowledge of Cd concentrations in the surface soil and how these compare with background Cd concentrations enables us to assess the present and future threat posed by Cd. This then permits the formulation and implementation of strategies to minimize the impact of Cd on the environment.

Views differ as to the most useful way of reporting Cd concentrations. The degree of soil contamination is best determined by total Cd, but Cd risk to the food-chain is best assessed by methods that identify plant-available Cd (De Temmerman *et al.*, 1984). In addition, inconsistency in soil sampling depth has introduced some confusion when comparing soil Cd levels on a global basis. Because the Cd concentration invariably decreases with soil depth (section 2.5), Cd concentrations reported for surface-soil samples taken to a deeper depth are diluted compared to those based on shallow sampling depths. Thus, Cd concentrations in New Zealand agricultural soils, where the

sampling depth is commonly 0 - 7.5 cm, may appear greater than those in European agricultural soils where sampling depths are more likely to be around 0 - 20 or 0 - 25 cm – the depth of the plough layer, Table 2.4 (Tjell and Christensen, 1992; Roberts et $al.$, 1994).

A global range for the concentration of Cd in soils has been suggested as 0.06 - 1.1 mg kg^{-1} by McBride (1994). The position of a soil in this global range will be influenced by human impact and environmental factors such as: its state of weathering; parent material concentrations (section 2.4.1); and its capacity to adsorb and retain metals – sandy soils, for example, generally have lower trace metal concentrations than silty or clayey textured soils (Peterson and Alloway, 1979).

The average global Cd concentration for surface soils has been estimated to be 0.53 mg Cd kg^{-1} by Kabata-Pendias and Pendias (1992). These authors further propose that soils showing Cd concentrations greater than this mean value are likely to be contaminated. However, in view of the wide range of Cd concentrations possible in soils (some examples are given opposite in Table 2.4), such a global value is of little use. Because New Zealand agricultural soils have relatively low Cd concentrations compared to the above global averages (Table 2.4), Cd contamination of soils in this country would be better assessed through a comparison with local, unpolluted soils (Tiller, 1989).

2.6.1 Unpolluted soils

Natural, normal or background Cd concentrations are those concentrations found in soils, waters, plants and other environmental matrices not impacted by pollution levels (Adriano, 1986). This requires the exclusion of soils experiencing obvious pollution from point sources, mining activities, roads or sewage sludge application (Kabata-Pendias and Dudka, 1991; Chen et $al.$, 1991; Holmgren et $al.$, 1993), but some studies also exclude contamination caused by normal agricultural practices such as fertilization (De Temmerman et $al.$, 1984; Roberts et $al.$, 1994). Thus there is some inconsistency when defining "background" concentrations.

On the whole, truly pristine New Zealand soils show low Cd concentrations since bedrock materials naturally high in Cd are not widely associated with New Zealand

Table 2.4 Mean total Cd concentrations in surface soils from around the world. The range for each survey is given in parentheses.

Country	Soil sample depth (cm)	Extraction method	Agricultural soils (mg Cd kg^{-1} dry soil)	No. of Samples	Non-agricultural soils (mg Cd kg^{-1} dry soil)	No. of Samples	Reference
New Zealand [†]	0 - 7.5	HClO$_4$-HNO$_3$	0.44 (0.04 - 1.53)	[312]	0.20 (0.02 - 0.77)	[86]	Roberts *et al.* (1994)
New Zealand	0 - 15	4 N HNO$_3$	0.69 (0.46 - 1.91)	[22]			Taylor and Percival (1992)
Poland [‡]		HF-HClO$_4$	0.41 (0.1 - 6.5)				Kabata-Pendias and Dudka (1991)
Mainland China		HNO$_3$-HF-HClO$_4$	0.097	[3947]			Chen *et al.* (1991)
Tibet		HNO$_3$-HF-HClO$_4$	0.080	[193]			Chen *et al.* (1991)
USA	0 - 20	HNO$_3$	0.265 (< 0.010 - 2.0)	[3045]			Holmgren *et al.* (1993)
Australia	0 - 5	0.1 M EDTA, 7 days at pH 6 [§]	0.18 (0.01 - 0.73)	[516]	0.11 (0.01 - 0.29)	[69]	Merry and Tiller (1991)
Denmark	0 - 20	Hot 6M HNO$_3$, 24 hrs	0.215 (0.012 - 0.494)	[65]			Tjell and Christensen (1992)
Sweden	0 - 20	2 M HNO$_3$, 2 hrs	0.22 (0.03 - 2.3)				Andersson (1977)
Netherlands Sandy soils Clay soils			0.32 0.41		0.08 0.25		Lexmond *et al.* (1986) and Salomons (1983), as cited by Harmsen (1992)
Canada					0.07 (0.01 - 0.1)		Alloway (1995a)

[†] Adjusted to a sampling depth of 20 cm, these become 0.27 and 0.12 mg Cd kg^{-1} soil for agricultural and non-agricultural soils respectively (Roberts *et al.*, 1994).
[‡] Expressed as geometric mean. Rural North-eastern Poland, believed to indicate soil Cd levels less affected by atmospheric pollution, gave 0.27 mg Cd kg^{-1} soil.
[§] Reported by authors to recover about 90% from polluted soils and 25 - 50% from unpolluted soils.

lithology (section 2.4.1). The average Cd concentration for native soils found by Roberts *et al.* (1994) (Table 2.4) falls well below the 1.0 mg Cd kg^{-1} which Jackson and Alloway (1992) estimate as a maximum for uncontaminated soils. This further demonstrates the irrelevance of global averages for establishing Cd contamination in New Zealand soils.

2.6.2   Contaminated soils

The term contamination is used to describe instances where a soil has statistically higher elemental concentrations than soils of the same classification which represent background concentrations, but the concentrations concerned may not always be detrimental to the environment (Dr. R. Chaney, pers. comm.). More serious cases of contamination, i.e. when concentrations reach levels capable of causing adverse effects on some part of the environment (e.g. plants, humans or soil organisms), are covered by the term "pollution". This may include instances of natural metal pollution (Mattigod and Page, 1983).

Based on the above definitions, it is apparent that New Zealand agricultural soils are showing signs of Cd contamination – Table 2.4 (Roberts *et al.*, 1994). Despite Roberts *et al.* (1994) being able to conclude that the Cd status of New Zealand soils generally falls at the lower end of the global range for Cd, a study targeting important agricultural regions in New Zealand has demonstrated the presence of soils with Cd concentrations greater than 1 mg Cd kg^{-1} (Taylor and Percival, 1992) (Table 2.4).

2.7   CADMIUM ACCUMULATION IN TOPSOIL

Numerous mass balance studies have reported the recovery of most added Cd in the surface horizon (Williams and David, 1973, 1976; Mulla *et al.*, 1980; Loganathan and Hedley, 1997). Loganathan and Hedley (1997), for instance, found that almost 90% of Cd applied to a New Zealand pasture over 10 years (as phosphatic fertilizer) could be accounted for in the top 12 cm of soil. However, not all studies have been able to detect measurable Cd accumulation. Work done on cropped land has found that low additions of Cd, such as from low Cd superphosphate, do not increase the soil Cd burden (Yost, 1979; Rothbaum *et al.*, 1986; Jones *et al.*, 1987; Mortvedt, 1987). Since current

international concern regarding this element centres on its potential to accumulate in soil, the reason why some studies fail to find evidence of Cd accumulation requires further investigation.

The apparent lack of Cd accumulation in some soils could arise from several factors: a difficulty in detecting the small Cd additions, particularly from low Cd fertilizers, that probably amount to less than 1% of the total surface soil Cd burden (Yost, 1979; Hutton, 1982); redistribution of the added Cd over large depths of soil through ploughing, thereby concealing increases in Cd concentration (Tiller, 1989); and Cd loss from the soil in numerous ways, for example through product removal (particularly crops), erosion and leaching (Williams and David, 1976; Rothbaum et al., 1986; McGrath and Lane, 1989; Tiller, 1989; Merry and Tiller, 1991). On the whole, however, Cd losses through the removal of grain, forage and livestock products, leaching and soil erosion are considered small compared to inputs, especially those from fertilizers containing Cd at high concentrations (e.g. 50 ppm) (Yost, 1979; Merry and Tiller, 1991; Korentajer et al., 1993; Mortvedt, 1996). In such cases, Cd accumulation in the soil profile is almost certain.

Accumulation rates of Cd in New Zealand topsoils have been estimated to be 9 g Cd ha^{-1} yr^{-1} (Rothbaum et al., 1986) and 11 g Cd ha^{-1} yr^{-1} (M. D. Taylor, pers. comm.). If a bulk density of 1 g cm^{-1} is assumed, and the sampling depth is taken as 7.5 cm, these accumulation rates will cause soil Cd levels to exceed the 3.0 mg Cd kg^{-1} soil guidelines (Department of Health, 1992) within 300 years.

Once in the soil, Cd can be expected to remain there for many thousands of years (McGrath, 1987; Witter, 1996; Loganathan and Hedley, 1997). This is especially the case in New Zealand with our animal grazing regime where little Cd is lost from the system through animal products. Loganathan and Hedley (1997) calculated that the residence time for Cd in soils under such a grazing regime would exceed 20 000 years. If this soil was cropped instead, the residence time would be only 200 - 700 years (Loganathan and Hedley, 1997). With such evidence of long-term, almost irreversible increases in soil Cd concentrations, actions to minimize the impact of Cd additions on the food-chain have become more widespread.

2.8 CONTROL POLICIES TO MINIMIZE THE CADMIUM THREAT

The greatest concern appears to be in preventing excessive Cd concentrations in edible foods, both present and future (Tiller, 1989; Roberts *et al.*, 1994). However, it should also be recognized that the soil is a living medium, and is the basis of food production for all species as well as being fundamental to the purification of ground water (de Haan *et al.*, 1987; Witter, 1996). Minimizing the Cd burden in the system as a whole is therefore desirable.

Many countries have legislation to restrict heavy metal loadings in soil caused by sewage sludge application. These are generally directed towards minimizing heavy metal contents of the sludge, regulating sludge application rates (based on soil factors and heavy metal concentrations), and the setting of maximum permissible heavy metal concentrations in agricultural soils (Tiller, 1989; Mortvedt, 1996; Witter, 1996). Such regulations must also consider the possibility of future changes in land use and soil properties that may influence Cd mobility.

As attention has turned towards Cd inputs accompanying fertilizer use, similar policies have been developed for phosphatic fertilizer, though regulations mainly focus on setting maximum permissible Cd concentrations of the fertilizer based on the Cd/P contents (Bøckman *et al.*, 1990; Mortvedt, 1996). Such limits (voluntary or otherwise) range from 35 mg Cd kg^{-1} P in the Netherlands to around 350 mg Cd kg^{-1} P in Australia and Japan (no limit exists in the USA) (Mortvedt, 1996).

Removal of Cd from phosphatic fertilizer or its precursors is difficult (Ghoshesh *et al.*, 1996). In New Zealand there is currently no commercial process to do this (M J Hedley, pers. comm.). Overseas, limited use is made of calcination processes to remove Cd from the phosphate rock (Ghoshesh *et al.*, 1996). Nonetheless, international research in this area continues. Thermal treatment for phosphate rock (Kossir and Chik, 1996), and processes to remove Cd from the fertilizer precursor, phosphoric acid (Davister, 1996; Ghoshesh *et al.*, 1996; Vermeul, 1996) are two such areas under study. In addition, Loganathan and Hedley (1997) recently reported an association between Cd and organic matter in the North Carolina phosphate rock. It may be that alkaline removal of the organic matter will provide another means of removing Cd (M. J. Hedley, pers. comm.).

With only finite global reserves of phosphate rock, low Cd phosphate rock will command a premium price, putting financial strain on the fertilizer industry and ultimately the farmer. Because of this and the inevitable depletion of low Cd phosphate rock sources, the higher (> 20 ppm) Cd rocks (about 60% of global reserves; Roberts and Stauffer, 1996) must continue to be used. Hence, Cd inputs to the soil environment look certain to continue in the near future.

Where the focus is on protection of human health, the threat of Cd can be minimized at several stages in the food chain (Chaney and Hornick, 1977; Simpson and Curnow, 1988; Roberts *et al.*, 1994; Grant *et al.*, 1997).

Soil to plant transfer: Transfer of Cd from soil to plant can be restricted through: liming to raise the soil pH, thereby reducing Cd solubility and consequently plant uptake; limiting the cropping species to those plants which show low Cd accumulation; elimination of micronutrient deficiencies, especially zinc; control of soil salinity (the effect of Cl^- is investigated in Chapter 6); and encouraging the growth of grasses and legumes over higher Cd-containing weeds in pasture swards through appropriate grazing management and fertilizer policies.

Plant to animal transfer: Because young sheep were found to accumulate Cd most rapidly up to 6 months of age (accumulation rates decline thereafter), Lee *et al.* (1996) propose that Cd concentrations in adult animals could be minimized by reducing their exposure to Cd when young.

Foodstuffs to humans: The final barrier preventing Cd entry into the human population through diet is the exclusion of produce which carries a high Cd risk. Current New Zealand regulatory policy, for instance, requires the exclusion from export sale of kidneys from all stock over 30 months of age. This assists compliance with the 1 mg Cd kg^{-1} FW maximum residue limit.

2.9 SUMMARY

Cadmium is a toxic element whose dispersion in the environment has become of

concern in recent years due to an awareness that chronic poisoning in humans can develop from long-term, low level exposure. It enters the food-chain mainly through plant uptake from soil, and accumulates in the kidneys and liver of domestic animals and humans causing a disruption to organ functioning at sufficiently high concentrations.

In view of the important role plant uptake plays in the Cd cycle, plant availability of soil Cd has received much focus. Many factors influence this availability, including the source and distribution of Cd in the surface soil, individual plant characteristics and soil properties, especially pH.

Evidence that surface soil Cd concentrations are increasing with time has prompted researchers and official organizations to assess the threat that this accumulating Cd poses to the human population. Consequent work has identified the predominant sources of soil Cd as atmospheric pollution and land management practices such as sewage sludge and phosphatic fertilizer application. Many countries now have guidelines to limit or reduce Cd additions through these means. However, increased plant concentrations have not always been correlated with increasing soil Cd concentrations and therefore views on the seriousness of the Cd threat vary substantially.

Work on the Cd cycle in New Zealand soils is sparse, but developing rapidly with the main focus being pastoral soils. Here, the Cd accumulation which has been found has generally been attributed to phosphatic fertilizer use. But a comprehensive study of Cd sources including parent material is lacking. This thesis therefore aims to advance current knowledge of Cd behaviour in the following areas:

- the concentrations and distribution of endogenous and fertilizer-derived Cd in a range of soil types on a typical hill country farm that has received regular applications of superphosphate fertilizer;
- and the factors involved in the redistribution of Cd in the soil profile and therefore its residence time in the plant root zone.

CHAPTER 3
MATERIALS AND METHODS FOR THE PREPARATION AND ANALYSIS OF SOIL AND HERBAGE SAMPLES

3.1   INTRODUCTION

Methods are described here for the preparation and chemical analysis of soil and plant material used in this study. The majority of analytical work involved the measurement of Cd concentrations at trace levels, consequently this forms the major focus of the research methodology (section 3.2). A brief discussion of several considerations pertinent to trace element analysis – contamination control, accuracy and precision of results – is also included. Determinations of other elements and soil properties were also carried out. The materials and methods for these are detailed in section 3.3. Methods unique to specific studies are described in the appropriate chapter. In addition, deviations from the generic methods presented below – as a consequence of some method development – are likewise detailed in the appropriate chapter.

3.2   TRACE CADMIUM ANALYSIS

Trace element analysis often demands low levels of detection. Although the detection levels attainable are essentially determined by the chosen instrumentation, the overall method detection limits are constrained by background contamination and sample preparation. Hence, highly sensitive analytical equipment, a clean environment and an awareness of potential element loss during preparation or storage of samples are all important to trace metal analysis. These aspects of trace metal analysis are discussed below in view of their relevance to the methods used in this study.

3.2.1   Contamination control
Contamination arises from numerous sources and includes: unclean laboratory equipment; airborne dust particles; and impurities in reagents (Slavin *et al.*, 1983). Clean-room facilities become mandatory for working on trace metals at low concentrations in complex matrices, especially when pre-concentration procedures are required because of the increased sample handling and increased risk of environmental contamination (Manning and Slavin, 1983). Several studies report that contamination

problems are more easily controlled with respect to Cd than elements such as copper, lead, zinc and iron (Manning and Slavin, 1983; Adeloju and Bond, 1985). Accordingly, although Adeloju and Bond (1985) found the analytical blank for Cd in a conventional laboratory was 5 times higher (0.050 ± 0.002 µg Cd L^{-1}) than a blank left exposed for 30 minutes in a clean room, the contamination was low enough to permit   accurate trace analysis without needing clean-room facilities. Work carried out during this study did not use clean-room facilities, but the consistently low procedural blank readings verified that contamination was under control.

In trace metal methodology, frequent mention is made of acid washing and deionized water rinsing of laboratory-ware. Furthermore, the use of high purity chemicals is standard. These measures safeguard against most extraneous Cd. However, other sources of contamination are not always so obvious. Because Cd compounds find use in colouring, most coloured plastic-ware or paint presents a risk of contamination. This is especially the case for yellow and red colours that are associated with cadmium sulphide, and cadmium selenide, (N. Kim, pers. comm.). As an example, Kim (1990) found that substantial amounts of Cd were leached from the red and yellow markings painted on a new batch of glass pipettes when these were acid washed. The use of Cd as a plastic stabilizer also introduces it into other coloured articles. On finding red and yellow plastic volumetric-flask tops to contain significant quantities of Cd, Kim (1990) opted for polypropylene and glass stoppers. For the same reasons, Manning and Slavin (1983) recommended avoiding yellow Eppendorf pipette tips.

During this study every effort was made to minimize contact of samples with sources of possible contamination. Colourless or white plastic-ware was used almost without exception in most stages of preparation and analysis. After testing for trace Cd contamination (by soaking in acid solution which was then analyzed) revealed no contamination risk, polypropylene storage tubes were used as new. All laboratory-ware was acid-washed at the start and kept clean by washing with Pyroneg detergent or soaking in acid, and rinsing in deionized water. High purity chemicals (Aristar) and deionized water were used for all Cd analyses.

3.2.2   Loss of cadmium from samples

Although contamination presents a major, obvious concern in trace element analysis, full recovery of the element from the sample is also important and potential losses should be considered (Versieck and Vanballenberghe, 1994). Cadmium can be lost from sample solutions through adsorption onto container walls or loss through volatilization during sample preparation. The first of these, Cd loss through sorption, can be minimized by acidifying the sample solution and analyzing as soon as possible after preparation. But, because Cd is a relatively volatile metal (boiling point 767 ^{o}C), loss during sample preparation (e.g. concentrated acid digestion) is best avoided by using procedures that do not require boiling (Förstner, 1980).

3.3   SOIL SAMPLE PREPARATION AND ANALYSIS

Field soil samples were air dried, coarsely ground using a porcelain mortar and pestle until they passed through a 1 mm (plastic) sieve, and stored in sealed plastic bags at room temperature. Subsamples for total elemental analysis were ground to fineness using the same mortar and pestle and similarly stored.

Risk of contamination from mechanical grinding equipment was avoided – with the exception of limestone rock from soils studied in Chapter 4 (these required ring-grinding) and topsoil samples from the bush sites studied in Chapter 5 (which required incorporation of the leaf litter by hammer mill).

In some cases, soil samples were collected and prepared as part of other studies (Chapter 4 and Chapter 8). However, the very low Cd concentrations found in some of these soils gave confidence that no systematic contamination from their collection and preparation had occurred.

Unless stated otherwise, Cd analysis was performed by the method of graphite furnace atomic absorption spectrometry (GFAAS) as summarized in section 3.5. The following sub-sections describe the chemical preparations used for soil samples and provide a comparison of these methods with respect to their Cd recoveries. Data collected during laboratory work for quality assurance purposes are also presented (section 3.3.4).

3.3.1   Extractable cadmium

Predicting the plant-availability of trace metals is an inexact science. Not all extractions produce strong correlations with plant metal-uptake for all situations. The true plant-availability of soil Cd depends on many factors, including: the form of Cd added to the soil (as fertilizer, atmospheric deposition, or bedrock); the properties of the receiving soil, in particular soil pH; and the ability of plants to absorb Cd from the soil solution (Hornburg and Brümmer, 1990; He and Singh, 1993a). In addition, correlations between chemically estimated plant-available Cd and actual plant-available Cd are confounded by the tendency of greenhouse-grown plants to show greater Cd absorption compared to the same plants cultivated under field conditions (Van Bruwaene *et al.*, 1986).

Selecting an extractant, therefore, seems to be a somewhat arbitrary decision with its subsequent effectiveness depending on many environmental factors (Neuhauser and Hartenstein, 1980; He and Singh, 1993b). The lack of an international standard method for determining plant-availability of soil Cd has resulted in a multitude of extraction methods (with associated variations) being applied world-wide. Each of these extractions varies in its ability to recover Cd from the soil. Recent research suggests, however, that better indications of plant-available Cd may be provided by the use of neutral salts such as $CaCl_2$ and NH_4Cl (Sauerbeck and Styperek, 1985; Krishnamurti *et al.*, 1995; Andrewes *et al.*, 1996).

In this study, a 0.1 M HCl extraction was used to indicate the potential plant-availability of Cd in soil samples. This extraction had previously been shown by Lee *et al.* (1993) to be strongly correlated with plant Cd uptake under New Zealand conditions where fertilizer was the main source of Cd. The method is described below.

Method for Extractable cadmium

Air-dried samples of 1 or 2 mm sieved soil (5 ± 0.0050 g) were weighed into 50-mL polypropylene centrifuge tubes and 25 mL of 0.1 M HCl was added. The mixture was shaken end-over-end for 16 hours. After centrifuging at 8000 rpm for 10 minutes the extract was filtered through Whatman No. 41 filter paper. This extract solution was then submitted to RJ Hill Laboratories, Hamilton, for analysis by flame atomic absorption spectroscopy with a slotted quartz atom trap to enhance sensitivity.

3.3.2   Total cadmium

Two digestion procedures were used during this study for determining total element concentrations. One method used concentrated nitric (HNO_3) and hydrochloric (HCl) acids, and is referred to as *pseudo-total Cd*, the other method involved hydrofluoric (HF) and concentrated nitric acids, and is referred to as *total Cd*.

Generally a close approximation of total Cd can be obtained by digesting with the mixture of HNO_3 and HCl concentrated acids. In many studies the Cd concentration determined by digestion with concentrated acids is regarded as 'total Cd' – for example De Temmerman *et al.* (1984), He and Singh (1993a) and Roberts *et al.* (1994). However, where there is an interest in Cd associated with resistant minerals such as silicates, HF acid is required to dissolve completely all components of the soil. In Chapter 4, for instance, it was necessary to identify all possible sources of lithogenic Cd, including any Cd that may have been incorporated in the silicate minerals of the parent material. For this reason most of the soil materials studied were subjected to digestion by HF acid.

The use of HF acid is hazardous and the selected digest procedure was slow. Consequently, with its less time consuming and less hazardous nature, the *pseudo-total Cd* digest replaced the HF-based *total Cd* digest during some other parts of this study – notably for analysis of Cd in soil samples taken from the soil columns discussed in Chapter 6. A comparison of the Cd recoveries for the two methods, *pseudo-total* and *total*, is presented later (see section 3.3.3).

During the course of laboratory work both the *pseudo-total* and *total* digest methods under went some degree of development. Soil samples low in organic matter were noted to give a cleaner digest (better for analysis by GFAAS), and so a step involving hydrogen peroxide was introduced at the beginning of both digest methods. The improved procedures described below are a culmination of this method development and include modifications such as: soaking the digested residue overnight in 1% w/v HNO_3 solution to improve dissolution and subsequent recovery of the Cd; the use of refluxing-funnels to improve digestion efficiency in the *pseudo-total* digest; the removal

of organic matter by an H_2O_2 oxidation step; and the addition of HF only once during the *total Cd* digestion thereby reducing the digestion time.

A dilute, 1% w/v HNO_3 solution was used as the diluent matrix for all soil digests. Nitric acid was chosen over HCl because of problems caused by chloride interference in the use of flameless AAS for Cd analysis (section 3.5). A 1% w/v HNO_3 solution would also minimize Cd sorption onto the plastic storage tube walls.

Method for total cadmium

Samples of air dried, finely ground soil (0.5 ± 0.0050 g) were accurately weighed into 100 mL polypropylene tri-pore beakers, 10 mL of 6% hydrogen peroxide solution added, and the beakers placed in a 100 $^{\circ}$C water bath (supported by a polypropylene rack). At this concentration of H_2O_2 only slight foaming from the reaction with organic matter was observed. The samples were evaporated to dryness, 5 mL of concentrated Aristar HNO_3 added, followed by 10 mL of 40% Aristar HF (using an acid-washed 20 mL Teflon measuring cylinder) shortly after. This mixture was left overnight and evaporated to dryness on the water bath the next morning. A further 2.5 mL of concentrated HNO_3 was added and HF boiled off by further heating on the water bath.

The dry residue was then warmed in about 10 mL of 1% w/v HNO_3 and left overnight before being made up to 25 mL with 1% w/v HNO_3. The solution was then decanted off into storage tubes ready for analysis by GFAAS (section 3.5). Procedural blanks (differing only in that they contained no soil) and standard soils (international standards and laboratory quality control standards) were included in all digest batches.

Method for pseudo-total cadmium

The ratio of HNO_3 to HCl used varies between workers, but in this study a ratio of 1:4 (HNO_3-HCl) was chosen (J. Lee, pers. comm.). Method development specific to this procedure included the use of glass funnels to give refluxing conditions (as a result of lower recoveries for standard soils during analysis of soils from Chapter 4) and overnight soaking of the digested material in the 1% w/v HNO_3 solution. The full method is described below.

Samples of air dry, finely ground soil (0.5 ± 0.0050 g) were weighed into 50-mL conical flasks and 10 mL of 6% H_2O_2 added. The conical flasks were then placed on a heating block and warmed gently, to prevent excessive foaming, until the reaction had finished. At this stage the heating-block temperature was increased to around 85 $^{\circ}$C and all liquid evaporated off. After allowing the flasks to cool, 10 mL of HNO_3-HCl mixture (1:4) was added, swirled and left to stand overnight with small, glass funnels (stem down) placed in each flask.

The solution was then refluxed until cessation of brown fumes (about 1 hour), at which stage the glass funnels were removed. The digest continued until samples reached near dryness, at which stage they were removed from the hot plate. Following cooling of the flasks, exactly 20 mL of 1% w/v HNO_3 was added by pipette to each digest sample. The flasks were then covered and left overnight to soak. Mixing, settling and decanting of the solution into storage tubes took place the following day.

Problems with this method were noted if the hot plate temperature was set too high. Acid solution was occasionally ejected from the flasks during digestion, and evaporating past the point of near-dryness caused baking of soil residue onto the flask bottom. In addition, there is the possible volatilization of Cd (Förstner, 1980). However, close attention to the above methodology, especially keeping evaporation to near dryness, minimized such losses.

3.3.3 Comparison of cadmium extraction efficiencies

Total cadmium versus pseudo-total cadmium

A comparison of the Cd concentrations, as determined by the HF digestion (*total Cd*) and concentrated HNO_3/HCl digestion (*pseudo-total Cd*) (section 3.3.2), is presented in Figure 3.1 for soil material taken from various depths from the soil profiles studied in Chapter 4.

It appears that the pseudo-total Cd digestion procedure used in this study is only recovering an average of 86% of the total Cd. This recovery often, but not always, decreased with depth down the profile and was also quite variable between soils (data not shown). Over the 17 soils for example, recoveries of Cd from the A horizon ranged
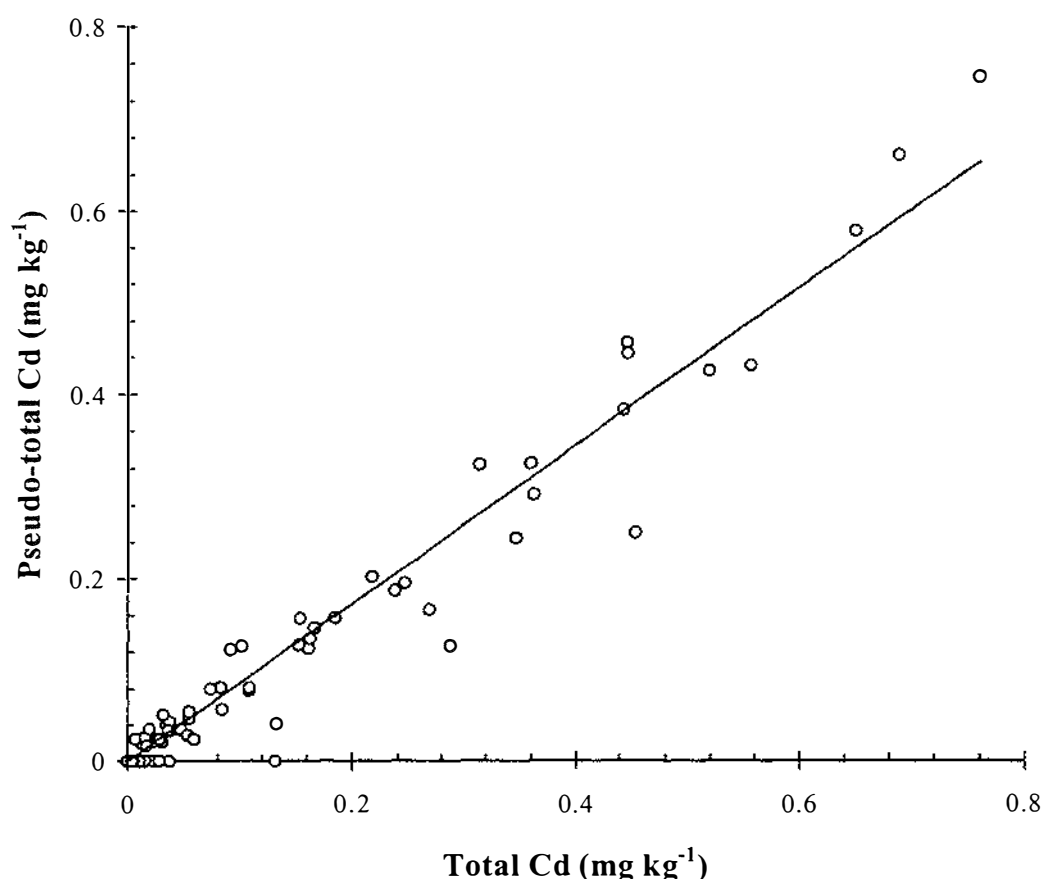
Figure 3.1   A comparison of pseudo-total Cd concentrations in samples taken from various soil profiles with the total Cd concentrations determined using HF acid digestion. The regression line has the equation: pseudo-total Cd = 0.86 * total Cd (R^2 = 0.95).

between 43 and 103%. Some method development took place to improve the digestion procedure (as discussed in section 3.3.2), and recoveries improved to around 90% for two standard soils (section 3.3.4). This digestion efficiency was considered satisfactory for determining soil Cd concentrations in the column leaching experiments of Chapter 6.

Extractable cadmium versus total cadmium

Although proposed as a means of determining the potentially plant-available Cd present in soils, 0.1 M HCl was found to be an effective extractant. On average, 0.1 M HCl removed 78% of the total Cd present (Figure 3.2), a high recovery when considered alongside the 90% recovered by the concentrated $HCl-HNO_3$ digest. This recovery rate is greater than that found from sludge by Neuhauser and Hartenstein (1980), but not

dissimilar to the extraction efficiency from soils for 0.2 M HCl seen by He and Singh (1993a).
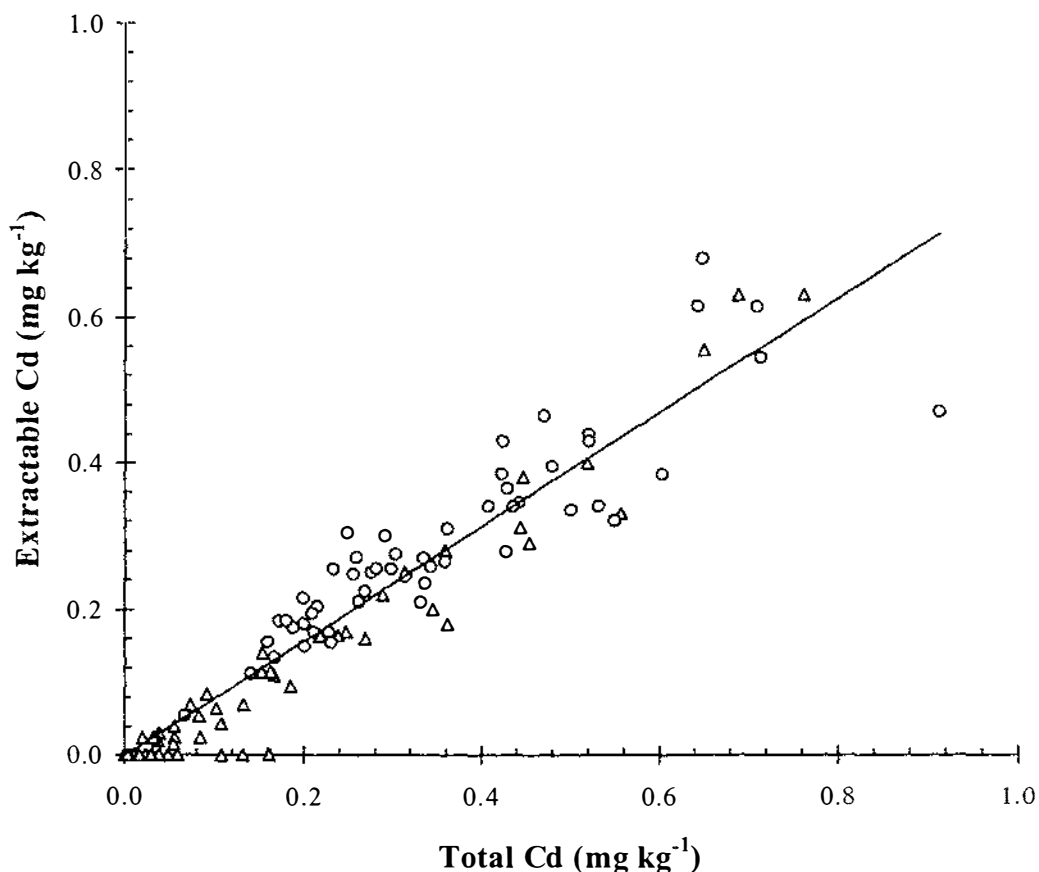
Figure 3.2   A comparison between extractable Cd concentrations and total Cd concentrations (determined using HF digestion) in surface soils (O) and soil material sampled by horizon from the A horizon down to the parent material (Δ).The regression line has the equation: extractable Cd = 0.78 * total Cd (R^2 = 0.91).

3.3.4   Quality assurance for soil analysis

In order to have confidence in analytical results, the accuracy of the analytical procedure needs to be established. As a means of measuring this accuracy certified, standard materials (for which there is an accepted value) are commonly incorporated into the analysis routine. These reference materials should be physically and chemically similar to the samples being analyzed (Thompson, 1983).

In this study, the accuracy of data obtained from the two "total Cd" digest methods (section 3.3.2) was monitored by analyzing in parallel an international standard lake sediment, International Atomic Energy Agency (IAEA) SL-1. This material was also used to calibrate in-house quality control soils (referred to as *in-house QC samples*). The results for repeated Cd analysis of these materials are presented in Table 3.1. *Total* Cd fell comfortably within the given range expected for the SL-1 standard. However, in accordance with the comparison of extraction efficiencies (section 3.3.3), values for soil Cd obtained by the *pseudo-total* method fell short of the certified value by around 10%.

The precision of soil analyses was monitored by analyzing some samples in duplicate. Where this was done for *total Cd*, the duplicates normally varied within ± 0.020 mg Cd kg^{-1}. Although the percentage error varied with actual soil Cd concentration, in surface soils (0-7.5 cm) this value was usually less than 6.3% (evaluated for 60 sets of duplicate analyses). In terms of the relative standard deviation (RSD), some soil samples analysed over several digestion batches showed a RSD of up to 10%. However, compared to the differences in soil Cd concentrations discussed in this study this analytical variability was acceptable.

Table 3.1 Results from repeated analysis of standard soil and herbage reference materials for total Cd. A 95% confidence interval for the average Cd concentration and the accepted values are also shown.

Sample material		Accepted Value	Measured Value [†]
		---------------(mg kg^{-1})---------------	
IAEA lake sediment	SL-1	0.26 ± 0.05	0.24 ± 0.01 (0.22 ± 0.01)
In-house QC soil sample	#265		0.19 ± 0.01 (0.17 ± 0.01)
In-house QC soil sample	#273		0.34 ± 0.01 (0.27 ± 0.02)
QC herbage sample from RJ Hill Laboratories	Pasture Lucerne	0.19 ± 0.01 0.17 ± 0.01	0.21 0.18

[†] Values given in parentheses are those for pseudo-total Cd (section 3.3.2)

Two herbage samples obtained from RJ Hill Laboratories were also routinely analyzed and provided quality control for herbage analyses. The accepted and measured values for these samples (pasture and lucerne) are also given in Table 3.1

3.4 PLANT SAMPLE PREPARATION AND ANALYSIS

Some herbage samples analyzed in this study had been collected earlier for other research projects and only required re-drying at 70 $^\circ$C prior to analysis. Other herbage was collected, oven dried at 70 $^\circ$C and finely ground in a Tecator Cyclotec 1093 sample mill. The ground sample was then stored in clean air-tight plastic bags ready for analysis.

About 0.2 g of plant material was weighed into 30 mL glass digest tubes and 2 mL of concentrated HNO_3 (Aristar) added to each tube. The tubes were then placed on a cold digestion block, small glass funnels (reflux funnels) placed on top (stems down), and heated for at least 4 hours at 150 $^\circ$C until the brown fuming ceased. The glass funnels were then removed and the heating-block temperature increased to 200 - 250 $^\circ$C. The sample digests were then boiled off until just dry (with care to avoid burning the sample as a black, insoluble residue would result) and removed from the digest block. While the tubes were still warm, 4 mL of 10% HNO_3 acid was added. After mixing on a vortex mixer, the solution was transferred into a 20 mL volumetric flask and made up to 20 mL with deionized water.

Procedural blanks and laboratory standard herbage samples were included in all batches.

3.5 ANALYSIS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GFAAS)

The determination of Cd in soils at concentrations commonly found in New Zealand soils (Table 2.4) frequently requires detection limits much more sensitive than that provided by either flame atomic absorption spectrometry or inductively coupled plasma emission spectrometry (ICP-ES) (Athanasopoulos, page 9-4; Millward and Kluckner, 1991). Graphite furnace atomic absorption spectrometry (GFAAS) allows detection

down to around 0.1-0.2 μg Cd L^{-1} – depending on the instrument operating conditions (Manning and Slavin, 1983; Baucells *et al.*, 1985; Millward and Kluckner, 1991). This permits analysis down to soil Cd concentrations of about 0.008 mg Cd kg^{-1} soil, a detection limit suitable for most soils studied in this work.

A brief outline of the instrumentation and techniques used to analyze for Cd in various sample matrices during this study is given below. Because of the wide range of sample matrices dealt with – soil extracts and leachates in various background solutions (e.g. water, $CaCl_2$, $CaSO_4$), and solutions from digested soil and herbage samples – some variation in sample analysis was encountered and subtle modifications to the arrangement of the graphite furnace were necessary. As a result, considerable method development often took place before a satisfactory analysis regime was obtained for each matrix. Published data, for example, the reviews of Slavin *et al.* (1983), Welz (1994), and the U.S. Environmental Protection Agency (1994) publication were found to help greatly with these modifications.

3.5.1   Instrumentation

Unless otherwise stated, all Cd analyses were performed on a GBC 909 AA with GBC GF 3000 graphite furnace, power supply and furnace work head, with deuterium lamp background correction, and a PAL 3000 Autosampler (GBC Scientific Equipment Pty Ltd, Australia). Background correction (BC) was used at all times – analysis of real samples (soil, herbage, leachate) by GFAAS without it is not advisable (Slavin and Carnrick, 1988; Welz, 1994). The hollow cathode lamp current was set to 3.0 mA, a slit width of 0.5 nm was used, and measurements were read at the 228.8 nm resonance line.

All analyses used pyrolytically coated graphite tubes and these tubes were replaced at regular intervals. Although the tube is enveloped by an inert gas to exclude oxygen and prevent it from burning, deterioration of the tube occurs over time (Chapple and Athanasopoulos, 1991). In commercial laboratories, for example, tubes may be renewed every day – after about 250 firings – to avoid the risk of changing sensitivity at the end of the tube's life (Slavin 1987).

3.5.2 Furnace programmes

In GFAAS, the injected liquid sample is taken through three heating stages: drying, ashing (to remove sample matrix components) and atomization. These stages are important to obtaining accurate and precise results. They are described briefly below.

The sample is dried over a series of temperature steps using ramp and hold times and temperatures which are dependent on the sample volume, sample matrix, modifier, solvent and whether a platform is in place. This is done slowly in order to avoid sample spluttering and dispersion and subsequent erroneous results. Only a small aliquot of sample is injected into the graphite tube, about 10 - 30 μL. Volumes at the lower end were generally used in association with the platform furnace arrangement.

During the ash (or char) step, the dried sample is subjected to temperatures just below that at which Cd loss through volatilization will occur. This stage minimizes interference from other components of the sample matrix by removing these components prior to atomization. The ash temperature is normally determined by the matrix modifier (see section 3.5.4) – in the case of $Pd(NO_3)_2$ it can be up to $800^{\circ}C$ (Creed *et al.*, 1992).

A one second gas stop following ashing ensures that gas flow has ceased completely before atomization of the Cd and reading of the absorbance signal. This cessation of gas flow during atomization increases the residence time of the analyte in the light path and gives GFAAS its greater sensitivity over flame AAS. Atomization takes place at a temperature which: 1) satisfactorily volatilizes all the analyte and 2) does not unnecessarily shorten the life of the graphite tube.

A clean cycle, where the furnace is heated for several seconds to a temperature higher than that required for analyte atomization, is also commonly included in the furnace programme. This ensures that residual analyte and residue build-up from the sample matrix are removed from the furnace, thereby preventing memory effects between firings. In this study a clean-out temperature of over $2000^{\circ}C$ was typically used.

Three furnace heating programmes are given in Appendix 1. These were typical programmes to which slight adjustments were made to optimize for specific matrices, changes in graphite tube age, use of the L'vov platform, sample signal response, and sample volume. Drying times and drying temperatures were frequently modified, while atomization temperatures were also varied in order to optimize the signal response – particularly where readings were taken on peak height. Peak area was the commonest method of signal evaluation, but sometimes peak height was also used. A general outline of programmes for particular sample matrices is given in section 3.5.3.

3.5.3   Standard solutions

Cadmium standard solutions were prepared from Spectrosol® *Cadmium nitrate standard solution for atomic spectroscopy*. Standards were made up in the background matrix of the sample, for example 1% HNO_3 when analyzing total and pseudo-total soil Cd digests (section 3.3.2) and 2.5 mM $CaCl_2$ when analyzing leachate samples collected from soil columns leached with 2.5 mM $CaCl_2$ (Chapter 6). In general, calibration was by the method of standard additions for all soil and herbage matrices after poor analyte recoveries were found when using a standard working curve. However, Cd concentrations in most leachates from Chapter 6 were able to be analyzed satisfactorily using a standard working curve in which the dominant solution components were matched (matrix matching).

Instrument detection limits were estimated to be around 0.1 $\mu g\ L^{-1}$ in the sample solution – calculated as three times the standard deviation of repeated blanks. This is equivalent to 0.004 mg Cd kg^{-1} soil for *total Cd* and *pseudo-total Cd* analyses in soils.

3.5.4   Modifiers and dealing with difficult samples

The major difficulties encountered in analyzing samples by GFAAS related to spectral and non-spectral interference during the atomization stage. Reports in literature indicate that the greatest interferences come from anions, in particular chloride compounds, though Ca and Fe have also been implicated (Baucells *et al.* 1985; Cabon and Le Bihan 1992; Carroll *et al.* 1992; Creed *et al.* 1992; Hulanicki *et al.* 1985; Smeyers-Verbeke *et al.* 1990; Yin *et al.* 1987). These reported interferences of Cl on Cd are in agreement with my experiences during this study.

Different furnace programmes were used for samples from different materials. In almost all cases the use of a modifier gave the best results. Matrix modification provides a means of controlling interferences caused by the sample-matrix by altering the behaviour of the analyte and/or background matrix during furnace firing.

Some chemical modifiers work by participating in reactions that remove problem matrix components at low ashing temperatures (e.g. oxalic acid on chlorides [Cabon and Le Bihan, 1992]), while others raise the possible ashing temperature, and therefore improve ashing effectiveness, by selectively delaying analyte volatilization (e.g. Pd [Creed et $al.$, 1992]). Essentially both these mechanisms maximize the amount of analyte (Cd) simultaneously volatilized while minimizing the amount of matrix concurrently vapourized into the light path.

The Merck-produced palladium modifier for graphite furnace AAS [$Pd(NO_3)_2$ in 15% HNO_3] worked well for soil and herbage digest samples. It was prepared by diluting the commercial product to 3 g Pd L^{-1} and adding 2 g L^{-1} $Mg(NO_3)_2$ (Creed et $al.$, 1992). Oxalic acid (25 g L^{-1} in deionized water) was the modifier most often used for samples containing high concentrations of chloride – for instance, leachates from the $CaCl_2$-leached soil columns (see Chapter 6) – because of its suppression of Cl interference (Smeyers-Verbeke et $al.$, 1990; Cabon and Le Bihan, 1992; Creed et $al.$, 1992). Normally, 5 µL of modifier and 10 µL of sample were injected for each firing. Leachate samples with a background matrix of water, $Ca(NO_3)_2$ or $CaSO_4$ (Chapter 6, Experiment 1) did not require a modifier of any form.

The palladium (Pd) modifier mentioned above requires a reducing agent, either in the form of ascorbic acid (present in the blank solution at 0.25% w/v) or H_2 (present in the GFAAS purge gas). When ascorbic acid was used as a reducing agent, several µL of blank solution also had to be injected along with the sample and modifier. Although both ascorbic acid and H_2 were used, under the instrument arrangement used for this study, the inclusion of 5% H_2 in the Argon (Ar) purge gas was preferred. Use of ascorbic acid led to the reduction of Pd on the inside wall of the injection probe where the modifier solution came in contact with residual blank solution.

Some samples, for instance those obtained from the HF-based *total Cd* digestion, proved difficult to analyze using only a graphite tube. In these cases, use of a L'vov platform improved the sample signal and reduced the background interference (Slavin and Carnrick, 1986; Creed *et al.*, 1992). An explanation and discussion of platform furnace technology is given by Slavin *et al.* (1983). Not all difficulties, however, related to spectral interferences. Sample injection into the graphite tube was frequently followed by creep of the solution up out of the injection hole. This was satisfactorily overcome by incorporating 0.2% v/v Triton-X 100 (detergent) and 0.6% v/v HNO_3 in the autosampler rinse solution (J. Rounce, pers. comm.).

3.6 MISCELLANEOUS ANALYSES

3.6.1 Phosphorus

Olsen P

One gram of air dry soil (1 - 2 mm sieved) was placed in a 50-mL centrifuge tube, mixed with 20 mL of 0.5 M sodium bicarbonate ($NaHCO_3$) at pH 8.45 and shaken for 30 minutes. Following centrifugation at 8000 rpm for 10 minutes, the solution was filtered through Whatman No. 2 filter paper, discarding the initial portion of the filtrate (Olsen *et al.*, 1954; Watanabe and Olsen, 1965). Five mL of the filtrate was analyzed for P using the molybdate blue method given by Watanabe and Olsen (1965). Absorbance readings were taken at 712 nm using a Philips PU 8625 UV/VIS spectrophotometer.

Total P

Total P was determined by digesting, under reflux conditions, 1 g of finely ground air-dry soil in a mixture of concentrated nitric (HNO_3), hydrochloric (HCl) and perchloric ($HClO_4$) acids in the ratio 5:5:7 at 260 °C until a build-up of white fumes. After adding 15 mL distilled water and heating, the digest was filtered and made up to 100 mL with distilled water (Bolan and Hedley, 1987). The resulting solution was then analyzed for P by the molybdate blue method of Murphy and Riley (1962) taking absorbance readings at 712 nm using a Philips PU 8625 UV/VIS spectrophotometer.

3.6.2 Zinc

Soils were digested as for *total* or *pseudo-total Cd* (section 3.3.2) and analyzed by flame

atomic absorption spectrophotometry, model GBC 904 AA spectrophotometer (GBC Scientific Equipment Pty Ltd, Australia) using an air-acetylene gas flame. Absorbance readings were made at 213.9 nm.

3.6.3   Cation exchange capacity

Cation exchange capacity (CEC) was determined by leaching 1-2 mm sieved soil samples with 1M ammonium acetate (NH_4OAc) at pH 7 according to the method of Blakemore *et al.* (1987). The measurement of exchangeable H and total exchangeable bases gives an approximation of exchange capacity and percent base saturation of the soil (Hesse, 1971). Exchangeable H was determined by leachate pH, while individual exchangeable cations (K, Na, Mg and Ca) were determined in the leachate by flame AAS or flame emission on a GBC 904 AA spectrophotometer (GBC Scientific Equipment Pty Ltd, Australia). Total CEC was then determined by summation.

However, there is criticism of this method for determining CEC because CEC is pH dependent and may differ significantly at the natural soil pH compared to that determined using a pH 7 buffered leaching solution (Orlov, 1992). Very few of the soils encountered in this study have a soil pH near neutral. Most soils are acidic and fall in the pH range 4 - 6. It is possible, therefore, that using 1M ammonium acetate (pH 7) has over estimated the cation exchange capacity of these soils.

3.6.4   Total soil carbon

Total soil carbon was determined using a Leco induction furnace in which all forms of carbon in the soil are converted to CO_2. During the early stages of laboratory work (data presented in Chapter 4), the equipment used measured soil carbon by the mass of CO_2 evolved during combustion with glucose as a calibration standard. All other samples were analyzed using a Leco FP-2000 Analyser which measured the carbon content, as CO_2, by infrared detection using sulphamethazine for calibration.

3.6.5   Soil pH

Soil pH was determined by mixing 10 g of air dried soil with 25 mL of distilled water and leaving overnight (16 hours) prior to measurement. Laboratory standard soils were included in all batches to monitor accuracy and precision.

3.6.6   Multi-element analysis by ICAP-OES

Soil samples digested using the total Cd digest methods from sections 3.3.2 were diluted with 1.0 M HCl in the ratio 2 mL : 2 mL (digest solution : 1.0 M HCl). These were then submitted for analysis by an inductively coupled argon plasma-optical emission spectrometer (ICAP-OES) – calibrated with multi-element standards in a background matrix of HCl. The analyses were performed by the Analytical Laboratory, Grasslands Research Centre, Palmerston North using an Applied Research Laboratories model 34000 ICAP-OES instrument.

CHAPTER 4

THE DISTRIBUTION AND ORIGIN OF TOPSOIL CADMIUM IN SOILS ON A REGULARLY FERTILIZED HILL-COUNTRY FARM

4.1 INTRODUCTION

With mounting evidence for Cd accumulation in food-producing soils (Williams and David, 1973 and 1976; Mulla *et al.*, 1980; Rothbaum *et al.*, 1986; Jones *et al.*, 1987; Simpson and Curnow, 1988), Bramley (1990) published a timely review of Cd in New Zealand agriculture. In it, he warned that use of superphosphate manufactured from high Cd phosphate rocks (Nauru and Christmas Island) was likely to have increased Cd concentrations in New Zealand pastoral soils. Since the publication of that review, several workers have presented data on Cd accumulation in New Zealand soils that support Bramley's prediction (Taylor and Percival, 1992; Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan and Hedley, 1997). In all cases, elevated Cd concentrations were found in New Zealand pastoral soils and these were consistently attributed to fertilizer application. This general trend towards elevated Cd concentrations in fertilized soils conceals, however, substantial variation in Cd concentrations between sampling points. Cadmium concentrations in topsoils often range over two orders of magnitude (Taylor and Percival, 1992; Roberts *et al.*, 1994). In order to fully appreciate the significance of Cd field data and the threat posed to New Zealand agriculture, it is important to also understand this underlying variation and the factors that produce it.

Trace metal heterogeneity in soils has been examined in several studies with the general conclusion that significant Cd variation exists in the field (Wopereis *et al.*, 1988; Boekhold *et al.*, 1991; Boekhold and van der Zee, 1992a and 1992b; Atteia *et al.*, 1994; Kuzel *et al.*, 1994).This variation can most probably be attributed to differences in Cd source and differences in the properties of the receiving soil that affect redistribution (Burrough, 1993).

Soil parent material, in particular, is considered a major influence on surface soil Cd concentrations (Pierce *et al.*, 1982; Blaser and Zimmermann, 1993). However, the relationship between Cd concentrations in parent material and the surface soil is often

modified by pedogenic processes, biocycling or over-ridden completely by the influence of non-lithogenic, non-diffuse and non-homogeneous Cd sources such as: phosphatic fertilizers; sewage sludge (Holmgren *et al.*, 1993; Kuzel *et al.*, 1994); and atmospheric deposition – from both localized point sources and regional diffuse sources (Grigal and Ohmann, 1989; Dudka, 1992).

Biocycling may have an significant influence on the distribution of trace metals in soil. Through this process Cd may be: 1) retained in the surface soil – thereby enhancing its accumulation; and 2) translocated Cd from depth to the surface through root uptake and leaf litter deposition (Martin and Coughtrey, 1982, as cited in Ross 1996c). It may be, for example, a factor in the unexplained surface accumulation of Cd in soils developed from Kimerigian rock material (0.15 mg Cd kg^{-1}) in the Swiss Jura. Despite the relatively low concentration of the parent rock, the surface soils showed Cd contents of more than 2 mg Cd kg^{-1} (J -P Dubois, pers. comm.). In the literature, though, biocycling has generally received little attention.

On a large scale (agricultural soils across the USA), variation in soil Cd concentration was reasonably explained by both taxonomic soil order (using 9 classes, e.g. Ultisol, Entisol, Histosol, to account for 45% of the variation) and soil series (whereby 307 classes explained 80% of the variation) (Holmgren *et al.*, 1993). At a local scale however, variability in soil-Cd concentrations is often linked to variations in soil pH and organic matter content as a result of the influence that these properties have on Cd solubility and retention in soils (Homann and Zasoski, 1987; Christensen, 1989; Eriksson, 1990; Boekhold *et al.*, 1991; Boekhold and van der Zee, 1992a and 1992b; Kuzel *et al.*, 1994; McBride *et al.*, 1997b). A review of the various factors instrumental in regulating Cd retention is provided in section 6.2.

Phosphorus is also a major soil component regularly found to correlate with soil-Cd. The presence of a strong correlation between P and Cd in agricultural soils is especially important as it usually provides evidence of a link between the Cd contamination of a soil and the soil's phosphatic fertilizer history (Williams and David, 1973 and 1976; Roberts *et al.*, 1994; Loganathan *et al.*, 1995). This relationship may also develop through the process of biocycling, however.

Some variability in soil Cd concentrations may also be attributed to the effect of topography on fertilizer inputs to various slopes and aspects. This applies similarly to other aerial sources of Cd such as point-source atmospheric pollution. The influence of topography is important for two further reasons. As a result of leaching and topsoil erosion, Cd can be lost from raised ground and accumulate in the surface soils of lower-lying areas (Thornton, 1986; Korentajer et al., 1993) – both processes being strongly dependent on topography. In addition, topography has a marked effect on the grazing behaviour of livestock on hill-country pasture. Around 99% of ingested Cd is returned to the soil via dung. However, this return of dung is uneven and is concentrated on low slopes (0 - 12°) (Gillingham et al., 1980). Thus, soils on low slopes receive higher inputs of Cd than soils on steep slopes (Loganathan et al., 1995). These above factors interact to produce a complex pattern of Cd distribution across the landscape.

In this chapter and the next, variation in soil Cd concentrations is examined to: (a) identify the source of Cd variability in surface soils, and (b) identify the likely origins of this Cd on a hill-country farm. These two aspects have become increasingly important with the growing awareness that we need to actively manage Cd accumulation in our pastoral soils.

4.2   STUDY LOCATION: LIMESTONE DOWNS – THE FARM

The spatial variation of Cd was studied on the semi-intensive sheep and beef cattle farm of Limestone Downs. The farm is located 15 km south of Port Waikato in the North Island of New Zealand, and covers 3,219 ha of flat, rolling and steep hill country. Around 2,800 ha of the property is under pasture, the rest remains in native bush.

Within its boundaries, Limestone Downs contains a diverse range of soil types – 17 in all (MacKay et al., 1985). These fall into 7 soil groups and have developed on either: peat, alluvial deposits, greywacke, argillite, calcareous sandstone and siltstone, non-marine siltstone, andesitic basalt, tephra, wind-blown sands or pumiceous alluvium (Table 4.1). Detailed soil profile descriptions for a modal profile from each soil series are given in Appendix 2. The farm soil map produced by MacKay et al., (1985) is presented as Map 1 (back pocket).

Table 4.1 Soil series present on the hill country farm of Limestone Downs, their soil groups and parent materials (MacKay *et al.*, 1985). Detailed soil profile descriptions are contained in Appendix 2.

Soil Series	Soil Group	Parent Material
Akatea steepland soils	Steepland soils related to yellow-brown earths	Calcareous siltstone with minor sandstone bands
Waingaro steepland soils	Steepland soils related to yellow-brown earths	Argillite and greywacke
Kapamahunga steepland soils	Steepland soils related to yellow-brown earths	Calcareous sandstone
Kohemarere hill soils	Yellow-brown earth	Calcareous sandstone, with local bands of siltstone and rare limestone
Ruakiwi hill soils	Yellow-brown earth	Calcareous siltstone, with prominent outcrops of bands of calcareous sandstone
Whangape clay loam	Yellow-brown earth	Rhyolitic alluvium
Wairama hill soils	Yellow-brown earth	Calcareous siltstone, may also contain local bands of sandstone and low grade limestone
Horea hill soils	Intergrades between yellow-brown earths and yellow-brown sands	Weathered black sand and admixed volcanic ash
Horea fine sandy loam	Intergrades between yellow-brown earths and yellow-brown sands	Weathered black sand and admixed volcanic ash
Tuahu sandy loam	Yellow-brown sand	Wind-blown sand and minor amounts of volcanic ash
Kotare hill soils	Brown granular loam	Hamilton ash
Kotare clay loam	Brown granular loam	Hamilton ash
Kotare fine sandy loam	Brown granular loam	Hamilton ash
Dunmore silt loam	Yellow-brown loam	Volcanic ash
Mangapiko clay	Gley recent soils	Alluvium of mixed origin
Mangapiko humic clay loam	Gley recent soils	Alluvium of mixed origin
Tauterei humic fine sandy loam	Gley recent soils	Peat and inwash alluvium

At the time of publication of the above referenced material (MacKay *et al.*, 1985), the soil classification system in use was the New Zealand Genetic Soil Classification system. Since then, a new New Zealand soil classification system has been adopted (Hewitt, 1993). However, because the only available soil map for Limestone Downs employs the old, New Zealand Genetic Soil Classification system, it was decided to continue with this soil classification system – both in the work presented here, and the thesis as a whole.

With the wide range in parent material and other soil forming factors present on this one farm property, the influence that these factors have on soil Cd concentrations can be investigated without regard to distortions caused by different farm management practices.

Heavy top-dressing with SSP was a notable aspect of the initial years of development following the purchase of Limestone Downs in 1926 by Charles Alma Baker, CBE. The first Romney flock was introduced in 1930 and, since then the farm has been well maintained and regularly fertilized. Currently the property is managed as a charitable trust "to further the science of agriculture" while maximizing the commercial viability of the farm (Lowe, 1992; Nelson, 1994), and runs about 13 stock units per hectare made up of breeding ewes, breeding cows, Friesian bulls and other sheep and cattle.

4.3   MATERIALS AND METHODS

A number of sites were located across the farm within each of the soil series identified in Table 4.1. From each site, a soil sample was collected to provide information on the variability of Cd concentrations in topsoil: (a) across the farm, and (b) within various soil groupings (section 4.3.1). At the same time, one site in each soil series was sampled to depth to provide information on the distribution of Cd within the soil profile and the likelihood that parent material was a significant source of Cd – and therefore a factor in explaining the variability of Cd in surface soils (section 4.3.2). A third study was also conducted to investigate Cd variability on a local scale, predominantly with reference to the possible impact of animal transfer (section 4.3.3).

4.3.1 Variability of cadmium and other related soil properties in topsoils under pasture

A number of samples of topsoil from each of the soil series on the farm were collected. The sampling sites were selected to cover the spatial distribution of the soil series across the farm. Each sample consisted of 10 soil cores, 7.5 cm deep, taken from a 1 m^2 site and bulked together. The soils were processed and analyzed for total Cd, extractable Cd (0.1 M HCl), total P, soil pH and soil carbon content, as described in Chapter 3.

4.3.2 Parent material as a source of cadmium and a cause of cadmium variability in topsoils

In a survey related to that above, one modal profile for each soil series was located on the farm by a pedologist (F. W. Krieger) and sampled by horizon down to, where possible, the parent material. The profile description of each modal site is presented in Appendix 2. Approximate locations for the profile sampling sites are shown in Map 1 (Reconnaissance Soil Map). The soil material from each horizon was analyzed for total Cd, 0.1 M HCl-extractable Cd , total P, pH and total carbon. General methods are described in Chapter 3, however, the method used for total Cd is described below.

During this early work the digestion of soil samples for total Cd differed from the procedure given in section 3.3.2. The reasons for this are explained in section 3.3.2.

Total cadmium: Approximately 0.5 g air dried, finely ground soil was accurately weighed into 100 mL polypropylene tri-pore beakers. Five mL of concentrated Aristar HNO_3 and 10 mL 40% Aristar HF acid was added sequentially. This mixture was left overnight and evaporated to dryness on a water bath the next morning. A further 3 mL concentrated HNO_3 was added to react with any remaining HF and was likewise evaporated off. The dry residue was then warmed in about 10 mL of 1% w/v HNO_3 and left overnight before being made up to 20 mL with 1% w/v HNO_3 and decanted into storage tubes to await analysis by GFAAS (section 3.5). These digest samples were also submitted for ICP-OES multi-element analysis as described in section 3.6.6.

Because the form and quantity of Cd in parent material on Limestone Downs was unknown, hydrofluoric acid was used to ensure a complete break down of all residual

minerals in parent material and soil material sampled from depth (section 3.3.2). This was necessary to clarify the source of Cd to soils on this farm and, in particular, the contribution from parent material.

4.3.3 Cadmium variability as a function of topography and animal transfer

A 25 m by 25 m area was selected with topography that progressed from low slope (0 - 12°), with evidence of stock camping activity, to steep slope (> 26°). From this area 121 topsoil samples (0 - 7.5 cm) were taken at 2.5 m intervals on the intersections of a square, 25 m by 25 m, grid. Each sample consisted of one soil core 7.5 cm deep and 2.5 cm diameter. These soil samples were analyzed for total P, total Zn, soil pH and total soil carbon according to the methods given in Chapter 3. Total Cd was determined according to the *pseudo-total* method given in section 3.3.2, but the soil samples were not subject to treatment by H_2O_2.

4.4 RESULTS AND DISCUSSION

4.4.1 Summary statistics for cadmium and other soil properties in topsoils under pasture

Summary statistics describing the fertility and Cd status of surface soils on Limestone Downs are presented in Table 4.2. Total Cd concentrations in the surface soil ranged from 0.067 mg Cd kg^{-1} to 0.912 mg Cd kg^{-1}. The distribution is positively skewed with the median Cd concentration, 0.32 mg Cd kg^{-1}, being slightly lower than the arithmetic mean, 0.36 mg Cd kg^{-1} (Figure 4.1 and Table 4.2). These Cd values are typical of those reported elsewhere for pastoral soils in New Zealand and for normal agricultural soils globally (Table 2.4).

Table 4.2 Cadmium concentrations and other soil parameters for topsoils (0 - 7.5 cm) sampled across Limestone Downs.

	Total Cd	0.1M HCl extractable Cd	Total P	Soil pH	Total carbon
	---------------------(mg kg^{-1})---------------------				%
Arithmetic mean	0.36	0.29	1332	5.3	7.1
Median	0.32	0.27	1371	5.3	6.4
Range	0.07 - 0.91	0.06 - 0.68	295 - 2738	4.6 - 6.3	0.8 - 14.2
Standard deviation	0.16	0.13	496	0.3	2.9
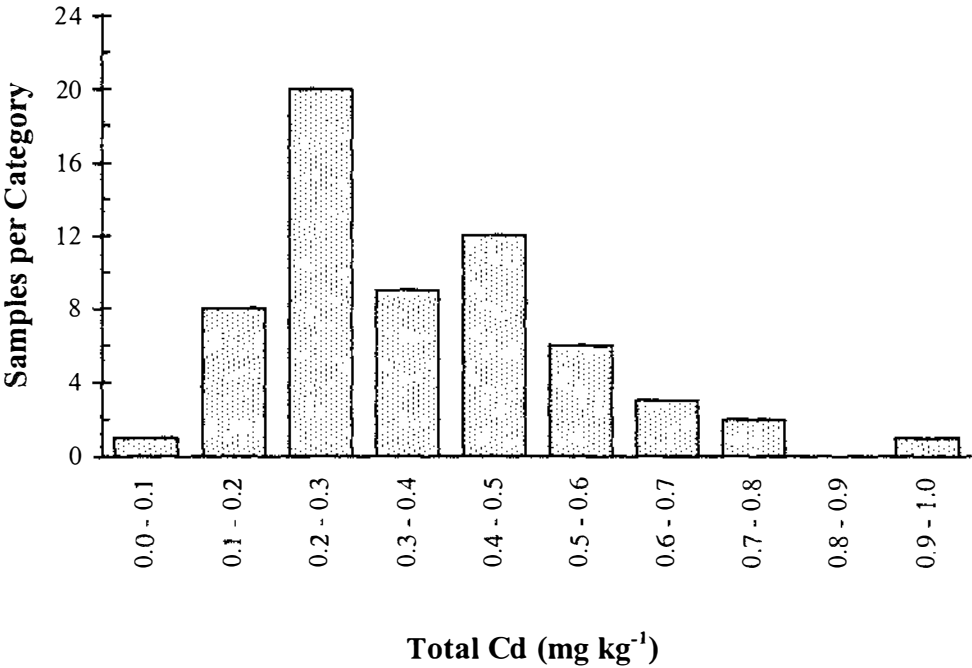
Figure 4.1 Frequency distribution of cadmium concentrations in the topsoil (0 - 7.5 cm) of pasture soils on Limestone Downs.

The total P concentrations of Limestone Downs soils appear consistent with other farmland soils studied in New Zealand (Table 4.2). Roberts *et al.* (1993) reported P concentrations nationwide as ranging from 400 to 6000 mg P kg^{-1}; while Moir *et al.* (1995) found between 430 and 1470 mg P kg^{-1} for predominantly Yellow-brown and Yellow-grey earth soils in the Wairarapa. The soils studied in this work reflect the farm's history of regular fertilizer application, particularly soils in the Brown-granular loam and Yellow-brown loam groups. Soils from these two groups commonly had the highest P concentrations, in keeping with their greater need for P fertilizer compared to, for example, the Yellow-brown earth soils.

Soil pH was acidic in all samples with a mean of 5.3. The soil carbon content also had a near-normal distribution, centred around 7% carbon and ranging from 0.8 to 14 %. These values are not unusual for New Zealand soils (McLaren and Cameron, 1990).

4.4.2 Parent material as a source of cadmium and a cause of cadmium variability in topsoils

In the above survey, Cd concentrations in topsoils were shown to have a skewed
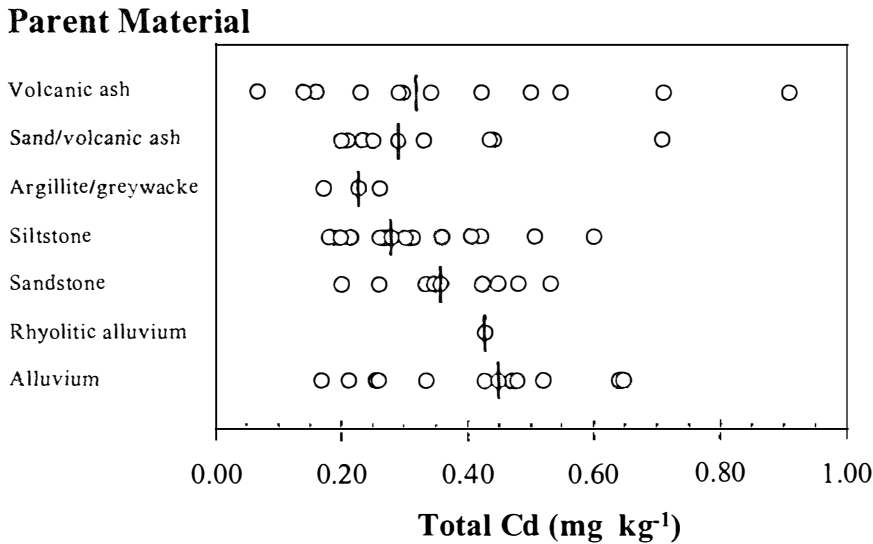
Parent Material

Figure 4.2   Variation in the cadmium concentrations of topsoils (0 - 7.5 cm) on Limestone Downs when grouped according to their parent material. Bars (|) represent the median value for each category.

distribution. Merry and Tiller (1991) reported a similar log-normal trend for both Cd and Pb in South Australian surface soils. They suggested that this reflected "inputs from external sources superimposed on variation in the metal compositions of the soils' parent rocks". If this applies similarly to the soils on Limestone Downs, then it would be expected that a high proportion of Cd variation in the surface soil could be explained by grouping soils according to their parent material.

Analysis of variance showed parent material to explain only 9% of the variability in topsoil Cd concentrations. Within each class of parent material, Cd concentrations in the topsoil still varied widely, Figure 4.2. This is consistent with observations that rock material in New Zealand generally has a low Cd content (section 2.4.1). However, in the absence of conclusive evidence to the contrary, debate continues to raise the possibility that parent material is an important source of the Cd found in pastoral soils. This is a significant issue for Cd management on pastoral farms where reducing the Cd content of phosphatic fertilizers is not an easy option because of both manufacturing difficulties and considerations of cost.

Recovery of all Cd present in the soil and rock material (using an HF digest) showed that, with one exception (the Ruakiwi Hill soil), Cd concentrations were always highest in the A horizon. Moreover, in all but four profiles, the Cd concentration decreased to

(a) **Dunmore silt loam (Yellow-brown loam)**
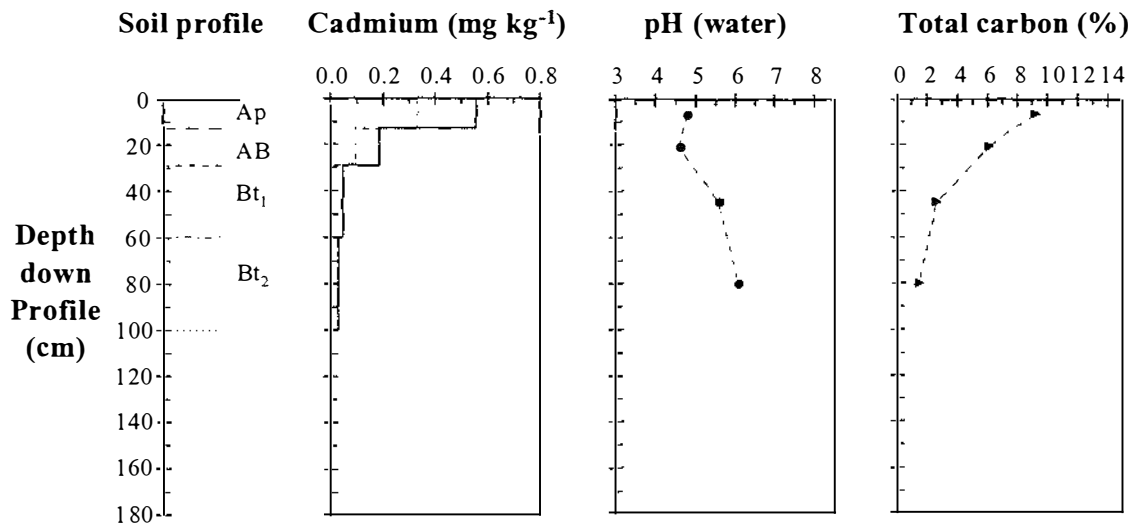
(b) **Waingaro steepland soil (Steepland soils related to yellow-brown earths)**
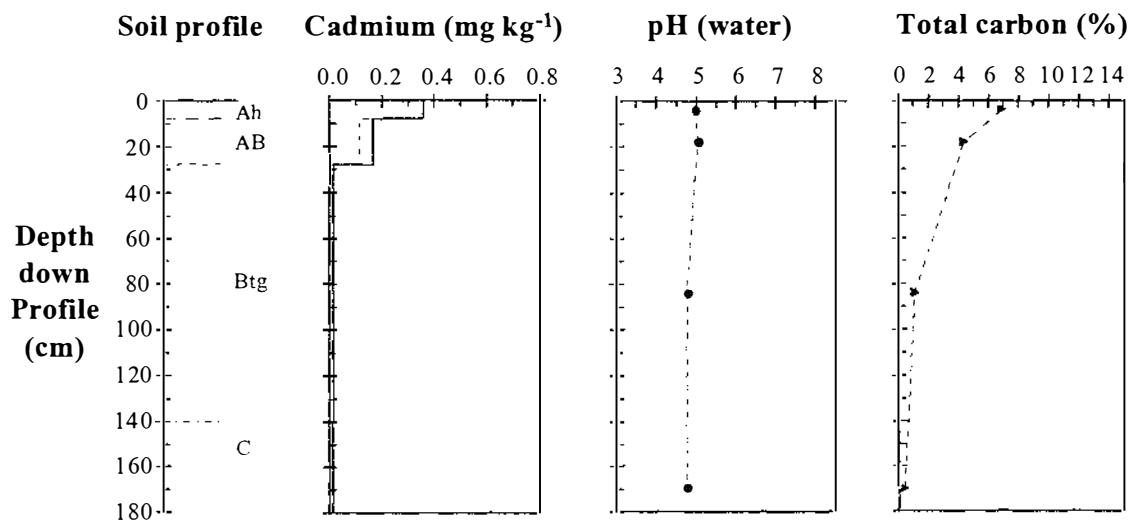
Figure 4.3 Horizon descriptions and vertical profiles of: total Cd (—) and 0.1 M HCl-extractable Cd (---); soil pH (●); and total carbon (▲) for two soils found on Limestone Downs. (*a*) Dunmore silt loam and (*b*) Waingaro steepland soil.

undetectable levels in the B and C horizons – indicating that parent material contributed little Cd to the surface soil. Two profiles are shown as examples in Figure 4.3 and the remainder are documented in Appendix 2. Profiles from the Wairama hill soil, Ruakiwi hill soil, Kapamahunga steepland soil, and Tuahu sandy loam did, however, contain measurable amounts of Cd in samples of their parent material (Table 4.3).

Of the four soils with Cd-containing parent material, the first three (Wairama, Ruakiwi and Kapamahunga) have formed from calcareous sandstone and/or calcareous siltstone (MacKay *et al.*, 1985). This information agrees with laboratory data obtained on rock samples from the Wairama Hill soil and Kapamahunga steepland soil profiles – basic pH, high calcium contents and comparatively high carbon contents (Table 4.3). In light of the known association of Cd with calcareous sediments and evidence for Cd substitution of Ca in calcite (McBride, 1980; Pierce *et al.*, 1982; Papadopoulos and Rowell, 1988), it is probable that the Cd present in these two parent materials was associated with their calcium carbonate content.

Table 4.3 Analytical data for the four soil profiles which showed significant levels of Cd in their parent materials.

Soil Series	Horizon	Depth (cm)	Total Cd (mg kg^{-1})	Total C (%)	Soil pH (H$_2$O)	Total Ca (%)
Wairama Hill soils	Ap	0 - 11	0.519	7.42	5.20	0.2
	AB	11 - 22	0.167	4.15	4.66	0.1
	Bt	22 - 35	0.038	2.09	4.90	0.1
	Btg	35 - 100+	0.008	0.84	4.60	0.0
	Parent material		**0.162**	**7.49**	**8.22**	**4.8**
Kapamahunga Steepland soils	Ah	0 - 20	0.238	5.50	5.08	0.2
	Bt	20 - 66	0.017	1.40	4.86	0.0
	Bts	66 - 110+	0.029	0.72	4.66	0.0
	Parent material		**0.108**	**5.57**	**7.61**	**2.7**
Ruakiwi Hill soils	Ap	0 - 17	0.153	5.41	5.70	0.2
	Bt	17 - 32	0.023	1.16	5.54	0.0
	Btg	32 - 74	0.029	0.94	4.97	0.0
	Cw	74 - 140+	0.017	0.28	4.93	0.0
	Parent material		**0.761**	**0.41**	**4.00**	**0.0**
Tuahu Sandy loam	Ah	0 - 31	0.346	6.37	5.53	0.3
	AB	31 - 59	0.084	3.35	6.03	0.4
	Bt	59 - 118	0.059	0.60	6.39	0.5
	Cw	**118 - 160+**	**0.132**	**0.36**	**6.35**	**2.2**

In contrast to the above soils, however, the low carbon, low Ca content and low pH found in material from the C horizon of the Ruakiwi Hill soil does not indicate a calcareous deposit. This weathered parent material had an unusually high Cd content, 0.76 mg Cd kg^{-1} (verified with a repeat sample) and is the only profile where Cd concentrations in the subsoil exceeded those in the A horizon (Table 4.3). Though possibly from deposits of marine detritus, the origins of this Cd are unknown.

The fourth parent material that contained significant Cd concentrations, the Tuahu Sandy loam, did not have characteristics typical of a carbonate deposits – these characteristics being high pH, high C and high Ca (Table 4.3). Moreover, no Cd was extracted by either 0.1 M HCl, or digestion with concentrated HNO$_3$ and HCl acids (Figure 4.4). It was only after treatment with HF that the Cd present in this material was released. On the basis of these observations it appears that the Cd was incorporated into

Soil Cd (mg kg^{-1})
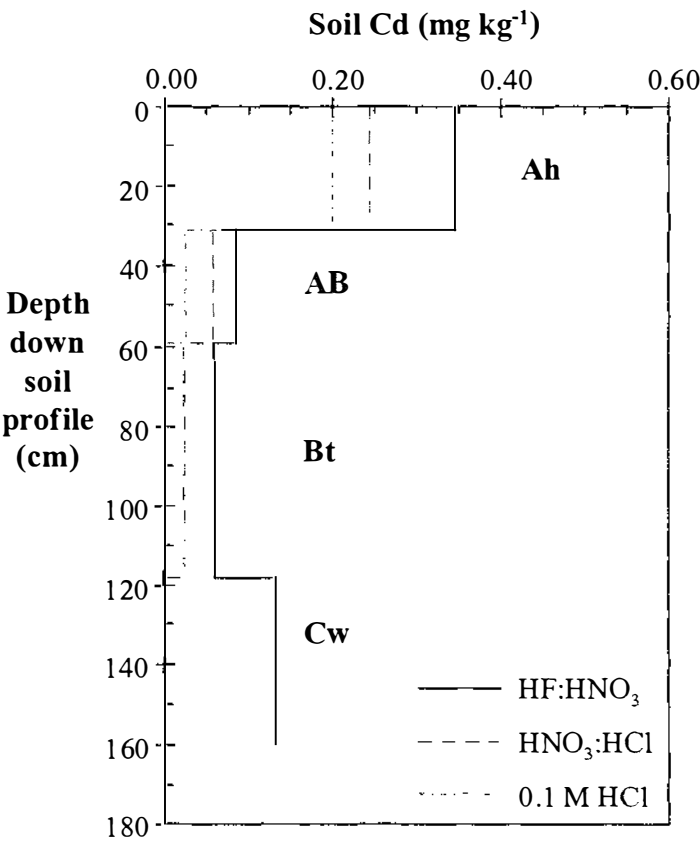
Figure 4.4. Cadmium distribution with depth in the Tuahu Sandy loam profile as determined by three extracting reagents ranging in strength from severe (HF:HNO$_3$) to mild (0.1 M HCl).

a highly resistant mineral, probably in association with the ironsand component. This theory was supported by the finding that raw ironsand from nearby dunes had a similar Cd content (0.15 mg Cd kg^{-1}) to that in the C horizon of this Tuahu sandy loam (0.132 mg Cd kg^{-1}, Table 4.3).

These Cd-containing ironsands present a special form of lithogenic input. In addition to *in situ* contributions during soil formation, they can also supply Cd to soils located some distance away through surface deposition of windblown material. Soil formed from the other parent materials discussed above would obviously have received contributions of Cd during development, and, where the soil is shallow, the proximity of Cd-containing rock to the surface means that this contribution will be on-going. In some Kapamahunga steepland sites, for instance, clearly discernible rock fragments in the surface soil ($0 - 7.5$ cm) are apparent, and outcrops of rock material (containing 0.143 mg Cd kg^{-1}) frequently occur. On the other hand, continued Cd inputs to surface soils from the parent material (through the process of biocycling, for example) may be limited where a reasonable depth of soil has developed. This is suggested by the low Cd concentrations in intervening horizons between the parent material and A horizon in the Wairama and Ruakiwi Hill soil profiles (Table 4.3).

4.4.3 Soil properties relating to variations in cadmium concentration

Although Holmgren *et al.* (1993) found taxonomic soil classifications to be useful in accounting for variation in Cd concentrations across the USA, this was not the case for the farm-scale study here. Categorizing on the basis of soil group only explained 13% of the Cd variation in the surface soils (Figure 4.5). This disparity may possibly be attributed to inherent differences between the two soil classification systems used.

While the New Zealand Genetic Soil Classification system focuses on soil genesis and the environmental processes involved in soil formation (Hewitt, 1992), the US Soil Taxonomy system relies more heavily on laboratory-based measurements of soil chemical and physical properties (A. S. Palmer, pers. comm.). Correlations between Cd and many important soil properties, for example, soil pH, organic matter, clay, CEC, have been reported (Eriksson, 1990; Boekhold *et al.*, 1991; Sánchez-Martín and Sánchez-Camazano, 1993; Ross, 1994b; Kabata-Pendias, 1997). With this emphasis by

62
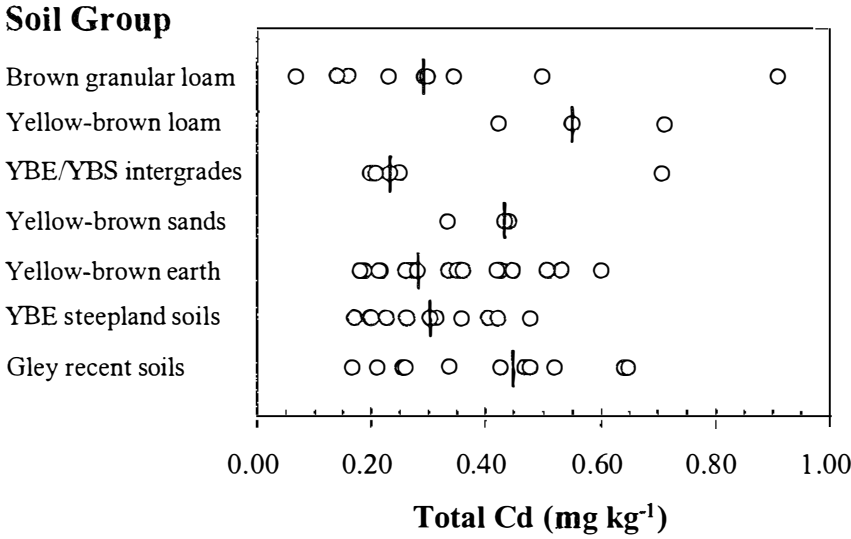
Soil Group

Figure 4.5   Variation in the cadmium concentrations of topsoils (0 - 7.5 cm) on Limestone Downs when separated into soil groups according to the New Zealand Genetic Soil Classification system. Bars (|) represent the median value for each category.

the US Soil Taxonomy system on measured soil properties, it seems reasonable that the interaction between Cd and some of these soil properties will also lead to some differentiation in Cd content between soil groups.
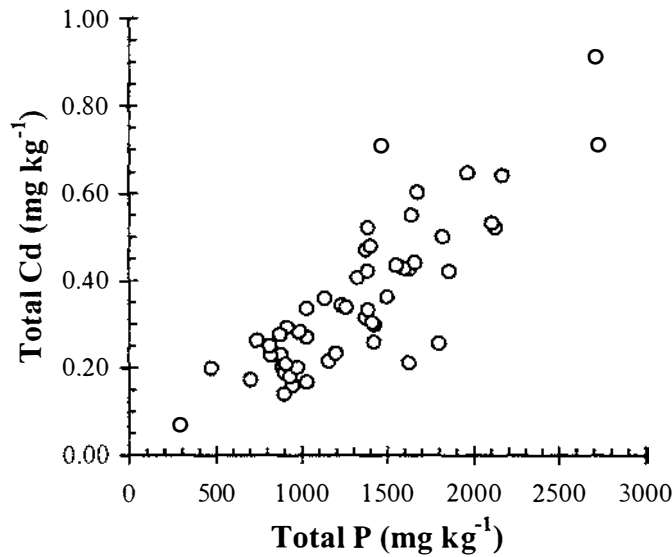
Figure 4.6   Total Cd concentrations in surface soils from across Limestone Downs plotted against their total P concentrations. The correlation coefficient (r) is 0.84 (P < 0.001).

Table 4.4 Correlation coefficients (r) between soil Cd, soil P and other soil properties in 53 surface soils sampled from across Limestone Downs.

	Total Cd	Total P	Soil pH
Total P	0.839		
Soil pH	-0.019	-0.018	
Total Carbon	0.514	0.635	-0.345

Of the soil properties measured, only total P concentrations were highly significantly correlated to total Cd concentrations (r = 0.84, Figure 4.6). This variation in P explained over 70% of the variation in Cd concentrations (Table 4.4) and strongly suggests an association between phosphatic fertilizer history and the Cd concentration of these surface soils.

The commonly reported influence of soil pH on Cd concentrations is not evident (Table 4.4). Similarly, soil carbon appears only weakly correlated to Cd concentration. But, removal of soils belonging to the Gley recent group from the Cd-carbon correlation causes the correlation coefficient (r) to improve from 0.51 to 0.79 (Figure 4.7). This happens because, in contrast to other soil groups, gley recent soils exhibit a weak, negative relation (P<0.1, r = -0.54) between Cd and soil carbon. In these organic rich
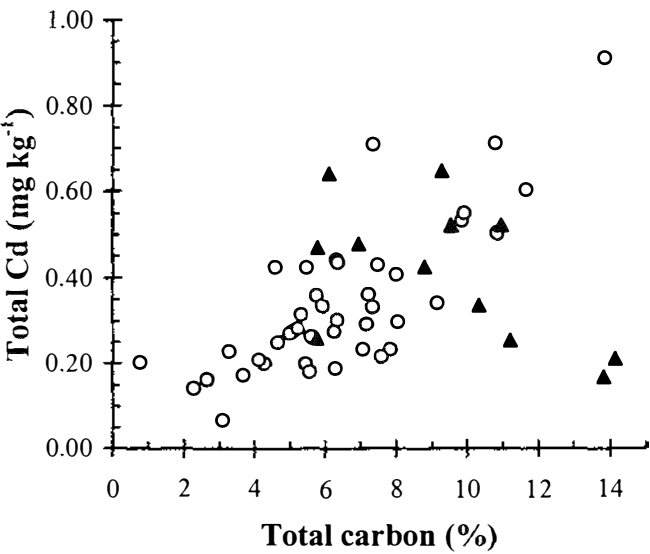
Figure 4.7 The relationship between total Cd and total soil carbon for surface soils from across Limestone Downs (O; r = 0.79, P < 0.001) excluding soils belonging to the gley recent soil group (▲; r = -0.54, P < 0.1).

soils, it is possible that surface oxidation of organic carbon in the aerobic layer has concentrated Cd in the topsoil (Holmgren *et al.*, 1993), thereby giving rise to a negative relationship between soil carbon content and soil Cd concentration.

4.4.4   Cadmium variability as a function of topography and animal transfer

While the strong correlation found between Cd and P in soil may derive from the close association of these two elements in phosphatic fertilizer, this correlation may also be a result of the concomitant redistribution of P and Cd through animal transfer.

It has been observed that different slopes and aspects in a paddock receive different proportions of dung and therefore different proportions of returned P. This results in a net gain of P on flat ground, where animals spend more time (referred to as stock camping sites), and a net loss of P from both medium and steep slopes (Gillingham *et al.*, 1980). Saggar *et al.* (1990) successfully applied this idea of unequal dung return in hill-country pasture to explain variations in soil P concentrations across the landscape.

Faeces also contain significant concentrations of Cd. In sheep faeces, for example, Cd concentrations can reach 5 μg Cd g^{-1} DM (J Rounce, pers. com.). As a result, unequal deposition of dung could also be expected to cause increased additions of Cd to stock camping sites. Using data from the same hill-country sites as those studied by Saggar *et al.* (1990), Loganathan *et al.* (1995) showed that animal transfer could reasonably account for the increased accumulation of Cd on low slopes over that on adjacent slopes of medium and steep topography. Longhurst *et al.* (1994) presented similar results in a separate study. In view of such evidence for the influence of animal transfer on soil Cd concentrations, a more detailed study of the effect of changing topography on Cd variability in soil was undertaken.

Despite the small area of the study site (625 m^2), the Cd and P concentrations in the soil were highly variable (Table 4.5). One sample was excluded from statistical analysis because of its extreme values for most measured parameters. The values for total Cd, total C and soil pH all fell outside 3 standard deviations from the arithmetic mean of the remaining 120 samples. On re-visiting the sampling site, this particular sample was

Table 4.5 Summary statistics for Cd, P and other measured parameters in 120 surface soils (0 - 7.5 cm) taken from a 25 x 25 m^2 area on Limestone Downs. The topography encompassed low and medium to steep slopes.

	Total Cd	Total P	Total Zn	Soil pH	Total carbon
	(mg kg^{-1})				%
Arithmetic mean	0.23	808	42.8	5.5	5.3
Median	0.23	733	42.5	5.5	5.4
Standard deviation	0.06	279	6.6	0.2	1.0
Range	0.06 - 0.36	338 - 2047	30.7 - 60.0	5.1 - 6.1	2.9 - 7.7
Skewness	0.09	1.73	0.33	0.20	-0.16

identified as having come from a small, isolated area affected by surface-soil erosion and therefore did not represent topsoil conditions.

As found previously across the farm, P and Cd concentrations in the soil at this site were positively correlated (r = 0.59, Table 4.6). On a sample by sample basis, fluctuations in the concentrations of these two elements and soil carbon coincided closely (Figure 4.8).

Phosphorus is a strong indicator of animal transfer effects because of the large proportion of fertilizer-applied P (possibly up to 50%[1]) that ends up being transferred to stock camping sites. In the study area, a marked decrease in soil P concentration occurs, both going from north to south and from west to east (Figure 4.9 (*a*)). This corresponds to a change in topography from low-slope (campsite) to steep-slope. A similar pattern is

Table 4.6 Correlation coefficients (r) between total Cd concentrations and other soil parameters in 120 surface soils from the 625 m^2 area encompassing campsite, medium and steep slopes.

	Total Cd	Total P	Total Zn	Total carbon
Total P	0.590			
Total Zn	0.316	0.222		
Total carbon	0.605	0.640	-0.086	
Soil pH	0.264	0.269	0.389	-0.055

[1] assuming an application rate of 15 kg P ha^{-1} yr^{-1}

66
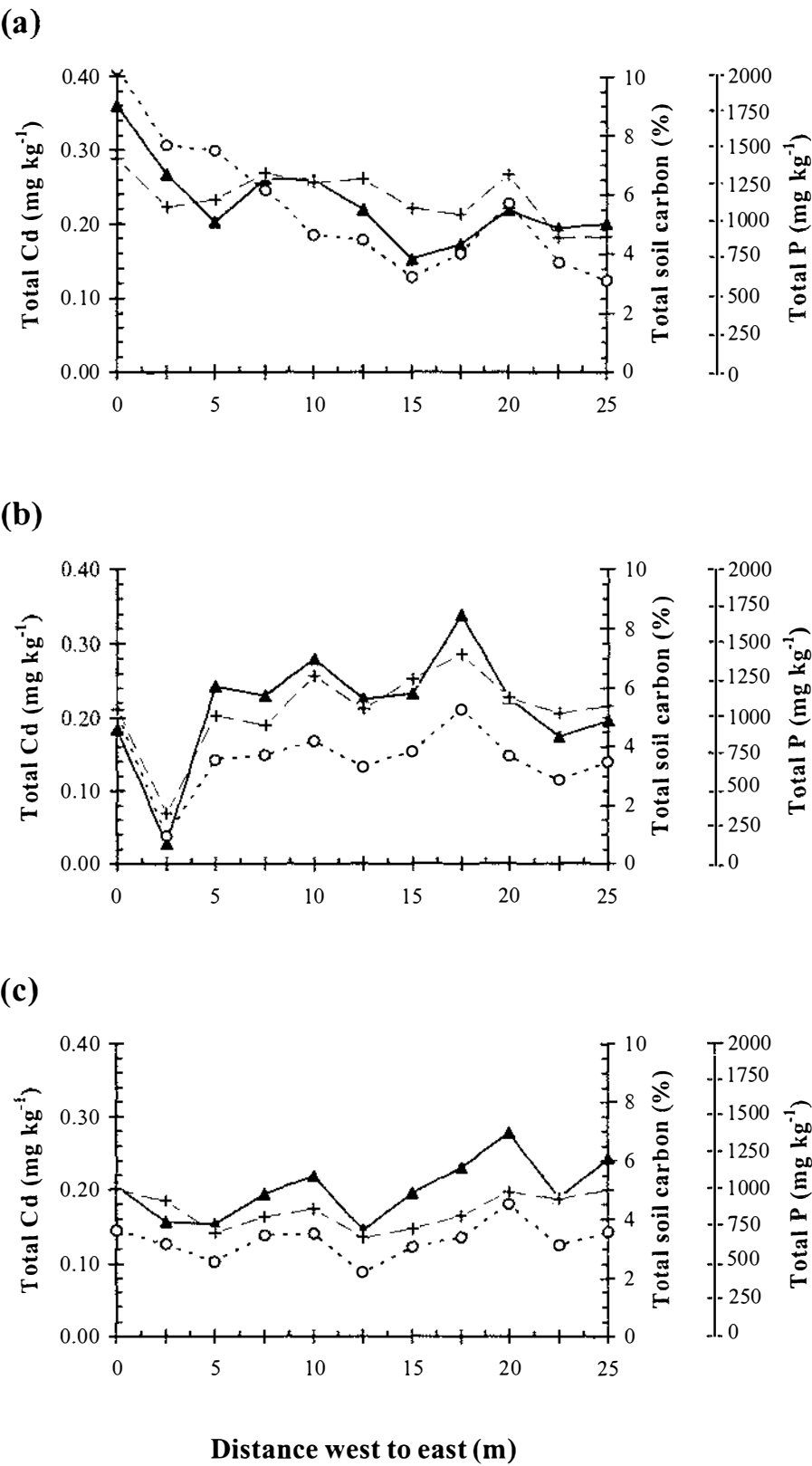
Figure 4.8 Representative plots of sample to sample fluctuations in the west-east
direction across a 25m x 25 m study area encompassing campsites,
medium and steep slopes: total Cd (▲); total P (O); and total soil carbon
(+). *(a)* 0 m south (S); *(b)* 7.5 m S; and *(c)* 20 m S. Directions correspond
to the orientation of the grid in Figure 4.9.

(a) PHOSPHORUS
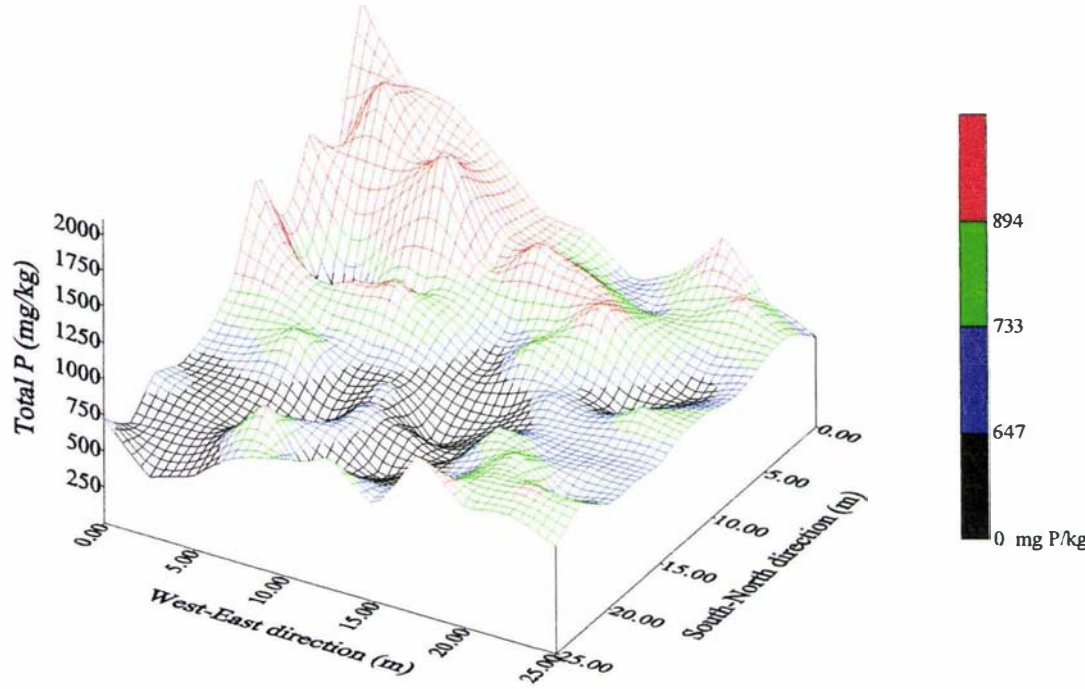
(b) CADMIUM
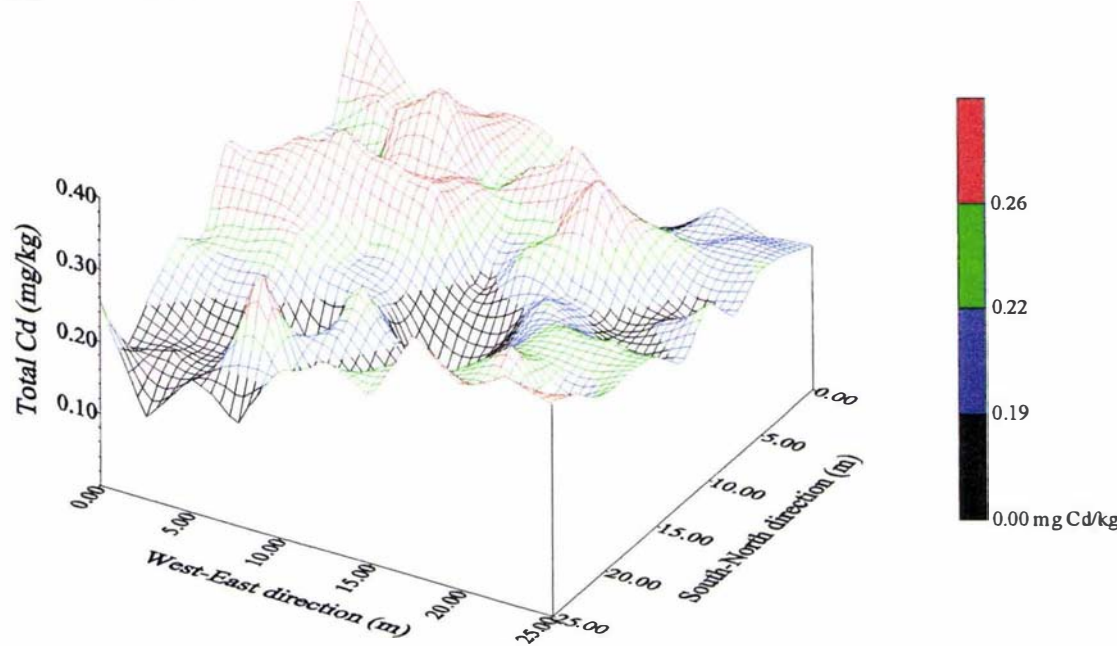
Figure 4.9 Three-dimensional plot of: (*a*) total P concentrations; and (*b*) total Cd concentrations in soil from a 25 m x 25 m study area encompassing campsites, and medium and steep slopes. The campsite is located in the north-west corner (0,0) and land slope generally increases in both the easterly and southerly directions. Divisions in the colour range are based on the median, and the lower and upper quartiles of each data set.

Table 4.7 Mean Cd and P concentrations, carbon content and soil pH for data when separated into low slope (campsite) and steep slope categories.

	Campsite (n = 72)	Steep slope (n = 49)	Difference P<
Total Cd (mg kg^{-1})	0.239	0.208	0.002
Total P (mg kg^{-1})	907	665	0.001
Total Carbon (%)	5.76	4.58	0.001
Soil pH	5.52	5.56	

also evident for Cd (Figure 4.9 (*b*)), and suggests that, as shown by Longhurst *et al.* (1994) and Loganathan *et al.* (1995), animal transfer effects have influenced Cd concentrations in the soil.

After visual inspection of the site, each sampling point was assigned to one of two slope categories: low slope (campsite); and steep slope. When categorized in this manner, the data reveal a highly significant increase in mean P concentration on the campsite compared to the steep slope (P < 0.001), and a similarly significant increase in mean Cd concentration (P < 0.002) (Table 4.7). However, in comparison to the findings of Loganathan *et al.* (1995), these increases are small. Whereas mean P and Cd concentrations on the campsite and steep slope differed by only 1.4 and 1.1 times respectively in this study, Loganathan *et al.* (1995) found them to differ by two-fold irrespective of site fertility (P Loganathan, unpublished data).

These differences in Cd concentration between the low and steep slope arise from not only the effect of animal transfer, but also slope-related variation in fertilizer application rate (Loganathan *et al.*, 1995) and erosion losses. If variation in the rate of fertilizer application is estimated using the cosine of the slope angle (after Loganathan *et al.* 1995), a 1.09 fold increase in concentrations on the low slope (12°) could be attributed to this factor alone. Thus there still appears to be an impact on soil P concentrations by animal transfer, but the impact on soil Cd concentrations appears limited. The lower accumulation of P in these low slope soils compared to that found in the study by Loganathan *et al.* (1995) suggest that this site has experienced less stock camping
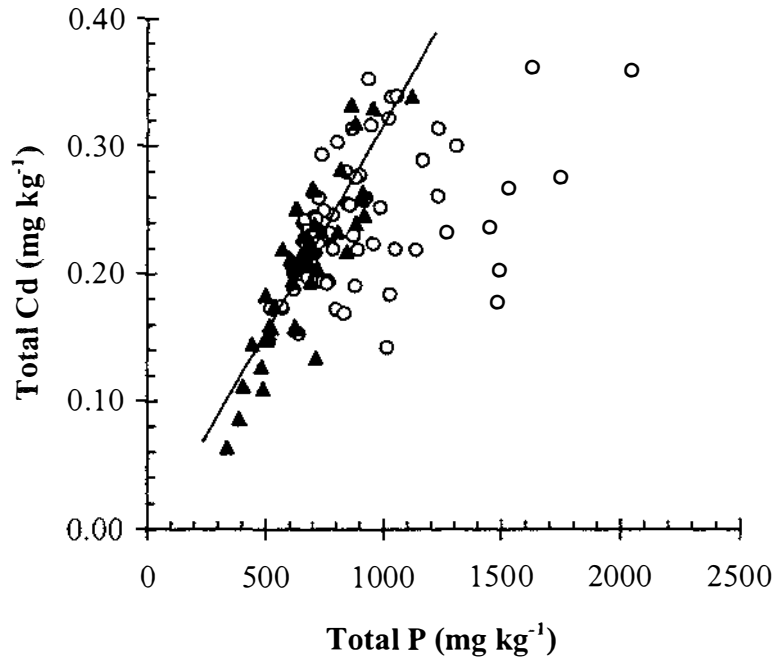
Figure 4.10 The relationship between total Cd and total P for soil samples taken from a 25m x 25 m study area encompassing campsites, medium and steep slopes. The 121 sample points have been categorized into two slope classes: low slope (O; r = 0.46) and medium to steep slope (▲; r = 0.86).

activity. Although, the smaller increase in Cd concentrations relative to P may likewise indicate reduced Cd redistribution in the paddock through dung.

Differentiating between the two slope categories, it is apparent that the P-Cd relationship changes from low slope to steep slope (Figure 4.10). On the one hand, Cd and P show a very strong linear correlation (steep slope, r = 0.88) while on the other, the points are dispersed and the relationship is markedly weaker (low slope, r = 0.46).

Closer inspection of the P-Cd relationship on the steep slope reveals that P concentrations increase by 3061 milligrams for each milligram increase in Cd. This corresponds to the relative increases in P and Cd which could be obtained through the application of phosphatic fertilizer. Compare, for example, the value 3061 (P:Cd) with an estimated P:Cd ratio in fertilizer of 2260 (Bramley, 1990; see also section 5.3.4). This observation, in conjunction with the strong correlation between P and Cd in these soil samples, suggests that the variation in Cd concentrations on the steep slope is probably a result of variations in the application of phosphatic fertilizer. Given the

impossibility of spreading granulated fertilizer perfectly uniformly, this would appear reasonable.

On the low slope, however, it is clear from the wide scatter of the points in Figure 4.10 that the P-Cd relationship inherited from fertilizer has been considerably weakened. Compared to soils on the steep slope, many of the soil samples taken from the low slope have proportionally more P than Cd. They, therefore, appear to have received additional P beyond that from phosphatic fertilizer. Since this low slope area has been identified as a campsite, it seems reasonable to presume that this additional P has come from dung.

Concentrations of P in herbage are relatively constant at 0.25 - 0.5 % (During, 1984). In contrast, Cd concentrations, while being much lower, are widely variable (from <0.05 to over 1.0 mg Cd kg^{-1} dry matter). Factors such as plant species, season, Cd concentration in the soil and mitigating soil properties, such as pH and organic matter content, all influence herbage Cd concentrations (Roberts *et al*., 1994; Loganathan *et al*., 1997). As a consequence, the ratio of P to Cd in herbage also varies widely – from 2500 to over 50 000 if the above-quoted figures are used, for instance. Under some conditions this ratio, and subsequently the P:Cd ratio in dung, may be much larger than that in soil [3000 to 8000 – from data by Roberts *et al*. (1994)] and in fertilizer (1000 to 5000, Table 2.3). Where this is the case, the P:Cd ratio in campsite soils may widen with the deposition of dung.

Bearing in mind the potential for widely varying P:Cd ratios in dung, two reasons for the weaker correlation between P and Cd on the low slope (compared with the strong correlation obtained for steep-slope samples) may be proposed. 1) A greater rate of P input, via animal transfer, relative to Cd; and 2) a large variability in the Cd concentrations in dung relative to P. In addition, though animal transfer will always act to increase the total amount of Cd in campsite soils, the magnitude of this effect on Cd accumulation in low slope soils (as indicated by the soil P:Cd ratio) will depend on the quantity of Cd transferred via dung. This depends, in turn, on the concentration of Cd in the herbage and, therefore, on the plant availability of Cd in the surrounding soil. Consequently, the impact of animal transfer on soil Cd concentrations will vary between sites. At the Limestone Downs study site, for example, the relatively high soil pH and

low soil Cd concentrations (Table 4.5) probably resulted in only limited transfer of Cd to campsites through dung deposition. This can be surmised from the lower accumulation of Cd compared to P and the resulting widening of the P:Cd ratio on low slopes. In contrast, data from the Ballantrae studies of Loganathan *et al.* (1995) showed a marked accumulation of Cd on campsites and no evidence of an effect from animal transfer on the P-Cd ratio. The difference between these studies is perhaps attributable to differences in the plant availability of Cd in the soil of the respective study sites.

4.5 CONCLUSIONS

The surface soils of Limestone Downs were found to have Cd concentrations between 0.07 and 0.91 mg Cd kg^{-1}. The arithmetic mean of this range (0.36 mg Cd kg^{-1}) is typical for New Zealand agricultural soils and is similar to the concentration of Cd in agricultural soils in other parts of the world.

Although variability in topsoil Cd concentrations may sometimes be attributed to pedogenic processes, categorizing topsoils according to their parent material and soil grouping could not explain the variation observed. This became understandable when analysis of soil and rock material from 17 representative soil profiles on Limestone Downs revealed that parent material was unlikely to contribute to topsoil Cd. In general, Cd concentrations in the soil profiles decreased rapidly with depth. Insignificant levels were normally seen by the C, and lower B horizons. There were, however, four profiles that deviated from this trend. In two profiles, the Cd content of the parent material (0.1 and 0.16 mg Cd kg^{-1}) could be related back to the presence of calcareous deposits in the parent rock. Cadmium in the parent material of a third profile (0.13 mg Cd kg^{-1}) was attributed to the presence of iron sand deposits. Though representing a potential source of Cd through both *in situ* weathering and aeolian deposition, the Cd in these ironsands was considered to be of very low plant availability (soluble in only HF acid), and, consequently, of no threat to plants and animals. In the fourth profile, an unusually large concentration of Cd was found in the parent material (0.76 mg Cd kg^{-1}). The origin of this Cd is unknown, but could possibly have come from marine detritus.

The only soil characteristics found to correlate significantly with Cd concentrations in topsoils across the farm were the P status ($r = 0.84$) and the total carbon content ($r = 0.79$) of the soil. In a localized area studied for the effects of topography and stock camping behaviour on Cd distribution, P and carbon continued to show a strong correlation with Cd. However, this correlation was strongly dependent on topography. Soils from the steep slope showed a very strong, linear correlation between P and Cd ($r = 0.86$). This was interpreted as indicating that variation in the spread of fertilizer granules had caused the variation in soil Cd concentrations. In contrast, the Cd-P correlation on the low slope was much weaker ($r = 0.46$).

As for P , Cd concentrations on the low slope were found to be statistically greater than those on the steep slopes. However, this difference (1.4 times for P and 1.1 times for Cd) was markedly less than that reported previously.

The greater impact of animal transfer on P concentrations compared to Cd suggested a greater redistribution of P through dung than Cd. This was considered reasonable in view of the fact that, unlike P, the concentration of Cd in herbage, and thereby in dung, is highly variable. Cadmium uptake by plants is strongly dependent on both the amount of Cd in the soil and soil properties which affect its plant availability – notably pH and organic matter. The impact of animal transfer on Cd will therefore be much more variable than is observed for P and the resulting Cd accumulation on campsites will differ as a function of the soil properties in the paddock.

Overall, the best explanation for Cd variability in soils appears to be the phosphatic fertilizer history. As a result of this finding, a more detailed investigation of the effect of fertilizer on soil Cd levels was conducted. Data from this study are reported and discussed in the next chapter.

CHAPTER 5

ANTHROPOGENIC INPUTS OF CADMIUM TO SOILS ON A REGULARLY FERTILIZED HILL-COUNTRY FARM

5.1   INTRODUCTION

In Chapter 4, the influence of soil parent material and soil forming processes were investigated to determine their impact on the Cd concentrations present in surface soils on the Limestone Downs Station. It was concluded that, on the whole, soil parent material was not a major contributor of Cd to these pastoral soils. Rather, the surface accumulation of Cd and the strong correlation of soil Cd with soil P suggested that phosphatic fertilizer was the dominant source of Cd currently resident in the topsoil.

Past and current studies have demonstrated that Cd present in phosphatic fertilizer will accumulate in surface soil with only limited translocation to depth (Williams and David, 1973 and 1976; Mulla *et al.*, 1980; Rothbaum *et al.*, 1986; Loganathan and Hedley, 1997; Taylor, 1997). Fertilizer-induced accumulation of Cd has been further illustrated by Roberts *et al.* (1994) in a New Zealand-wide survey. This work showed that soils from pastoral farms receiving fertilizer had significantly higher Cd concentrations in the 0 - 7.5 cm depth than soils at unfertilized (non-agricultural) sites.

There is, nonetheless, continued debate over the significance of fertilizer as a source of Cd to pastoral soils. As a regularly fertilized property, Limestone Downs offers a unique opportunity to investigate the importance of fertilizer-derived Cd inputs to pastoral soils. Adjacent to the farm is an area of undisturbed native bush that allows for the comparison of fertilized (pasture) and unfertilized (native bush) soils within the same soil group. In this manner, disparity in Cd accumulation between soils as a result of widely differing soil properties is avoided. This chapter reports on the results of two such comparisons and explores the data for evidence of significant Cd inputs from fertilizer.

5.2   MATERIALS AND METHODS

In November of 1993, two pedologically matched sites were located on Limestone

Downs farm for each of two different soil groups (Yellow-brown loam and Yellow-brown earth) and sampled. One of each of the pedologically matched sites was under unfertilized, undisturbed native bush. The other was under regularly fertilized, permanent pasture (Figure 5.1). A description of each soil profile was recorded from pits dug in the vicinity of sampling (A. S. Palmer, Appendix 3) and soil bulk density was determined on samples taken from these pits at four depths spaced between 0 and 30 cm.

Vegetation is known to influence soil chemical properties, such as pH and carbon content (Riha *et al.*, 1986; Ross, 1994c), and this in turn influences trace element behaviour in the soil (Bergkvist, 1987; Werner *et al.*, 1987; Krosshavn *et al.*, 1993). In order to recognize such variation, separate soil samples were collected at the native bush sites from around the base of two different tree types – broadleaf and podocarp. The physical locations of each site are shown on Map 1 (Reconnaissance Soil Map of Limestone Downs).

At each site, about 10, 30-cm deep soil cores were taken from a 1 m^2 area and sectioned to give bulked samples for depths of 0 - 3.5, 3.5 - 7.5, 7.5 - 15.0 and 15 - 30 cm. The individual samples were bulked to give an average 'soil' so as to reduce sampling error. Following treatment as described in section 3.3, the soils were analyzed for total Cd, total Zn, total P, total carbon, soil pH and soil cation exchange capacity as described in Chapter 3. Samples of herbage from the two native tree species were also taken and analysed for total Cd (section 3.4).

For the purposes of this study, Cd in soil will be referred to by one of three terms:
1) Native Cd – describing Cd which has originated from parent material and any other natural sources;
2) Resident Cd – a general term used to cover Cd present in field soils, both native and that derived from anthropogenic sources such as industrial air pollution or the application of soil amendments, for instance phosphatic fertilizer; and
3) Added Cd – which has been introduced to the soil as a $Cd(NO_3)_2$ treatment for the purposes of studying Cd behaviour in soil (used specifically in Chapter 6, the laboratory leaching studies).

Limestone Downs farm
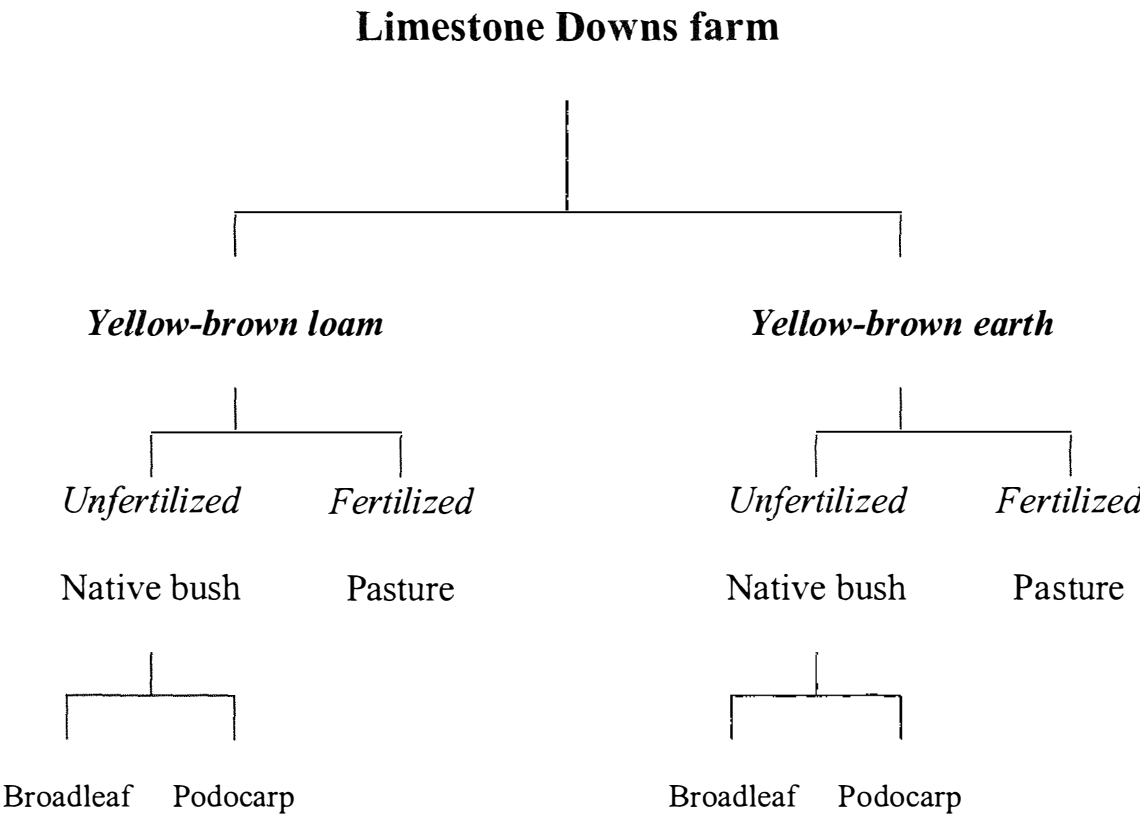
Figure 5.1   Sampling scheme for comparison of pedologically matched fertilized and unfertilized sites from two soil groups on Limestone Downs farm.

5.3   RESULTS AND DISCUSSION

5.3.1   Comparison of soil properties between sites

The diverse behaviour of Cd in soils is largely related to differences in soil properties (He and Singh, 1993c; Ross, 1994b and 1994c). For example, increasing the (organic) carbon content of a soil and increasing the soil pH normally increase the soil capacity to bind Cd, and may therefore enhance Cd accumulation – such factors are considered in greater detail in Chapter 6. In addition, it has been suggested that Cd concentrations in a forest soil may be lower than adjacent grassland because conditions in the forest soil are more conducive to the leaching of Cd (Jensen and Svensmark, 1989). Consequently, in order to investigate the impact of fertilizer on the Cd concentrations in the soils of this

study, it was necessary to verify first that the matched, fertilized and unfertilized soils were sufficiently comparable in their soil properties.

For all sites soil pH shows little variation with depth and, except in the case of the Yellow-brown earth (YBE) broadleaf site, it is similar between fertilized and unfertilized sites of the same soil group, (Table 5.1). Under the broadleaf species, soil pH in the YBE is notably lower than under pasture. An effect of tree species is possible, but this situation is not repeated on the Yellow-brown loam (YBL). Between soil groups, pH is consistently higher in soils of the YBL compared to those of the YBE. This trend is typical due to the buffering effect of the amorphous colloidal allophane (NZ Soil Bureau, 1968a).

As expected, total soil carbon is always higher and more variable in the 0 - 3.5 cm depth. Other depths show little variation between fertilized and unfertilized sites. The higher carbon values recorded in the top depth at the unfertilized (bush) YBE sites compared to the fertilized (pasture) site are probably due to inclusion of some leaf litter when sampling. Comparing carbon values between soil groups, it is seen that the YBL has a notably greater carbon content than the YBE soil. As with the trend in soil pH, this is typical for New Zealand conditions (NZ Soil Bureau, 1968a).

Though soil cation exchange capacities (CEC) vary considerably with depth and site, it appears that the fertilized YBE soil has a consistently greater CEC and exchangeable calcium content below 3.5 cm than its unfertilized counterpart (Table 5.1). This most likely reflects periodic lime, and annual SSP applications on the pasture soil. Generally these activities also raise the soil pH, though, as noted previously, only one of the bush sites – the broadleaf site – shows a lower soil pH than the pasture site. Cation exchange capacity is often included in regulations governing metal loadings to agricultural land because of its importance to metal accumulation (King, 1988). As a measure of sites available for Cd sorption, the higher CEC lower down the profile of the fertilized YBE soil may indicate a slightly greater capacity for Cd accumulation at depth in this soil compared to its unfertilized counterparts.

From the results presented in Table 5.1, it does not appear that tree species has consistently influenced any of the soil properties. This is perhaps not surprising given

Table 5.1 Selected properties for soil sampled from paired sites, one fertilized (pasture) and one unfertilized (native bush - with separate profiles collected from under two tree types: broadleaf and podocarp), for two soil groups on Limestone Downs.

Vegetation	Depth down soil profile (cm)	Bulk Density (g cm^{-3})	Total Carbon (%)	Soil pH (water)	Exchangeable Cations (mEq/100 g) H$^+$	Ca^{2+}	Total CEC	Total Cd (mg kg^{-1} air dry soil)	Total P	Zn:Cd [†] (weight:weight)
Site 1:	**Yellow-brown loam**									
Pasture	0 - 3.5	0.54	16.8	5.5	27.6	14.1	47.6	0.64	2208	102
	3.5 - 7.5	0.60	13.0	5.6	28.9	8.1	39.8	0.44	1461	152
	7.5 - 15	0.59	9.6	5 7	22.7	3.9	28.1	0.19	688	346
	15 - 30	0.64	6.7	6.0	12.7	3.7	17.5	0.12	486	519
Broadleaf	0 - 3.5	0.47	11.9	6.0	18.9	11.2	36.9	0.18	648	294
	3.5 - 7.5	0.53	10.3	5.9	19.1	8.2	31.8	0.16	551	326
	7.5 - 15	0.49	10.5	5.9	17.6	8.1	30.2	0.15	506	320
	15 - 30	0.55	6.7	5.9	14.4	4.0	21.1	0.10	386	422
Podocarp	0 - 3.5	0.47	20.2	5.6	34.2	12.3	55 3	0.13	642	265
	3.5 - 7.5	0.53	13.8	5.6	28.0	4.8	37.0	0.10	511	341
	7.5 - 15	0.49	12.3	5.7	24.7	4.0	32.5	0.11	483	279
	15 - 30	0.55	11.2	5.6	23.8	3.1	30.2	0.11	489	330
Site 2:	**Yellow-brown earth**									
Pasture	0 - 3.5	0.94	8.8	5.1	16.7	11.7	33.9	0.61	1642	77
	3.5 - 7.5	1.12	5 9	5.1	16.7	9.0	29.7	0.33	779	132
	7.5 - 15♦	1.17	3.9	5.2	16.1	7.0	27.5	0.10	339	433
	15 - 30	1.14	2.4	5.3	14.4	7.1	27.1	0.03	198	1700
Broadleaf	0 - 3.5	0.94	18.7	4.6	29.5	5.6	41.4	0.03	354	738
	3.5 - 7.5	1.09	4 9	4.7	17.9	0.6	19.9	0.01	195	3900
	7.5 - 15	1.15	3.9	4.6	18.3	0.3	19.6	0.00	171	∞
	15 - 30	1.27	2.1	4.6	11.4	0.2	12.3	0.00	103	∞
Podocarp	0 - 3.5	0.94	10.5	5.1	18.9	9.3	35.0	0.03	296	720
	3.5 - 7.5	1.09	4.4	5.1	12.7	3.1	18.3	0.01	190	2675
	7.5 - 15	1.15	3.1	5.2	9.5	2.7	14.3	0.01	150	3283
	15 - 30	1.27	1.7	5.1	8.7	1.7	12.0	0.00	103	∞

[†] ∞ indicates a very large number.

that these native bush sites were mixed stands and soil sampling was generally conducted away from the trunk-base area. Consequently, the soil sampled is likely to have been influenced by litter and throughflow from both tree families. What is more, there appears to be sufficient similarity in soil properties between the paired pasture and bush sites for one to assume similar behaviour in terms of potential Cd accumulation. Thus, any disparity in the amounts of Cd accumulated between these fertilized and unfertilized sites can be attributed to differences in their anthropogenic inputs.

5.3.2   Impact of fertilizer application on soil cadmium concentrations

At all sites, Cd concentrations were always highest in the very top layer (0 - 3.5 cm). The concentrations ranged from 0.03 - 0.2 mg Cd kg^{-1} in the unfertilized soils to over 0.6 mg Cd kg^{-1} in fertilized soils under pasture (Table 5.1). Cadmium concentrations in the topsoil of the pasture were similar for the two soil groups (0.64 and 0.61 mg Cd kg^{-1} for the YBL and YBE respectively), but on a mass per unit volume basis the Cd concentration is less in the YBL (0.35 μg Cd cm^{-3}) than in the YBE (0.57 μg Cd cm^{-3}). This results from the greater bulk density in the YBE compared to the YBL (Table 5.1).

In both soil groups, the fertilized soils contained significantly higher Cd concentrations in the top 3.5 cm than their matched unfertilized soils (Figure 5.2 *(a)* and *(b)*). This difference ranged from 3.6 times to 20 times the concentration of Cd in the unfertilized YBL and the YBE respectively. Furthermore, as found for the soil profiles examined in the previous chapter, the Cd concentrations under pasture decreased markedly with depth (Figure 5.2 *(a)* and *(b)*). Cadmium concentration profiles in the soil at depth are similar for both unfertilized and fertilized sites. This suggests that the native Cd concentrations in these soils have been supplemented by anthropogenic additions from the surface.

Also noteworthy is the marked difference in the native Cd concentrations between the soil groups. Whereas Cd concentrations in the unfertilized YBE soils reduce to undetectable concentrations by 15 cm, both unfertilized sites on the YBL still contain Cd (0.1 mg Cd kg^{-1}) in the 15 - 30 cm depth. This was an unexpected observation since none of the YBL profiles discussed in Chapter 4 were found to contain sufficient Cd in the parent material to produce significant native Cd concentrations (section 4.5.2).

(a)   Yellow-brown loam
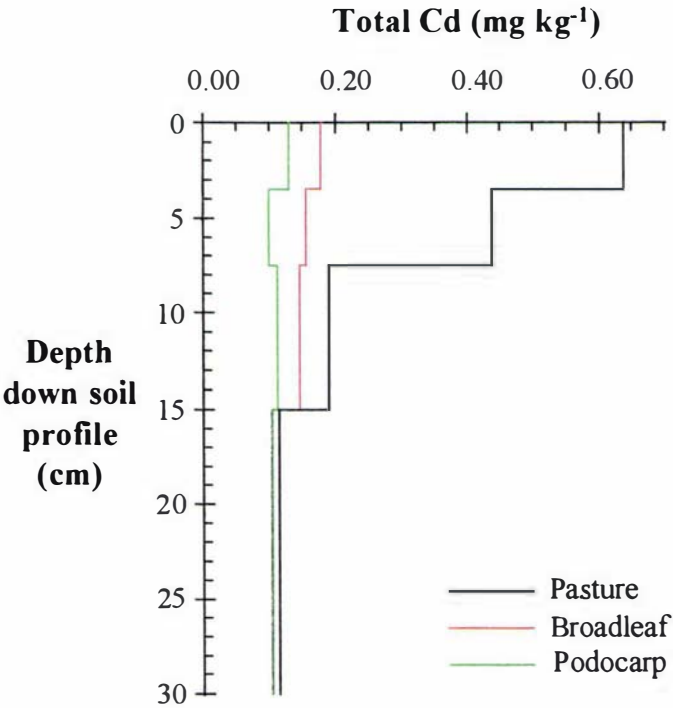
(b)   Yellow-brown earth
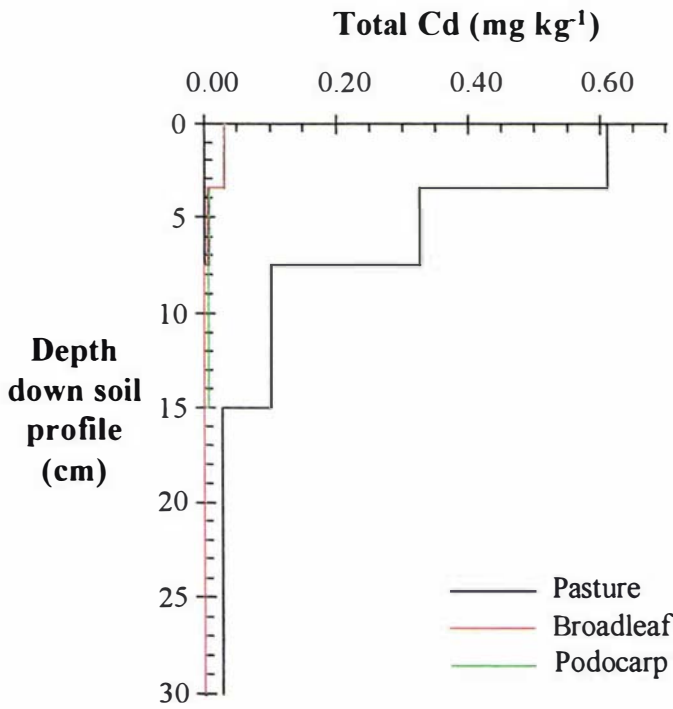
Figure 5.2   Soil profiles of: *(a)* a Yellow-brown loam and *(b)* a Yellow-brown earth showing the difference in Cd concentration between sites fertilized with phosphatic fertilizer (pasture) and unfertilized sites under two tree species (broadleaf, podocarp) in undisturbed native bush.

Hence, while accepting that the Cd in the YBL bush soils is mainly native, it is noted that the close proximity of these soils to the farm (Appendix 3) may have exposed them to some addition of Cd through fertilizer drift during aerial top-dressing of adjacent pasture.

The Zn:Cd ratios in these soils also show a noteworthy trend. Ratios calculated for the fertilized, pastoral soils are lowest in the topmost layer (increasing with depth) and are between 2.5 and 10 times lower than in their matched, unfertilized native bush soils (Table 5.1). Zinc and Cd exhibit very similar soil chemistry and are found closely associated in phosphate rock at a ratio smaller than that found naturally in soils (section 2.4.2). A lower soil Zn:Cd ratio is, therefore, generally seen following repeated applications of phosphatic fertilizer (Roberts *et al.*, 1994).

Finally, it is evident from Table 5.1 that there has also been an accumulation of P in the surface soil of the fertilized sites. This and the above observations are all consistent with the regular use of fertilizer over many decades and the absence of frequent mechanical mixing of the topsoil through tillage. However, before drawing a conclusion on the importance of fertilizer as a Cd source, two other aspects require consideration. There is: 1) the possibility of additions through anthropogenic atmospheric deposition; and, more importantly, 2) the chance that native Cd reserves have been under-estimated due to large amounts of Cd being stored in the above-ground biomass of the native bush.

5.3.3 Atmospheric Pollution

Many European studies have implicated urban and industrial air pollution in the accumulation of Cd in rural soils (section 2.4.3), especially in the dominant downwind direction from a major point source where pollution may persist for at least 20 km (Tiller, 1988). The probability that atmospheric pollution may be a source of Cd to the soils on Limestone Downs was briefly considered.

Estimates using a 1:350 000 regional map indicate that, of several possible pollution sources (including the cities of Hamilton and Papakura), the nearest (Glenbrook Steel Mill) is at least 33 km away. At this distance the deposition rate could be assumed similar to that found at a rural site, 37 km west of Christchurch city. At this locality,

Fergusson and Stewart (1992) recorded 0.015 μg Cd m^{-2} day^{-1}, or 0.055 g Cd ha^{-1} yr^{-1}. Compared with estimated fertilizer inputs of between 5 - 20 g ha^{-1} yr^{-1} for the New Zealand situation (Rothbaum *et al.* 1986; Loganathan *et al.* 1995), such a deposition rate is negligible. Furthermore, atmospheric pollution would affect both bush and pasture sites similarly, thus the difference in Cd status between these two systems is unlikely to be from atmospheric Cd input.

5.3.4 Cadmium reserves in native bush biomass

Data from international studies suggest that a significant proportion of Cd stored in a forest ecosystem can be contained in the above-ground biomass (Table 5.2, over page). This raises the possibility that, in reporting only soil Cd concentrations, I may have underestimated the total Cd store in the native bush, and consequently underestimated the native Cd store in the pasture profiles. Further, should the bush biomass contain significant quantities of Cd, any Cd which was returned to the soil surface during clearing in the form of ash (from burning) may, once under pasture, be erroneously categorized as having come from fertilizer additions. Accordingly the potential Cd store in the bush biomass was investigated.

Samples of foliage were collected from native tree species and analysed for their Cd concentrations. The Cd concentrations in the trunks, branches and stems were then estimated using these leaf concentrations in conjunction with data from European studies (Heinrichs and Mayer, 1980). This gave an idea of the relative concentrations of Cd within each part of the tree (Table 5.3) as trunks and branches could not realistically be sampled for this study. In the absence of data for the native bush on Limestone Downs, figures from a podocarp-hardwood forest in Westland, New Zealand (Levett *et al.*, 1985) were used to estimate the total bush biomass. Understorey vegetation was omitted from the calculations as, at 2.5 x 10^3 kg ha^{-1} (Levett *et al.*, 1985), it would not significantly change the total Cd stores.

The results of the above calculations are presented in Table 5.3, and are based on either an entire stand of Broadleaf or an entire stand of Podocarp. Compared to the Cd concentrations in vegetation of the Solling Mountains, foliage samples taken from Limestone Downs are very low. Consequently the total Cd estimated to be contained in

Table 5.2 Cadmium loadings in forest soils and forest biomass from other countries.

Country	Soil Type	Depth (cm)	Soil Cd store (g ha^{-1})	Vegetation species	Above-ground biomass (10^3 kg ha^{-1})	Biomass Cd store [†] (g ha^{-1})	References
Switzerland	Acid-brown [‡]	0 - 20 [§]	212	Spruce	-	155	Keller *et al.* (1992) [¶]
	Alpine podzol	0 - 30 [§]	306	Mixed forest	-	40	
Central Germany	Typic Dystrochrept	0 - 30	220	Beech	274	50	Heinrichs and Mayer (1980) [¶]
		0 - 30	223	Spruce	245	120	
Poland	-	-	-	Oak-Hornbeam	151	154	Weiner and Grodzinski (1984)
	-	-	-	Pine	110	133	
Ontario, Canada	-	-	-	Sugar maple-Yellow birch	168	41	Morrison and Hogan (1986)

[†]   Excluding that contained in roots.
[‡]   In this soil, the majority of Cd is contributed by the B horizons.
[§]   These depths are approximately the base of the lowest A horizon.
[¶]   Totals have been calculated from tabulated data given by the authors. Loadings for further depths are also given, but not included here.

Table 5.3 Estimating the store of Cd in the above-ground biomass of native bush on Limestone Downs.

Tree compartment	Solling Mountains (Central Germany) [†] Cd concentration (mg/kg dry weight)		Podocarp-hardwood forest (New Zealand) [‡] Biomass dry weight (10^3 kg ha^{-1})	Estimates for native bush stand, Limestone Downs (New Zealand) Cadmium Content (mg/kg dry weight) [§]		Total Cd in compartment (mg Cd ha^{-1})	
	Beech	Spruce		Broadleaf	Podocarp	Broadleaf	Podocarp
Foliage	0.66	0.31	5.8	**0.018**	**0.027**	104	157
Twigs	0.17	0.91	10.7	0.005	**0.074**	54	792
Branches	0.17	0.91	25.5	0.005	0.079	128	2015
Branches/Stems	0.19	0.36	209.8	0.005	0.031	1049	6504
Total cadmium contained in above-ground biomass (g Cd ha^{-1})						1.3	9.5

[†] Heinrichs and Mayer (1980)

[‡] Levett *et al.* (1985)

[§] Cd concentrations for foliage collected at the YBL study site on Limestone Downs are shown in bold type.
The Cd concentrations in the branches and stems of the Broadleaf and Podocarp species on Limestone Downs have then been estimated by assuming that their ratio of Cd in the foliage to that in the branches will be similar to this ratio in similar tree species in the Solling mountains.
For example:

$$\frac{([Cd]_{foliage})_{Broadleaf}}{([Cd]_{branches})_{Broadleaf}} = \frac{([Cd]_{foliage})_{Beech}}{([Cd]_{branches})_{Beech}} \quad \text{or:} \quad \text{Cd in Broadleaf branches} = 0.018\,/(0.66/0.17)$$

the bush biomass is also low – compare the totals from Table 5.3 with the figures given in Table 5.2. With a 50% margin of error on the estimated Cd concentrations in the foliage and wood of the native trees on Limestone Downs, the amount of Cd stored in the biomass could range between 0.7 and 2 g Cd ha^{-1} for the Broadleaf species and between 4.8 and 14.3 g Cd ha^{-1} for the Podocarp. These figures are still significantly less than the total Cd stored in the soil of the fertilized pasture sites (Table 5.4).

If the bush contains 10 g Cd ha^{-1} as estimated, and this entire store is returned to the soil on burning, it will account for just over 2% of the total Cd found under pasture (Table 5.4). Such a contribution could not reconcile the difference in native bush and pasture soil Cd reserves found in section 5.3.2.

5.3.5 Fertilizer as the cadmium source: an estimated mass balance

All evidence indicates that the additional Cd found in the fertilized pasture soils is a consequence of their having received phosphatic fertilizer. Assuming that native Cd levels are indicated by concentrations in the unfertilized soils, almost 97% of Cd in the YBE pasture profile (0 - 30 cm) is of fertilizer origins (Table 5.4). This proportion reduces to 66% in the YBL profile as a result of the higher Cd load of the native bush soils. However, it is apparent that fertilizer has had a major impact on the Cd loads in both these soils. A simple mass balance calculation is able to demonstrate that the elevated Cd levels seen in the pasture profiles can be accounted for by Cd additions through phosphatic fertilizer (Table 5.4).

By assuming that P present in the unfertilized soils (Table 5.4) represents native P, the difference between fertilized and unfertilized sites can be taken as P added via phosphatic fertilizer (Table 5.4). In ignoring above-ground P losses through animal products or animal transfer, an estimate of the minimum amount of fertilizer P added during pasture development is obtained and equals a rate of 12 - 15 kg P ha^{-1} yr^{-1} over 67 years. Using this as the minimum fertilizer application rate one can then estimate the likely minimum addition of Cd.

Examples of Cd:P ratios in phosphate rocks (which transfer across to the fertilizer product) are given in Table 2.3. Here, however, I have taken the value used by Bramley

Table 5.4 Accumulated Cd and P in fertilized (pasture) and unfertilized (native bush: Broadleaf and Podocarp) soils of a yellow-brown loam and a yellow-brown earth compared with estimates of Cd inputs from phosphatic fertilizer.

Soil Type	Vegetation	P accumulated in soil to 30 cm (kg ha^{-1})	Cd accumulated in soil to 30 cm (g ha^{-1})	Cd accumulated in topsoil [†] (g ha^{-1})	Cd MASS BALANCE FOR FERTILIZED (PASTURE) SOILS		
					P added by fertilizer [‡] (kg ha^{-1})	Cd added with this fertilizer P (g ha^{-1}) [§]	Anthropogenic Cd found in soil (g ha^{-1}) [¶]
Yellow-brown loam	Pasture	1539	420	226	778	347	234
	Broadleaf	728	202	63			
	Podocarp	795	170	43			
Yellow-brown earth	Pasture	1525	482	347	1000	443	466
	Broadleaf	545	13	13			
	Podocarp	506	19	13			

[†] Topsoil is soil from the depth 0 - 7.5 cm.

[‡] The difference between the accumulated P value given for the pasture and the average accumulated P values of the two bush sites (Broadleaf and Podocarp).

[§] The amount of Cd being applied with the fertilizer is based on a 50:50 mix of Nauru and Christmas Island phosphate rocks with a Cd:P ratio 4.43×10^{-4} (Bramley, 1990).

[¶] This value is the difference in accumulated Cd between the fertilized (pasture) and unfertilized (bush) sites for the 0 - 30 cm depth.

(1990). He estimated a Cd:P ratio of 4.43×10^{-4} for a 50:50 mix of Nauru and Christmas Island phosphate rocks. Multiplying the fertilizer-added P by this Cd:P ratio gives Cd additions of 350 and 440 g Cd ha^{-1} for the Yellow-brown loam and Yellow-brown earth pasture sites respectively (Table 5.4). The resultant annual rates of Cd additions (5.2 and 6.6 g Cd ha^{-1} yr^{-1} for the YBL and YBE respectively) are lower than the 8.9 g Cd ha^{-1} yr^{-1} predicted by Bramley (1990), but still account adequately for the extra, non-pedogenic Cd found in both pasture profiles (Table 5.4).

5.3.6   Distribution of fertilizer-derived cadmium in the soil profile

Because most concern over the accumulation of Cd in soils stems from entry of Cd into the food chain, the distribution of Cd with depth in the soil profile holds considerable importance. Most studies to date indicate strong surface accumulation of fertilizer-derived Cd in pasture soils and recovery of between 50 and 90% of the Cd applied (Williams and David, 1976; Rothbaum *et al.*, 1986; Nicholson *et al.*, 1996; Loganathan and Hedley, 1997). In this study, between 67 and 100% of the Cd estimated to have been applied as fertilizer was recovered from the pasture profiles (to a 30 cm depth). These values compare favourably with those of the other studies mentioned above. Of this fertilizer-derived Cd still residing in the soil, almost three-quarters was found in the top 7.5 cm of soil (Table 5.4) – the active rooting zone of pasture plants. If this trend continues, Cd transfer to plants and grazing animals will become of increasing concern.

On the other hand, these data suggest that over a quarter of the Cd applied to the surface has moved more than 7.5 cm deep. Mechanical mixing is unlikely to have been responsible for such translocation since many New Zealand hill-country pastures, once established, are left undisturbed. Therefore, it appears that Cd migration down these soil profiles has occurred under the influence of normal soil processes – possibly leaching.

5.4   CONCLUDING DISCUSSION

A comparison of developed pastoral soils (fertilized) with soils from an undeveloped native bush reserve (unfertilized) has confirmed that the application of phosphatic fertilizer to pasture causes a 3- to 20-fold increase in soil Cd loading. Cadmium which may be stored in the above-ground biomass of the native bush is insufficient to account

for the difference and deposition of atmospheric pollution in the area is considered minimal. All evidence, therefore, leads to the conclusion that the elevated Cd concentrations of soils under pasture are attributable to phosphatic fertilizer application during pasture development. Since this study was conducted, results published by Roberts *et al.* (1994), Loganathan and Hedley (1997) and Taylor (1997) have also attributed the accumulation of Cd in New Zealand pasture soils to fertilizer application.

The strong accumulation of Cd in the main rooting zone of pastoral plants should cause concern with regards to future fertilizer application and the effect on plant uptake and entry of Cd into the food chain. However, there is also a suggestion from this study that significant quantities of Cd may be moving below the active rooting zone. This raises the possibility that some Cd loss from these soils may be occurring. The literature suggests that leaching could be responsible for the apparent loss of Cd from topsoils. In view of the results presented here, this possibility was investigated and the findings are presented in Chapters 6 and 7.

The findings of this chapter also enable better interpretation of the results presented in Chapter 4 on Cd variability in the landscape. With such a large influence from fertilizer on Cd concentrations in soil, it is unsurprising that variation in parent material and soil group could not explain the variation in Cd – even with several parent materials containing measurable quantities of Cd. The strong correlations between total P and total Cd in the soil, the evidence for fertilizer-related variability, and the distinct surface accumulation of Cd all support the premise that phosphatic fertilizer is the major source of Cd to soils on Limestone Downs.

CHAPTER 6
CADMIUM REDISTRIBUTION IN SOIL

6.1   INTRODUCTION

Evidence presented in Chapters 4 and 5 indicates that most Cd in the soils of Limestone Downs originates from the surface application of fertilizers. However, while there is a marked accumulation in the surface horizons of these soils, some Cd can be found at depths of up to 50 cm. This raises the issue of Cd movement down the soil profile.

Redistribution within the soil profile is important when considering the accumulation of Cd in soils and its transfer to the food chain. There are two reasons for this. Firstly, an accurate assessment of the risk associated with the presence of Cd in soils must include a quantitative description of the rate of Cd accumulation in topsoil – a function of the rate of Cd input and the rate of Cd loss. In moving to depths beyond the active rooting zone, Cd is effectively removed from the soil-plant system and accumulation rates of Cd in the topsoil are reduced. If some leaching of Cd does occur, long-term management of Cd inputs to soils could be possible once a sustainable concentration is established. The application of some Cd-containing P-fertilizer could then be permitted without causing increased risk to consumers in the food chain.

Secondly, redistribution within the rooting zone, though perhaps restricted to only a few centimetres, may have a significant impact on Cd availability. In comparison to soil several centimetres deeper, the surface soil is generally a region characterized by high organic matter and high pH. Movement of Cd below this surface zone could take it from an environment of generally   low plant availability, to a region of increased availability in accordance with changes in soil chemical and physical properties (Loganathan and Hedley, 1997).

To predict future trends in soil Cd concentrations and the risk these pose to plants and animals, an understanding is required of the basic chemistry which regulates Cd interactions with the solid and solution phases of soil. The most important aspects of this chemistry are summarized in the following literature review. Methods used for soil column leaching studies and a preliminary investigation into anion concentrations in

some coastal soils are described. The remainder of the chapter discusses results from several leaching experiments that investigate Cd mobility in a range of New Zealand soils.

6.2   LITERATURE REVIEW

Cadmium mass balance studies for agricultural systems are often unable to account for all the Cd originally applied (Williams and David, 1976; Rothbaum *et al.*, 1986; McGrath, 1987; Williams *et al.*, 1987; Nicholson *et al.*, 1996; Loganathan *et al.*, 1997). Some of this loss has been attributed to lateral movement off treatment plots (McGrath and Lane, 1989), while some is presumed to be through vertical redistribution – possibly leaching (Rothbaum *et al.*, 1986; Nicholson *et al.*, 1996; McBride *et al.*, 1997a).

In general, losses of Cd from the soil system, either through leaching or plant uptake, are found to be small (Weiner and Grodzinski, 1984; Bergkvist *et al.*, 1989; Merry and Tiller, 1991; McGrath and Jarvis, 1993; Loganathan *et al.*, 1997) and this is reflected in the hundreds to thousands of years predicted as residence times for Cd in soil (Bowen, 1979; McGrath, 1987; Witter, 1996; Loganathan and Hedley, 1997). However, when constructing balances of Cd fluxes to and from agricultural soils, Folke and Landner (1996) noted that variations in the estimates of Cd leaching rates could exceed the calculated difference between Cd inputs and losses. To assess accurately the long-term threat of Cd to shallow rooted food and fodder crops, a more thorough understanding of its behaviour (in particular its leachability) under a greater variety of soil conditions and management regimes is needed.

6.2.1   Sorption as the mechanism regulating cadmium mobility in soils

Metal mobility in soils is governed by many aspects of the soil system – soil texture (particle size) and surface area, bulk density, temperature, aeration and redox status, pH, ion exchange capacity, amount and form of organic matter, amounts and forms of hydrous metal oxides and clay minerals (Sposito and Bingham, 1981; Mattigod and Page, 1983; Ross, 1994b; Wolt, 1994). In the case of Cd, it is how these various factors influence the sorption processes regulating Cd mobility that is important. Precipitation reactions are usually unimportant at environmental Cd concentrations since soil solution

concentrations are usually too low (McBride, 1980; Tjell and Christensen, 1992; Ross, 1994b).

Sites for Cd sorption in soil are mostly provided by clay minerals, organic matter, oxides of iron and manganese and calcium carbonate deposits. These surfaces provide sites that may be highly specific for Cd and other trace metals or non-specific. For the latter, Cd must compete with other macro-cations such as Ca^{2+} and Na^+ (Hendrickson and Corey, 1981; Ross, 1994b).

Clay has the greatest surface area to volume ratio of any soil fraction and, therefore, it is the most reactive component of the soil (Orlov, 1992). Clay provides both non-specific bonding sites for competitive adsorption and variable-charge edge sites which specifically adsorb heavy metals and can contribute significantly to metal sorption at trace concentrations (Hendrickson and Corey, 1981; McLaren and Cameron, 1990). Irreversible sorption into the crystal lattice can also be found with illites and smectites (Brümmer et al., 1986). The resulting decrease in sorption reversibility with increasing contact time, sometimes referred to as "ageing" (Christensen, 1984b; Pickering, 1980), may provide a means of removing "mobile" Cd from the soil-plant-animal system (Pickering, 1980; Barrow, 1986).

Organic matter makes a significant contribution to the CEC of a soil through its functional groups. These provide a range of exchange sites, with the charge being pH-dependent (Orlov, 1992). Organic matter can, therefore, participate in regulating Cd mobility (He and Singh, 1993c; McBride, 1989). The order of affinity that Cd has for donor atoms (S > N > O), which is opposite to that of cations such as Ca^{2+}, Mg^{2+} and Na^+, enables Cd^{2+} to compete successfully for the S-containing ligands in humic substances in spite of large concentrations of macro-cations (McBride, 1989; Senesi, 1992).

A significant relationship between Cd and soil organic content is often found in the field (Andersson, 1977; Keller et al., 1992; this study, Chapter 4), and some laboratory-based studies have been able to replicate this (Levi-Minzi et al., 1976; Andersson, 1977; Elliot et al., 1986; Eriksson, 1988; Kim and Fergusson, 1992).

Reactions between Cd and organic matter are difficult to generalize. Cadmium sorption can be either increased, decreased or unchanged by the presence of organic constituents. This depends on the nature of the organic molecules, the size and type of functional groups available for complexing and the interactions between organic molecules and other soil components. Other variables are the number and stability of other trace metals and surface phases (Riffaldi and Levi-Munzi, 1975; Baham *et al.*, 1978; Inskeep and Baham, 1983; Fischer, 1986; König *et al.*, 1986; Puls *et al.*, 1991; Berggren, 1992; Taylor and Theng, 1995). For example, organic material associated with the solid phase is able to remove Cd from solution, but dissolved organic matter (DOM) may solubilize and hold it in solution (Puls *et al.*, 1991; Berggren, 1992).

In contrast to interactions with organic matter, reduced Cd solubility in the presence of iron and manganese oxides and hydrous oxides has been regularly shown in laboratory studies (Tiller *et al.*, 1984; Slavek and Pickering, 1986; Gerth *et al.*, 1993; Ainsworth *et al.*, 1994). These oxides and hydroxides occur as coatings on soil particles, fillings in cracks and veins and as concretions or nodules (Kabata-Pendias and Pendias, 1992). After adsorption of Cd, subsurface diffusion into the crystal lattice and/or incorporation of Cd into developing oxide coatings or concretions (depending on the redox potential) can remove Cd from the potentially mobile pool (Kinniburgh and Jackson, 1981; Anderson and Christensen, 1988; Brümmer *et al.*, 1988; McLaren and Cameron, 1990; Singh and Gilkes, 1992).

The importance of calcium carbonate ($CaCO_3$) with respect to Cd behaviour in soil is most often related to its effect on soil pH (lime being commonly applied to raise soil pH); this aspect is discussed later. But studies have also found that Cd has a high affinity for the calcite surface and undergoes chemisorption at surface sites by substituting for Ca^{2+} (McBride, 1980; Papadopoulos and Rowell, 1988). Cadmium in solution can compete successfully against concentrations of Ca^{2+} which are 100 to 5000 times greater, and this may provide an important process for Cd immobilization in calcareous or limed soils (McBride, 1980; Papadopoulos and Rowell, 1988).

The rate at which Cd migrates through soil, movement to groundwater or to plants for example, is regulated by the equilibrium established between the soluble Cd pool and

that sorbed onto solid phases. Quantifying the threat that Cd poses to the environment, both short and long term, requires an assessment of the potential for desorption of soil-bound Cd. This is often done by partitioning the Cd into various phases (water soluble, exchangeable, Mn oxide, Fe oxide occluded, organic and residual Cd fractions [Keller *et al.*, 1992]) using a sequential extraction scheme. Alternatively, a distribution coefficient (K_d) can be determined to describe numerically the relationship between concentrations of metal sorbed to the solid phase and metal concentrations in solution at equilibrium. Large values of K_d indicate strong retention of the metal onto the solid phase and consequently reduced migration (Anderson and Christensen, 1988).

With improvements in analytical instrumentation, the ease of studying Cd at environmentally relevant (trace) concentrations has led to observations that the behaviour of Cd in soil differs depending on concentration (Garcia-Miragaya and Page, 1978; Hendrickson and Corey, 1981; Christensen, 1987a and 1989; McBride, 1994).

When present at low concentrations, adsorption on to highly specific binding sites allows Cd to compete effectively against the macro-cations (Papadopoulos and Rowell, 1988). Under these conditions, the distribution coefficients are generally large and mobility will be much lower than that predicted by non-selective cation exchange reactions (McBride, 1994). However, increasing the Cd concentration pushes adsorption into the region of non-specific cation exchange and distribution coefficients subsequently decrease (Egozy, 1980; Hendrickson and Corey, 1981). It is apparent, therefore, that to understand and accurately assess metal behaviour in the natural environment, studies should be done at appropriately low concentrations.

Evidence from the literature points to Cd^{2+} as the sole species through which adsorption of Cd to the solid phase takes place (Neal and Sposito, 1986; Boekhold *et al.*, 1993). This species, therefore, provides the key to regulating Cd mobility in soils and factors which most affect its concentration in solution and interaction with the solid phase will be of greatest interest with regards to leaching and residence times in soil.

6.2.2 Soil and solution pH

Soil and solution pH have been repeatedly identified as among the most important

factors in determining Cd mobility (Christensen, 1984a; Anderson and Christensen, 1988; Christensen, 1989; Hornburg and Brümmer, 1993; Naidu *et al.*, 1994). Soil solution pH has a major effect on many of the components involved in cation adsorption. It directly affects the speciation of Cd by influencing the stability and dominance of various metal complexes in solution, in particular the metal-hydroxy species which are involved in adsorption reactions (Hahne and Kroontje 1973; Egozy, 1980; McBride, 1989; Naidu *et al.*, 1994). Through its relationship with the H^+ concentration, pH provides a measure of the competition for binding sites by H^+ (Plant and Raiswell, 1983). Furthermore, a change in pH causes a change in the variable charge and solubility of organic molecules, metal hydrous oxides, and the variable charge on clay minerals (Barrow, 1993).

In general, Cd has been found to be much more soluble in the pH range 4-5 than pH 5-7 (Brümmer and Herms, 1983). A soil's sorptive capacity can increase rapidly over a narrow pH range. Christensen (1984b), for example, observed sorption to increase three times for each unit increase in pH. This is also illustrated by Cd adsorption on to iron oxides, a process normally completed (0 to 100% adsorption) within 2 pH units (Benjamin and Leckie, 1981; Sposito, 1983; Brümmer *et al.*, 1988; Gerth *et al.*, 1993). Considering this, organic acids released into the rhizosphere by plant roots are especially important with their ability to reduce soil pH by up to one pH unit (McLaren and Cameron, 1990) and thereby cause local mobilization of Cd.

This dominant effect of pH on Cd mobility has also been seen in experimental leaching studies. Soils differing only in pH often show large variation in Cd mobility, the greatest degree of movement occurring at acid pH (McBride, 1994; Holm *et al.*, 1995, as cited by Folke and Landner, 1996). In acid soils, therefore, Cd movement can be detected over years to decades as opposed to centuries – the time frame required for other more strongly held metals (McBride, 1994).

Low Cd solubility is normally observed above pH 6 - 7 (McBride, 1994), though this depends on the sorbing surfaces present and solution characteristics (Elliott *et al.*, 1986; Brümmer *et al.*, 1988; Gerth *et al.*, 1993; Naidu *et al.*, 1994). However, in highly alkaline soils, Cd becomes mobile again due to monovalent hydroxy ion species not

easily occupying sites on cationic exchange complexes (Kabata-Pendias and Pendias, 1992).

6.2.3   Redox Potential

Changes in redox potential occur when the oxygen content of the soil becomes depleted. This frequently occurs with waterlogging, and is accelerated by the respiration of micro-organisms (Iu et al., 1981a; McLaren and Cameron, 1990). Cadmium mobility is greatest under oxidizing, acidic conditions – i.e. high positive values of E_H, the redox potential (Plant and Raiswell, 1983; Hermann and Neumann-Mahlkau, 1985; Gambrell et al., 1991). Because Cd only exists in the +2 oxidation state, changes in redox potential do not affect its speciation directly. Instead Cd mobility is influenced indirectly by changes in the oxidation state of elements with which it forms chemical bonds. The most important elements are sulphur and transition metals such as Fe and Mn which exist in different oxidation states over the normal range of surface soil conditions (Sposito 1983). Under severe reducing conditions, transformation of SO_4^{2-} to S^{2-} causes immobilization of Cd as the CdS precipitate (Hermann and Neumann-Mahlkau, 1985; McLaren and Cameron, 1990). This process was suggested by Poelstra et al. (1979) as the reason why soil columns ceased to lose Cd during a period operating under anaerobic conditions.

Under more moderate reducing conditions where Fe and Mn hydrous oxides become soluble, Cd^{2+} ions previously sorbed are released into solution, and Cd mobility may increase (Iu et al., 1981a; Brown et al., 1989; McLaren and Cameron, 1990). Re-precipitation of the Fe and Mn oxides following a return to oxidizing conditions again provides sites for adsorption of Cd, but may also lead to Cd^{2+} ions being occluded into the re-forming oxide structure making them unavailable for future desorption (Brown et al., 1989; McBride, 1994). Cadmium mobility in acid soils can also decrease as a result of anaerobic conditions causing soil pH to shift towards neutral (Iu et al., 1981b; Singer and Munns, 1987).

In general, the effect of redox potential on Cd mobility is mainly through the changes experienced by Fe and Mn oxides. Iu et al. (1981b) summarize the impact of waterlogged conditions as: decreasing E_H through microbial respiration; increasing soil

pH if acid; decreasing stability and crystallinity of Fe and Mn oxides with resulting increased surface area; and possible precipitation of colloidal oxides should ferrous and manganous ions reach oxygenated zones. These factors are all considered to increase the sorptive capability of Fe and Mn oxides towards Zn and, based on the similarity in chemistry, it is reasonable to suppose that this would also apply to Cd.

6.2.4   Ionic Strength

In several field studies, ionic strength has been found to be at least as important as pH in regulating Cd solubility (Andersson, 1976; McLaughlin *et al.*, 1994; Mitchell *et al.*, 1997). On the whole, increasing ionic strength results in decreasing Cd sorption (Garcia-Miragaya and Page, 1976; Puls *et al.*, 1991; Boekhold *et al.*, 1993; Naidu *et al.*, 1994; Temminghoff *et al.*, 1995). In soils with variable charge, however, this trend can be reversed below a certain, soil-specific, pH (Naidu *et al.*, 1994).

This influence that ionic strength has on Cd sorption comes from the effect that ionic strength has on Cd^{2+} activity, Cd-anion complexation, competition for exchange sites by other cations, and the electrostatic potential in the plane of sorption (Garcia-Miragaya and Page, 1976; Plant and Raiswell, 1983; Christensen, 1984a; Barrow, 1986; Naidu *et al.*, 1994). Changes in ionic strength also cause changes in the soil-suspension pH due to exchange acidity (Andersson, 1976; Barrow and Ellis, 1986) and this will affect Cd mobility as discussed previously. These effects of ionic strength are likely to cause localized increases in heavy metal solubility following fertilizer application – irrespective of the fertilizer Cd content (Andersson, 1977; Lorenz *et al.*, 1994).

Cation competition

As a significant contributor to the effect of ionic strength on heavy metal solubility, increasing cation competition for exchange sites is often cited as the cause for decreases in Cd adsorption (Garcia-Miragaya and Page, 1977; Christensen, 1984a; Homann and Zasoski, 1987; Puls *et al.*, 1991; Boekhold *et al.*, 1993; Temminghoff *et al.*, 1995). Christensen (1984a), for example, concluded that an increase in Ca^{2+} concentration from 1 mM to 10 mM was responsible for reducing Cd sorption by approximately one third. Naidu *et al.* (1994), however, argue that these observations also reflect, in part, changes

in the electrostatic potential of the surface region caused by changes in solution composition.

The ability of a particular cation to compete for non-specific exchange sites generally follows an order defined by the size to charge ratio: $Al^{3+} > Ca^{2+} > K^+ > Na^+$ (Garcia-Miragaya and Page, 1977). For example, compared to Na^+ the Ca^{2+} ion can decrease Cd sorption by approximately 80% (Boekhold et al. 1993). Such competitive adsorption is not restricted to the macro-cations either. Zinc and other heavy metals (Ni, Co, Cr, Cu and Pb) have also been found to reduce Cd sorption in soil and this may be important where sludge application has resulted in elevated concentrations of these other heavy metals (Tiller et al., 1979; Christensen, 1987a and 1987b).

Complexation of cadmium by inorganic ligands

While cation competition is frequently accorded the greatest responsibility for decreases in Cd sorption, it is also recognized that a major part is played by complexing reactions between Cd^{2+} and anions in solution (Hahne and Kroontje, 1973; Garcia-Miragaya and Page, 1976; Benjamin and Leckie, 1982; Bingham et al., 1983 and 1984; O'Connor et al., 1984; Boekhold et al., 1993; McLaughlin et al., 1994; Temminghoff et al., 1995). By reducing the activity of Cd^{2+} in solution, complexes such as $CdCl^+$ are able to reduce Cd sorption and hence enhance its mobility. In this way, Cd-chloro complexes could account for elevated Cd concentrations in potato tubers grown in the saline soils of southern Australia (McLaughlin et al., 1994).

The dominant Cd form in soil solutions is the Cd^{2+} aqueous species, but complexes with anions are also found, predominantly $CdSO_4^0$ and $CdCl^+$ in acid soils, and $CdCl^+$, $CdSO_4^0$ and $CdHCO_3^+$ in alkaline soils under oxic conditions (Sposito, 1983; Mullins and Sommers, 1986; Hirsch and Banin, 1990). Though the NO_3^- ion can also form weak complexes with Cd (Roy et al., 1993; Temminghoff et al., 1995), in comparison to Cd complexation by Cl^- and SO_4^{2-} it is commonly considered to be non-complexing (Egozy, 1980; Benjamin and Leckie, 1982; Homann and Zasoski, 1987; Hirsch and Banin, 1990; see also Table 6.1).

Table 6.1.   Stability constants for nitrate, sulphate and chloride complexes with Cd (Lindsay, 1979).

Reaction	log K^o
$Cd^{2+} + Cl^- = CdCl^+$	1.98
$Cd^{2+} + 2Cl^- = CdCl_2^0$	2.60
$Cd^{2+} + SO_4^{2-} = CdSO_4^0$	2.45
$Cd^{2+} + NO_3^- = CdNO_3^+$	0.31

However, while Cl^- is consistently found to decrease Cd sorption (Garcia-Miragaya and Page, 1976; O'Connor *et al.*, 1984; Roy *et al.*, 1993), results from studies on the effect of SO_4^{2-} complexing have not been so clear. Harmsen (1992) suggests that formation of the neutral species $CdSO_4^0$ should significantly increase Cd mobility in soils because it is non-interacting. But, though Benjamin and Leckie (1982) generally found reduced Cd adsorption with the addition of both Cl^- and SO_4^{2-}, Homann and Zasoski (1987) found no significantly greater decrease in Cd sorption when in 5 mM $CaSO_4$ than when in 4 mM $Ca(NO_3)_2$.

These above comparisons are affected, however, by differences in the dissociation of the various (background) electrolytes. O'Connor *et al.* (1984) calculated that up to 22% of the Ca^{2+} ions in a 5 mM $CaSO_4$ solution would be complexed with SO_4^{2-}. In contrast, only 2% of Ca^{2+} was complexed in 5 mM $CaCl_2$. This reduction in the free Ca^{2+} activity decreases the competition which Ca^{2+} presents for exchange sites while also reducing the proportion of associated SO_4^{2-} ions able to complex with Cd^{2+}. Thus, in solutions of equal ionic strength, Cd can be expected to show greater sorption in $CaSO_4$ than $CaCl_2$. This aspect of solution chemistry appears to be commonly overlooked in sorption studies.

The importance of metal chloro complexes under conditions such as saline soils, soils exposed to road deicing salts and sea water was recognized by Hahne and Kroontje (1973). But, even under normal fertilization practices, agricultural soils can contain up to 20 mM Cl^- in the soil solution (Wiklander and Andersson, 1974). The influence that this anion has on the soil chemistry of Cd is therefore important.

Chlorides may be regarded as being selective towards heavy metals such as Cd because they do not complex strongly with Al(III), Ca^{2+}, Mg^{2+}, Na^+ and K^+ (Hahne and Kroontje, 1973; Garcia-Miragaya and Page, 1976). In addition, chloro complexes form independently of pH and therefore have the ability to increase Cd concentrations in solution whether the soil is acidic, neutral or basic (Bingham *et al.*, 1984; Roy *et al.*, 1993; McLaughlin *et al.*, 1994).

Formation of the $CdCl^+$ complex has been calculated to begin at 1 mM Cl^- (Hahne and Kroontje, 1973). But a significant effect of Cd-Cl complexation on Cd sorption by clays has generally been found to begin only above 10 mM Cl^-, typically around Cl^- concentrations of 30 mM or 15 mM $CaCl_2$ (Garcia-Miragaya and Page, 1976; Egozy, 1980; Roy *et al.*, 1993). For an acid soil, Bingham *et al.* (1984) calculated that, at 5 mM Cl^-, between 16 and 24% of dissolved Cd existed as the $CdCl^+$ complex. This figure rose to between 38 and 41% in the presence of 15 mM Cl^-. Similar partitioning of Cd species was found by Boekhold *et al.* (1993); again in an acid soil, they estimated 50% of dissolved Cd to be in the Cl-complexed form when exposed to 20 mM Cl^-.

These Cl^- concentrations – where Cd mobility has been found to be significantly increased through complexation – are similar to those that were found in saline soils of southern Australia (11 to 34 mM Cl^-) and were thought to have caused increased Cd concentrations in potato tubers (McLaughlin *et al.*, 1994). However, normal soils are also exposed to high Cl^- concentrations following, for instance, the application of sheep and cattle urine (Haynes and Williams, 1992; Williams and Haynes, 1994). With Cl^- concentrations of between 10 and 25 mM, these soils may likewise experience localized mobilization of soil Cd. Further sources of Cl^- that are common to pastoral soils in New Zealand include K fertilizer and atmospheric sea-salts. Both sources have the potential to elevate Cl^- concentrations; the second of these was studied for its impact on the anion balance of soil solutions from Limestone Downs – results are presented in section 6.5.1.

6.2.5 Solid-solution ratios, temperature and physical means of cadmium transport

While the distribution of Cd between solid and solution phases in soil has been found useful for describing potential Cd mobility, several workers report finding that changes

in the proportions of solid phase (either soil, or synthetic clay minerals) and solution phase produce different values for this distribution coefficient (Puls *et al.*, 1991; Bajracharya *et al.*, 1996). Decreasing the solid-to-solution ratio (i.e. decreasing the concentration of the solid phase) increased the value of the distribution coefficient leaving more Cd in the adsorbed phase. Changes in temperature also affect this adsorption equilibrium. Under conditions of low pH, cation adsorption will, generally, increase with an increase in temperature (Barrow, 1992). These two phenomena are probably of most interest when distribution coefficients intended for modelling Cd movement in field soils have been determined from laboratory-based batch sorption isotherms under controlled conditions.

The soluble complexes discussed in the previous section are not the only means by which topsoil Cd is translocated down the profile. Other physical, chemical and biological processes that have the same end result also operate within the field environment. Cadmium redistribution can occur through migration in association with the particulate fraction (Keller and Domergue, 1996); physical mixing caused by particles washing or falling down cracks formed by root growth or wetting-drying cycles; and farm practices such as tilling and ploughing to break up pans. Mechanical mixing by soil biota (e.g. worms) and plant uptake followed by surface deposition and redistribution via root growth and sloughing are other mechanisms.

In addition, though loss through runoff water does not constitute leaching, removal of Cd from a soil profile in association with eroded sediment has also been found to account for over 50% of Cd applied to surface soil (Korentajer *et al.*, 1993). Thus, erosion processes may be another important consideration when calculating Cd mass balances and estimating residence times in soils.

6.3   OBJECTIVES

An understanding of how Cd behaves in soils, particularly those factors controlling the concentration of Cd in soil solution and leaching, is essential for: 1) assessing its potential residence time and subsequently 2) for predicting the future trend in Cd accumulation in New Zealand soils.

When reviewing the literature, however, the number of studies that had investigated Cd mobility in New Zealand soils were limited (Kim, 1990; Kim and Fergusson, 1992; Naidu *et al*, 1994; Smith, 1994; Gray *et al*, 1998). More extensive research in this field has been done overseas, but this has largely been based on adsorption isotherms or leaching experiments in which the first reaction is the adsorption of *freshly applied* Cd to the solid media (Poelstra *et al*., 1979; Christensen, 1985; Selim *et al*., 1992; Kookana *et al*., 1994; Hinz and Selim, 1994).

Data that describe the mobility and redistribution of Cd already resident in the soil, for which desorption is the initial step, are rare. In view of the potential for adsorption and desorption isotherms to show time-dependent hysteresis (caused, for instance, by essentially uni-directional solid state diffusion) (Brümmer *et al*., 1986 and 1988; Mann and Ritchie, 1994; Ainsworth *et al*., 1994; Verburg and Baveye, 1995), studies which quantify only the adsorption reaction of Cd to soil material may describe less well the mobility of resident soil-Cd. Furthermore, it is clear from evidence presented in the literature that the soil-solution composition has a major impact on Cd sorption. This is particularly so with regard to the presence of inorganic ions which have the ability to complex Cd. Hence, to be environmentally applicable, mobility studies require a background electrolyte which is of similar composition and concentration to the soil solution of the soils under study.

Bearing in mind these observations on the literature and the focus of my studies on Cd in the soils of Limestone Downs, this chapter aims to:
1)   Characterize the anions present in coastal New Zealand soils (Limestone Downs) that have the ability to complex Cd, and
2)   Investigate the potential for leaching of soil-bound Cd in several New Zealand soils as influenced by electrolyte composition and soil properties.

6.4   MATERIALS AND METHODS

6.4.1   Preliminary analysis of soil solution from Limestone Downs

In order to determine the concentrations of charge balancing anions in soil solution and to confirm the importance of Cl^- as an anion with potential to accelerate Cd movement,

soil from the coastal property of Limestone Downs was collected in July, 1995 (mid-winter in New Zealand). Bulked samples of 5 cores, 2.5 cm diameter and 7.5 cm deep, were taken from 6 locations on the Wairama Hill series (yellow brown earth). The soils were placed in a refrigerator at $4^{o}C$ and extracted the following day using centrifugation. Sufficient solution (6 - 7 mL) was obtained from each sample by centrifuging 80 g of soil for 30 minutes at 10 000 rpm.

An aliquot of the solution was used immediately to measure the soil solution pH. The major anions (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were determined by ion chromatography after filtration through a 0.22 μm Millipore filter. The instrument involved was a Waters Ion Chromatograph equipped with an IC-PAK A anion guard column and an IC-PAK A anion chromatography column (H. Percival, Landcare, Palmerston North, pers. comm.).

Electrical conductivity (EC) was measured on another portion of the soil solution extracts and standardized against KCl solutions at $25^{o}C$.

6.4.2   Laboratory leaching studies on repacked soil columns

As outlined in Chapter 5, Cd present in soil was divided into three categories based on its source, namely: native Cd, resident Cd, and added Cd. The latter was introduced into the soil as $Cd(NO_3)_2$ for the purposes of studying Cd mobility in this and the following Chapter. Cadmium loadings of between 1 and 2 mg Cd kg^{-1} soil were chosen for these studies so as to be relevant to the New Zealand situation where Cd concentrations in the topsoil rarely exceed more than a few parts per million (Table 2.4 and Chapters 4 - 5).

Soil materials

Four soils differing in chemical and physical properties were studied: Manawatu, Kohemarere, Wharekohe [Developed] and Wharekohe [Undeveloped]. The classification and general characteristics of each soil are given in Table 6.2; their sampling locations within the North Island of New Zealand are shown in Figure 6.1. The soil properties were characterized using the methods described in Chapter 3. Clay mineralogy was determined according to the methods of Whitton and Churchman (1987).

103

Wharekohe fine silt loam
Northern podzol
Undeveloped: Manuka & bracken (A horizon)
Developed: Pasture, 25 years fertilizer (A horizon)

Kaikohe ●

Limestone Downs ●

Kohemarere fine sandy loam
Northern yellow-brown earth
Pasture (A horizon)

Palmerston North ●

Manawatu fine sandy loam
Central recent alluvial
Pasture (A/B horizon mix)
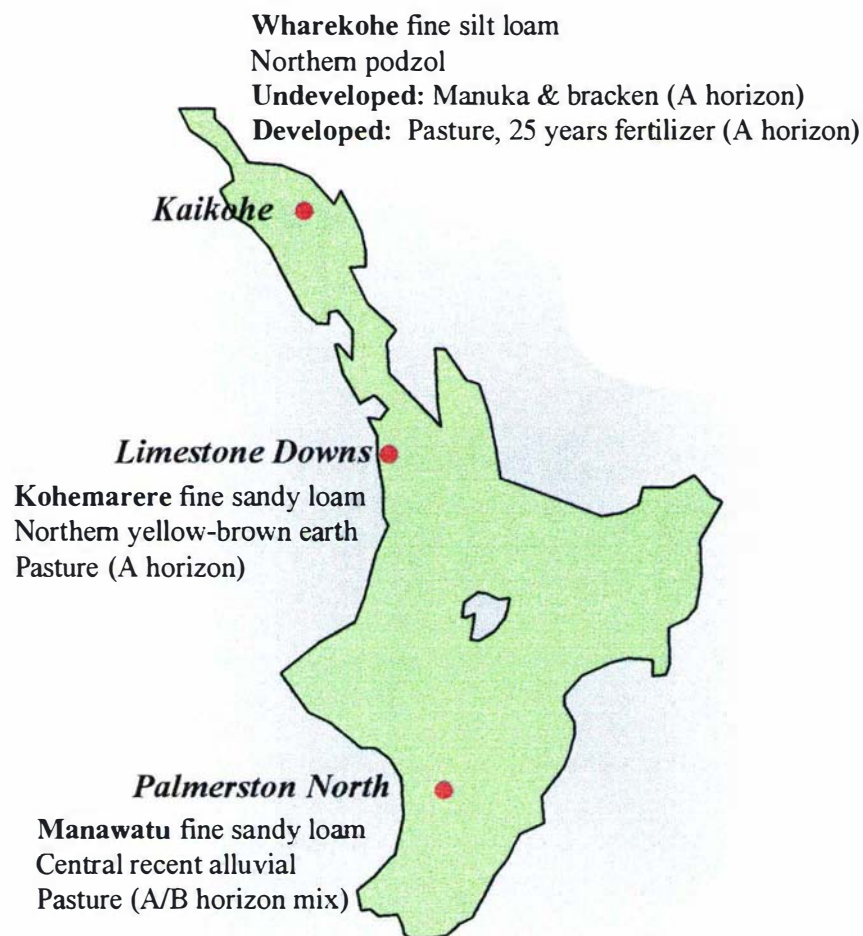
Figure 6.1.   Geographical location of (North Island, New Zealand), and sample site information on soils studied in the column leaching experiments.

Table 6.2 Selected characteristics for four soils used to study Cd redistribution in columns of soil leached under laboratory conditions with a range of electrolyte compositions and concentrations.

Soil properties [†]	Manawatu	Kohemarere	Wharekohe [Undeveloped]	Wharekohe [Developed]
Soil type	Manawatu fine sandy loam	Kohemarere fine sandy loam	Wharekohe fine silt loam	Wharekohe fine silt loam
Soil Group	Central recent alluvial	Northern yellow-brown earth	Northern podzol	Northern podzol
Resident Cd ($\mu g\ g^{-1}$) [‡]	0.050	0.272	0.013	0.430
Soil pH	5.45	4.95	4.48	6.02
Total carbon (%)	1.6	6.5	4.8	7.5
Moisture content of air dry soil (%) [§]	1.5	5.5	10.3	4.5
Dominant clay minerals	Mica - 75% Vermiculite - 10%	Kandite - 40% Smectite - 40% Quartz - 15%	Quartz - 90% Vermiculite - 3%	Quartz - 85% Vermiculite - 5%

Cation exchange capacity (meq per 100 g) [‡]

	Manawatu	Kohemarere	Wharekohe [Undeveloped]	Wharekohe [Developed]
Total CEC	10.5	33.5	15.3	21.5
H^+	3.75	21.72	13.22	6.31
Ca^{2+}	4.25	7.30	0.70	13.16
Mg^{2+}	1.13	3.58	0.76	0.76
K^+	1.32	0.69	0.45	1.08
Na^+	0.09	0.19	0.15	0.19

†   On air dry soil unless otherwise indicated
‡   On oven dry soil
§   Gravimetric moisture content of air dry soil (%)

Manawatu soil

The Manawatu soil was collected as a laboratory standard soil from the Massey No. 1 Dairy farm (L. D. Currie, pers. comm.). The 0 - 15 cm soil cores (a mixture of A and B horizons) were dried and sieved to 2 mm. It is low in carbon, available P (Olsen P) and total Cd.

Kohemarere soil

Collection of the Kohemarere soil from Limestone Downs took place in July 1995 near to the profile pit dug for its description, Profile 16 (Chapter 4). After removal of the herbage and root mat, a sample of the top soil (about 0 - 7.5 cm) was taken. At sampling it was noted that, despite the very wet ground surface, under the root mat this soil still had a dry appearance. The soil was laid out to air dry, then crushed to pass through a 1 mm sieve.

Wharekohe soil[1]

Two sites on the Wharekohe silt loam were sampled, one from under long-term pasture and another from under Manuka and bracken scrub. This gave rise to two soils virtually identical in mineralogy but differing in properties such as soil pH, CEC and Cd content, which can be influenced by soil management practices. In the following studies these soils are referred to as Wharekohe [Developed] and Wharekohe [Undeveloped]. Soil samples were collected mid-August in 1995 from the AgResearch research station, Kaikohe (Figure 6.1). The Wharekohe [Developed] soil came from near the L Block site studied as part of the Wharekohe chronosequence discussed later in Chapter 8. Similarly, the Wharekohe [Undeveloped] soil here was taken from a site comparable to that of the Undeveloped sites in this later study.

As northern podzols (Table 6.2), these soils have been subjected to severe disturbance, firstly during gum digging at the turn of last century, and later through ripping of the hard E horizon for drainage in preparation for pasture development. Pugging by stock is also a problem. As a result, they were difficult to sample to a consistent depth; the maximum depth was around 10 cm and care was taken to exclude the eluvial horizon. After air drying, both soils were crushed to pass through a 1 mm sieve.

---

[1] The effort of Dr. J. Edwards in locating and sampling these soils is gratefully acknowledged

Soil columns

The plastic permeameters used in these leaching studies were constructed using perspex tubing with an internal diameter of 4.5 cm, a base mesh of 44 μm polyester-sieve fabric and a removable front section to facilitate partitioning of the soil column into 5 mm segments (after Kim, 1990). A waterproof, silicone-based sealant (*Selleys Window and Glass Sealant*) was used to hold the removable section in place during leaching. No Cd contamination from the use of this sealant was observed. The permeameter design is illustrated in Figure 6.2.

As a way of more closely relating laboratory investigations of Cd movement to normal pasture soils, the soil columns used for these leaching experiments had a two-layer arrangement (Figure 6.2). The top soil layer consisted of 20 mm of Cd-amended soil with a Cd concentration of at least 1 μg Cd g^{-1} – thereby simulating natural topsoil with its accumulated Cd (section 2.7). The bottom layer consisted of unamended, low Cd soil (40 mm) to simulate the rapid decrease in Cd concentration with depth found in the soil profiles of Chapter 4. However, with this arrangement, it was necessary to know the position of the original high-Cd/low-Cd boundary in order to assess the extent of Cd movement induced by leaching. Because soil compaction during leaching caused changes in soil depth, this boundary point had to be located by a physical marker within the soil column. Hence, a piece of Whatman 41 filter paper was placed between the top and bottom layers.

The different Cd concentrations required for the top and bottom layers were obtained by taking subsamples of the air-dried bulk soil described previously and treating as follows:

Cadmium-amended soil

The Cd-amended soil was produced by adding Cd, as $Cd(NO_3)_2$ (Spectrosol) diluted in deionized water, to air-dry soil in the ratio: 1 μg Cd to every gram of oven dry soil. The concentration of the added Cd solution was such that soil gravimetric water contents of between 12 and 17% would be achieved. At these moisture contents the Manawatu soil appeared quite moist while the Kohemarere remained dry to the touch.

Removable front
section of perspex
column

Cd-amended soil (1 µg g⁻¹ added Cd)

High-low Cd boundary from which to
measure Cd movement - marked by a
filter paper

Unamended soil

Base mesh, 44µm

Column diameter, 4.5 cm
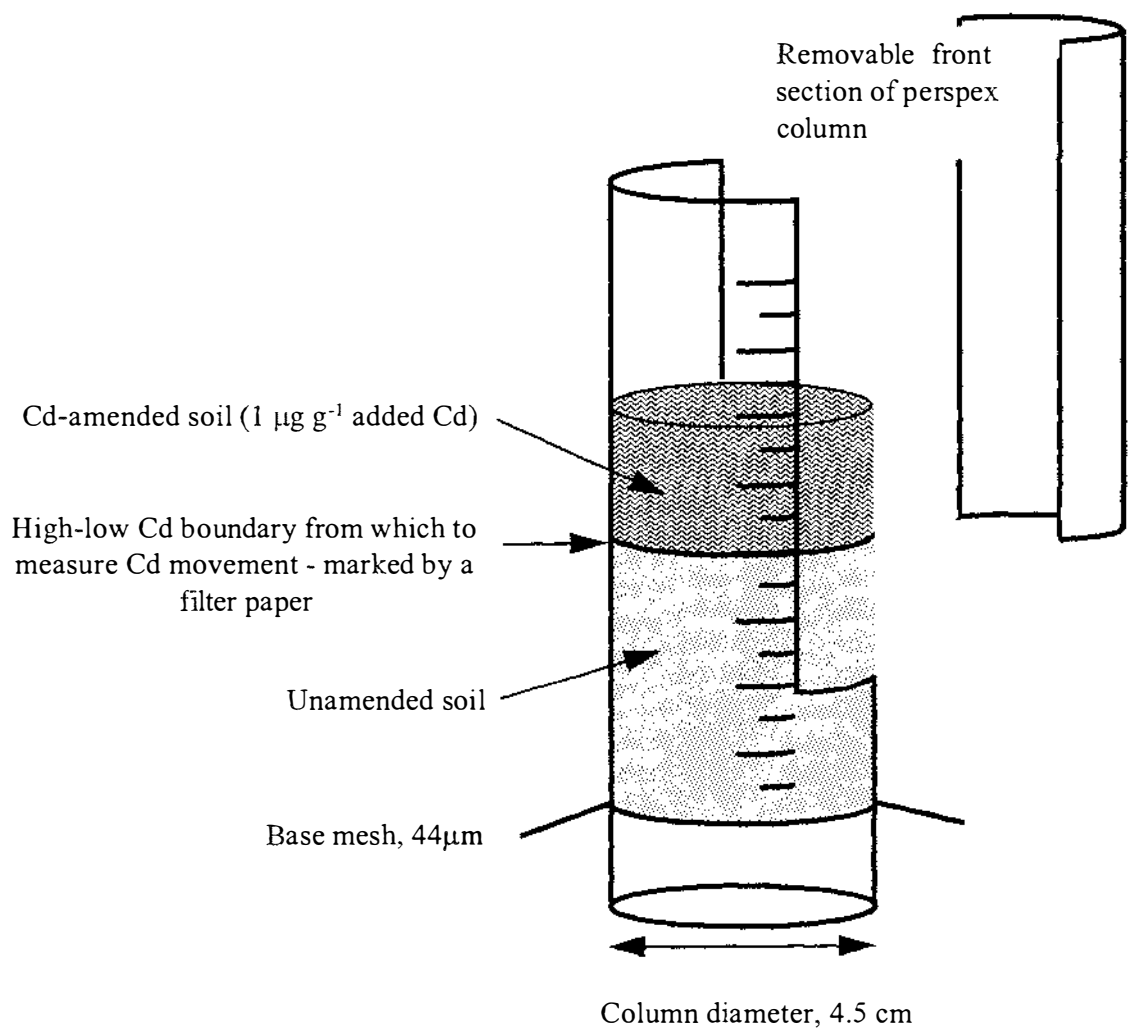
Figure 6.2.   Schematic diagram of the permeameter design and soil arrangement used
for studying Cd movement.

Although different soils had different resident Cd concentrations (Table 6.2), each soil received the same amount of added Cd – and no attempt was made to bring the soils to the same total Cd concentration.

Unamended soil

Each unamended soil received the same quantity of deionized water as was added to the Cd-amended soils – giving moisture contents of between 12 and 17% – but received no Cd. This provided the bottom soil layer discussed earlier.

Each soil treatment was incubated in closed plastic bags for 20 days at about $21^{\circ}C$. At regular intervals the bags were opened to ventilate, and the soil was mixed. Following incubation, the soils were weighed and their final moisture content was determined to allow the calculation of equivalent oven dry weights (in order to standardize the mass of soil packed in each column). To homogenize the soil and break up aggregates, each soil was pushed through a 1 mm sieve prior to packing in the columns.

Consistency in soil mass and the mass of added-Cd between columns was maintained by packing the same equivalent oven dry soil weight for all soils. This soil weight was taken as the mass of Manawatu soil required to give the 40 mm deep bottom layer and the 20 mm deep top layer in the 4.5 cm diameter permeameter. These weights were 68 g oven dry soil and 34 g oven dry soil respectively. Because of the variation in bulk density between soil types, the height of soil in each column differed between soil type. The total height of soil in a column ranged from 60 mm for columns of Manawatu soil to 92 mm for columns of Wharekohe developed soil. Specifications for all columns are summarized in Table 6.3.

In addition to **Cd-amended** columns composed of Cd-amended and unamended soil, **control columns** containing only unamended soil were also prepared. These control columns were required to distinguish between resident Cd entering the leachate from the bottom soil layer, and added-Cd from the Cd-amended top soil layer which had leached down through the column. A second piece of filter paper was placed on the soil surface to distribute leaching solution and prevent soil disturbance.

Solution application and leachate collection

All leaching solutions were prepared by dissolving Analar-grade chemicals in deionized water. When freshly made, the pH of these solutions were similar at pH 5.6 ± 0.044 (95% confidence level). The solutions were stored in acid washed, deionized water-rinsed plastic bottles before and during the experiments.

Leaching solutions were applied to the top of the soil columns via plastic tubing and allowed to percolate through the soil column under the influence of gravity. The application rate was regulated by a peristaltic pump calibrated to deliver 0.05 mL min.$^{-1}$. This flow rate was chosen to accommodate the lowest hydraulic conductivity found in a preliminary experiment (data not presented), while also approximating the low rainfall infiltration rates which field soils commonly experience (Yao and Hendrickx, 1996).

Leachate flow rates did not always conform to the 0.050 mL min.$^{-1}$ rate, but varied from 0.004 to 0.112 mL min^{-1} over the duration of leaching. This variation was attributed to several factors, including: temporal differences in soil hydraulic conductivity; inconsistency in peristaltic pump-tube brands; and mechanical wear of both the pump tubes and the peristaltic pump over the experimental period. However, evidence from the literature suggests that changes in flow rate do not significantly affect the Cd sorption/desorption equilibria (Alesii *et al.*, 1980; Bajracharya *et al.*, 1996).

Individual leachate samples were collected manually using pre-weighed 100 mL plastic beakers and sample volumes were determined by assuming that for a dilute solution, at room temperature, 1 g of solution equalled 1 mL. Subsamples of the leachate were placed in clean storage tubes and kept in cold storage (5°C) until analysis. These samples were not acidified so that anion determinations could be made if required.

Leachates were analyzed directly for total Cd as described in section 3.5. Subsamples of leachate were analyzed for pH and in some cases electrical conductivity. Other elements in the leachate were determined by inductively coupled argon plasma-optical emission spectrometer (ICAP-OES, Applied Research Laboratories model 34000).

Determining the cadmium distribution within the soil column

Following collection of the last sample of leachate, each column was disconnected from

the peristaltic pump and left to stand for 5 minutes. The column was then weighed to give the saturated water content required for the modelling work presented in Chapter 7. Where columns had ponded, solution application stopped some time prior to finishing leaching and excess surface ponded solution was removed before weighing.

After drying to reduce moisture content, the front partition of the perspex column was removed by cutting through the silicone sealant, and the soil column sliced into 0.5 cm increments. Some distortion of the soil columns occurred during leaching – increased packing density and reduced column height, and some stretching of the base mesh so that the soil column centres dropped relative to the edge – and this created difficulties when trying to section each column accurately. In addition, care was also needed to avoid cross-contamination between soil sections.

The soil sections were transferred to clean plastic bags and dried to a constant weight in a 45°C oven (air dried). Following drying, the sections were weighed to calculate the recovered soil weight and then crushed. Mass balances on the recovered soil indicated that, for these small samples of soil, oven drying at 45°C gave recoveries very close to the initial oven dried (105°C) weight of soil (102 g). The exception was the Kohemarere soil for which 104 g of soil was generally recovered. As this soil contains smectite, an expanding clay, a harsher drying regime would have been required to remove water from the interlayer spacing.

The column soil sections were analyzed for *pseudo-total* Cd (section 3.3.2) and soil pH (section 3.6.5). In the case of some Manawatu soil sections, other elements were determined by ICAP-OES (section 3.3.6) following digestion in concentrated acid (section 3.2.3.1).

Contamination was identified by mass balance calculations in five columns out of fifty. This contamination was significant in three columns in Experiment 1, but untraceable – where possible these were repeated. Other minor contamination also occurred in Experiment 4. I attributed this to siphoning of leaching solution, which had ponded above some columns, back into the solution storage bottles – consequently contaminating the leaching solution with Cd. Later it was found that the 2.5 mM $CaCl_2$

solution used to leach the columns in this experiment had Cd concentrations of between 0.37 and 0.68 $\mu g\ L^{-1}$ (ppb).

The soils and leaching solutions used in each of the following four experiments are summarized in Table 6.4.

Table 6.4 Leaching solutions and soils used to study Cd redistribution in re-packed soil columns under laboratory conditions.

SOILS	LEACHING SOLUTIONS	
Experiment 1:	**Cadmium movement in columns of Manawatu soil as influenced by the presence of anions and cations**	
Manawatu	2.5 mM Ca(NO$_3$)$_2$	2.5 mM KCl
	2.5 mM CaSO$_4$	5.0 mM KCl
	2.5 mM CaCl$_2$	7.5 mM KCl
	50.0 mM CaCl$_2$	Deionized water
Experiment 2:	**Effect of increasing CaCl$_2$ concentration on cadmium movement in Manawatu soil columns**	
Manawatu	5.0 mM CaCl$_2$	20.0 mM CaCl$_2$
	10.0 mM CaCl$_2$	35.0 mM CaCl$_2$
Experiment 3:	**Response of leachate cadmium concentrations to wetting-drying cycles**	
Manawatu	2.5 mM Ca(NO$_3$)$_2$	2.5 mM KCl
	2.5 mM CaSO$_4$	5.0 mM KCl
	2.5 mM CaCl$_2$	7.5 mM KCl
	50.0 mM CaCl$_2$	Deionized water
Experiment 4:	**Cadmium movement in soils of differing chemical and physical properties when leached with 2.5 mM CaCl$_2$**	
Manawatu Kohemarere Undeveloped Developed	2.5 mM CaCl$_2$	

6.4.3   Experiment 1:   Cadmium movement in columns of Manawatu soil as influenced by the presence of anions and cations

The influence of anion complexation on Cd mobility was studied by comparing Cd movement in columns of Manawatu soil leached with deionized water, 2.5 mM $CaCl_2$ (replicated), 2.5 mM $Ca(NO_3)_2$ and 2.5 mM $CaSO_4$. A salt concentration of 2.5 mM was chosen to give solutions with an ionic strength close to that normally found for soil solutions in the topsoils of New Zealand grasslands. The resulting ionic strengths of 0.0075 to 0.01 are slightly higher than the typical value of 0.005 reported by Edmeades *et al.* (1985), but lie within the 0.003 - 0.016 range given. An additional treatment of 50 mM $CaCl_2$ (replicated) was included in this experiment, but results from columns leached with this solution are presented as part of Experiment 2.

Competition for sorption sites by other cations in solution increases the potential for Cd leaching. In order to resolve the separate contributions made by anion complexation and Ca^{2+} competition on Cd movement in columns, additional leaching solutions of KCl were studied and compared with the 2.5 mM $CaCl_2$ treatment. Because of the different valencies of K^+ and Ca^{2+}, three concentrations of KCl solutions were used to match the 2.5 mM $CaCl_2$ solution. These were: 2.5 mM KCl (to give equal cation concentrations); 5.0 mM KCl (equal anion concentrations); and 7.5 mM KCl (equal ionic strengths).

For the above comparison, K^+ was chosen over the other frequently used cation , Na^+ (Boekhold *et al.*, 1993; Naidu *et al.*, 1994; Temminghoff *et al.*, 1995) because of adverse effects which Na^+ has on soil structure. Whereas Ca^{2+} promotes clay flocculation, Na^+ deflocculates clay particles (Greene *et al.*, 1988). This opposing effect on aggregate surface area may itself influence the relative Cd sorption (Pulford, 1986), This was avoided by comparing Ca^{2+} and K^+.

A total volume of 1000 mL of leachate was collected for each column over a period of 9 to 22 days at an average flow rate of 0.063 mL min^{-1} (equivalent to 0.24 cm h^{-1}). Leachate collection volumes varied from 2.5 - 10 mL at the start, to 40 - 50 mL later in the experiment. A preliminary experiment suggested that Cd generally appeared in the leachate as a sharp, brief peak at the start of leaching. To capture this event small volumes were used for the first 10 collections, but resulted in delayed reading of the

leachate pH. The pH data recorded later using a micro-electrode showed unexplainable variability and are not shown. Later experiments and repeated treatments from this experiment (2.5 mM $Ca(NO_3)_2$, deionized water and 2.5 mM $CaCl_2$ repeated as part of Experiment 4) had pH values recorded at the time of collection, on subsamples of leachate not used for Cd analysis, and these results are presented later in Figure 6.5.

6.4.4 Experiment 2: Effect of increasing $CaCl_2$ concentration on cadmium movement in columns of Manawatu soil

Columns of Manawatu soil were prepared as described in section 6.4.2 and leaching procedures were changed as follows: Solutions of $CaCl_2$ at concentrations of 5.0 mM, 10 mM, 20 mM and 35 mM $CaCl_2$ were each percolated through one Cd-amended and one control column for between 20 and 22 days until a total of 1000 mL of leachate had been collected. The average effluent flow rate over the eight columns was 0.033 mL min^{-1}. These treatments were not replicated.

6.4.5 Experiment 3: Response of leachate cadmium concentrations to wetting-drying cycles in columns of Manawatu soil

After collecting 1000 mL of leachate, the Manawatu soil columns used in Experiment 1 were allowed to drain and left for 8 days at room temperature without the application of any solution. This drying period was intended to allow the restoration of equilibrium between Cd sorbed on to the solid phase and Cd ions in solution. After 8 days the columns were again subjected to leaching (with the solutions used prior to drying, e.g. 2.5 mM $CaCl_2$, 50 mM $CaCl_2$, deionized water, 2.5 mM KCl) until 50 mL had been collected in 5 mL aliquots. The procedure was to be repeated if Cd concentrations in the leachate showed a marked response to the new wetting cycle.

6.4.6 Experiment 4: Cadmium movement in soils of differing chemical and physical properties when leached with 2.5 mM $CaCl_2$

In this study, the objective was to investigate Cd movement in New Zealand soils which varied in soil pH, particle size, bulk density, CEC, organic matter and clay minerals.

Four soils were selected for this study: the Manawatu fine sandy loam, Kohemarere fine sandy loam, and the Wharekohe fine silt loam in two stages of pasture development, Undeveloped and Developed. The distribution of Cd down soil profiles of Kohemarere, Wharekohe Undeveloped and Wharekohe Developed at field sites have been studied elsewhere in this thesis. Physical and chemical properties for all soils are presented in Table 6.2.

Duplicate Cd-amended and control columns of each soil were prepared as described in section 6.4.2 and leached with 2.5 mM $CaCl_2$ until 1000 mL of leachate was collected. This took 19 - 22 days for the Manawatu and Kohemarere soils, and between 22 and 35 days for the Wharekohe soils. A 2.5 mM $CaCl_2$ leaching solution was chosen to approximate field soil-solution ionic strengths with a view to gauging the potential for Cd movement in these soils under field conditions. Between Experiment 1 and Experiment 4, the 2.5 mM $CaCl_2$ treatment-Manawatu soil combination was repeated four times to give a total of four Cd-amended columns and four control columns. These are presented collectively in Appendix 4 to illustrate the reproducibility of the leaching results.

Average flow rates for each soil type were: 0.033 mL min^{-1} for the Manawatu soil; 0.036 mL min^{-1} for the Kohemarere soil; and 0.026 mL min^{-1} for the Wharekohe soils. The lower flow rate of the Wharekohe columns reflects the severe surface ponding which occurred during the later stages of leaching. Under these ponded conditions their flow rates gradually dropped to reach about 0.010 mL min^{-1} after approximately 900 mL (560 mm) of effluent had passed.

6.5   RESULTS AND DISCUSSION

Preliminary studies

Because of the coastal location of Limestone Downs, soils on the property are subjected to higher inputs of Cl^- than inland regions through sea spray. With the greater mobility of the $CdCl^+$ species (section 6.4.2), this additional Cl^- in the soil solution presents the potential for increased Cd movement within these soils.

6.5.1 Analysis of soil solution from Limestone Downs

Analysis of soil solution from Limestone Downs identifies Cl⁻ as the dominant anion (Table 6.5). A similar finding was reported by Heng *et al.* (1991c) for a site located 30 km from the coast where Cl⁻ concentrations in drainage water regularly exceeded 2 mM Cl⁻. This was attributed, in part, to the application of KCl fertilizer, but also to a substantial input from the atmosphere. However, the general order of anion concentrations for New Zealand top-soils under pasture has been found to be: nitrate > sulphate > chloride (Edmeades *et al.*, 1985).

Comparing anion concentrations in Table 6.5 with the ranges given by Edmeades *et al.* (1985): nitrate, 0 - 6.86 mmol L^{-1}; sulphate, 0 - 1.99 mmol L^{-1}; and chloride, 0.06 - 1.13 mmol L^{-1}; it can be seen that, while NO_3^- and SO_4^{-2} concentrations at Limestone Downs fall at the lower end, all but one of the Cl⁻ concentrations exceed the maximum found by Edmeades *et al.* (1985). This illustrates the significant impact that a coastal location has had on the anion balance in the Limestone Downs soils.

The low concentrations of NO_3^- and SO_4^{-2} may be a reflection of leaching during a period of unusually high rainfall just prior to sampling (110 mm in 14 days, Mr. W. Deighton, Farm Manager limestone Downs). This being the case, Cl⁻ concentrations may also be lower than normal. Had soil solutions been sampled during summer instead

Table 6.5 Anion composition of soil solution samples taken from the coastal property of Limestone Downs during the winter of 1995. Exposure of the sampling sites to coastal breezes are also indicated.

Sample	Aspect	Exposure	pH	EC	Cl⁻	SO_4^{2-}	NO_3^-
				(μS cm^{-1})		(mmol L^{-1})	
S1	westerly	moderate	5.74	372	1.60	0.12	0.87
S2	westerly	moderate	5.54	397	1.42	0.17	1.17
S3	easterly	sheltered	5.68	218	0.94	0.14	0.6
S4	north-west	exposed	5.56	286	1.81	0.22	0.12
S5	north-west	moderate	5.43	264	1.32	0.24	0.29
S6	hill top	exposed	6.22	391	1.70	0.22	0.65

of winter, the accumulation of sea salt deposits between infrequent rainfall events may have elevated chloride concentrations even further.

Although sampled at increasing distances from the coast (S1 to S6), soil solution Cl⁻ does not show a corresponding decrease in concentration. Instead, concentrations appear to be most strongly influenced by local geography – those sites most exposed to the coastal wind show the highest Cl⁻ concentrations. Certain aspects and locations on the landscape may, therefore, be susceptible to greater Cd mobility because of locally higher Cl⁻ concentrations. As a result, they may show higher leaching losses of Cd from top-soil, and/or greater uptake by plants. The influence of Cl⁻ on Cd movement in such soils is an important aspect which needs further investigation.

Laboratory leaching studies

The results from replicated columns showed close agreement, both in leachate Cd and the final soil Cd profile. To illustrate this, results from replicated columns of Manawatu soil leached with 2.5 mM $CaCl_2$ (four Cd-amended and four control columns) are presented together in Appendix 4. Within this chapter, therefore, results from only one Cd-amended and one control column are presented for brevity.

6.5.2   Experiment 1:   Cadmium movement in columns of Manawatu soil as influenced by the presence of anions and other cations

Effect of anion (Cl^-, SO_4^{-2}, and NO_3^-) on cadmium movement

A small peak of Cd appeared in the initial leachates collected from both Cd-amended and control columns. Otherwise, no notable loss of Cd to the leachate occurred for any of the different leachate treatments: deionized water, 2.5 mM $CaCl_2$, 2.5 mM $Ca(NO_3)_2$, or 2.5 mM $CaSO_4$ (Figure 6.3). As a result, total Cd recovered in leachate from the Cd-amended columns was less than 0.3 % of that initially present in the soil, Table 6.6.

Within the soil itself, however, redistribution of added-Cd in the top soil layer of the Cd-amended columns was clearly apparent where the leaching solution had contained a
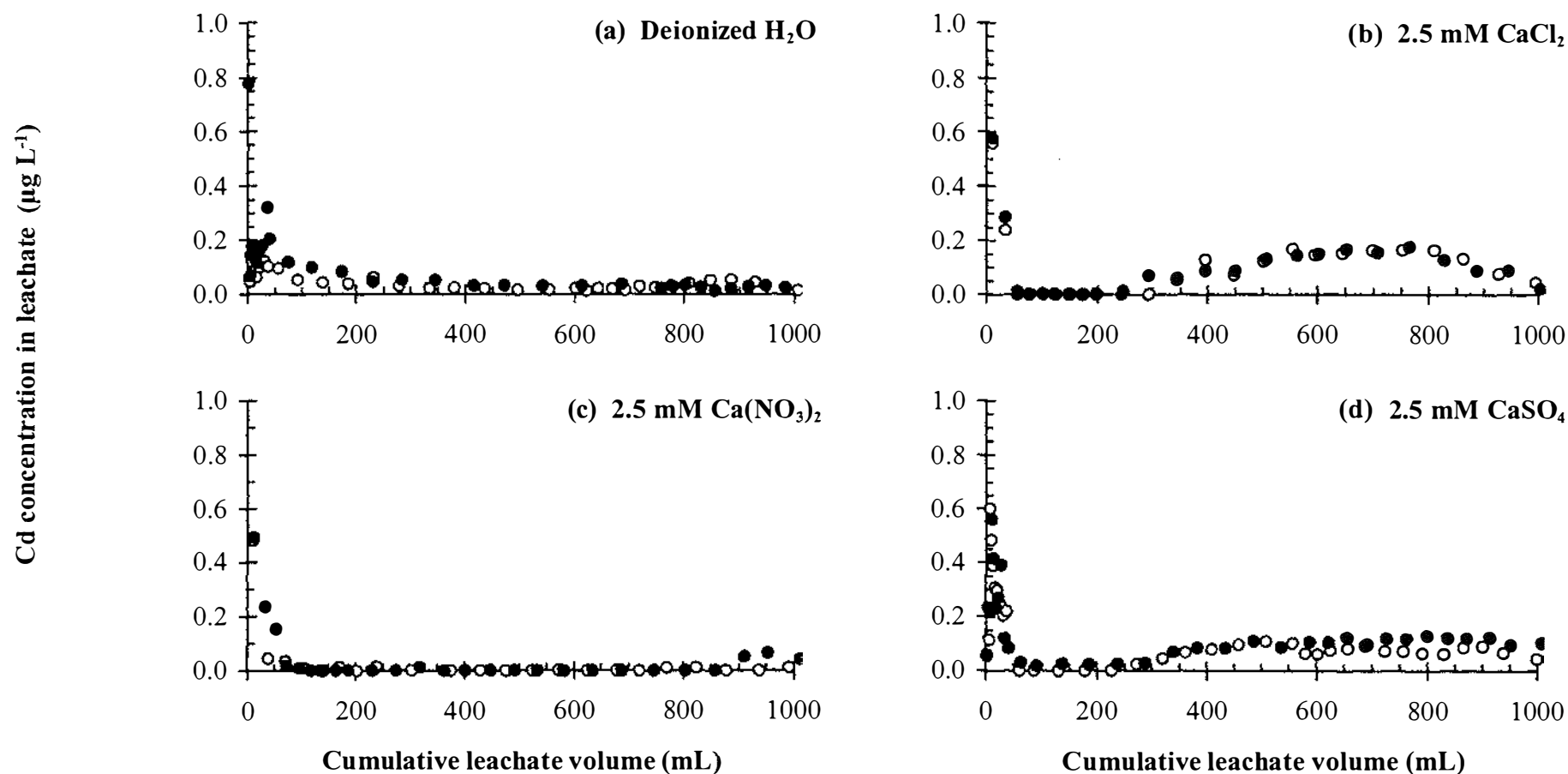
Figure 6.3. Concentrations of Cd in leachate from columns of Manawatu soil leached with 1000 mL of: *(a)* deionized water; *(b)* 2.5 mM CaCl$_2$; *(c)* 2.5 mM Ca(NO$_3$)$_2$; or *(d)* 2.5 mM CaSO$_4$. Cd-amended columns which contained added-Cd in the top soil layer are indicated by closed symbols; control columns are indicated by open symbols.
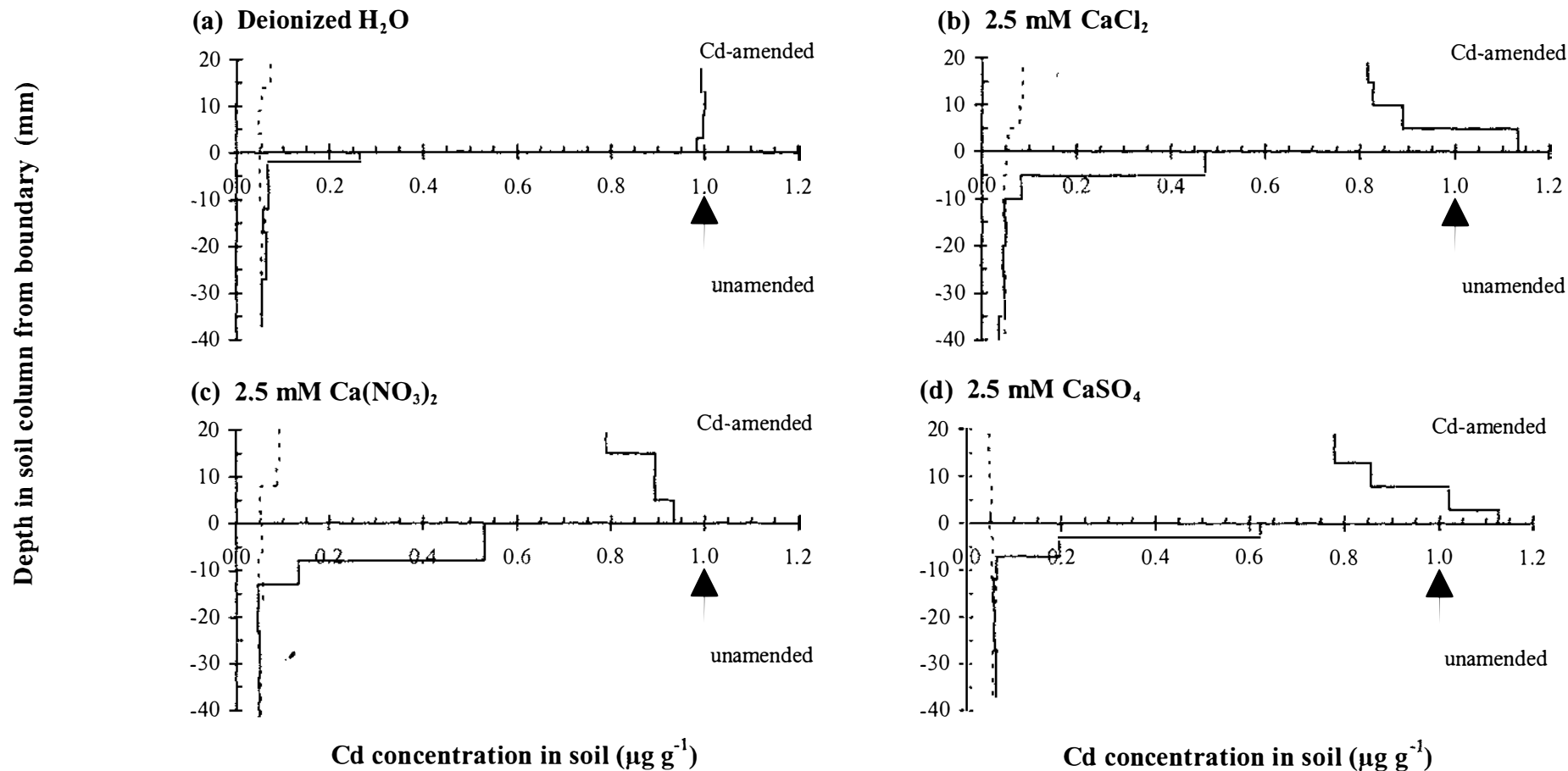
Figure 6.4. Final distribution of Cd in columns of Manawatu soil leached with 1000 mL of: *(a)* deionized water; *(b)* 2.5 mM CaCl₂; *(c)* 2.5 mM Ca(NO₃)₂; or *(d)* 2.5 mM CaSO₄. Cd-amended columns which contained added-Cd in the top soil layer are shown as a solid line; control columns are shown as a dashed line. Arrow indicates initial Cd concentration in the Cd-amended soil of the top layer.

Table 6.6. Amount of Cd recovered in the leachate and that remaining in columns of Manawatu soil (Cd-amended) leached with 1000 mL (630 mm) of salt solution.

Leaching solution	Cd collected in leachate		Cd lost from topsoil	Cd recovery for treatment
	(μg)	(%)[†]	----------------(%)----------------	
Deionized water	0.05	0.1	6	98
2.5 mM Ca(NO$_3$)$_2$	0.02	0.1	13	100
2.5 mM CaSO$_4$	0.09	0.2	9	106
2.5 mM CaCl$_2$	0.10	0.3	10	103
2.5 mM KCl [‡]	0.03	0.1		118
5.0 mM KCl	0.02	0.1	3	105
7.5 mM KCl	0.08	0.2	3	105

[†] Expressed as % of the total Cd present in the soil column at the start of leaching (Table 6.4)
[‡] Contamination found in the topsoil of this column following leaching makes the calculation of Cd loss from the topsoil meaningless.

calcium salt, Figure 6.4. This contrasted sharply with the very limited movement caused by deionized water and is in agreement with the general effect of increasing ionic strength on Cd adsorption on the solid phase (Garcia-Miragaya and Page, 1976; Naidu et al., 1994). This redistribution in the columns leached with CaCl$_2$ and CaSO$_4$ appears restricted to the top layer with an apparent accumulation of Cd immediately above the filter paper. At the apex of the Cd profile in this region the Cd concentration is actually greater than that of the original Cd-amended soil (indicated by the arrow in Figure 6.4). For this to have happened, a change in the equilibrium relationship between Cd sorbed onto the solid phase and that in solution must have occurred. Such an increase in Cd concentration was not seen in the column leached with Ca(NO$_3$)$_2$ (Figure 6.4 (c)). Later studies demonstrated this accumulation effect to a greater extent and possible explanations for these observations are discussed in section 6.5.3.

The proportions of Cd lost from the top soil layer during leaching are compared in Table 6.6 (10 %, 9 % and 13 %, for Cl$^-$, SO$_4^{2-}$ and NO$_3^-$ respectively). These results show that Cd movement in the Manawatu soil was similar for each of the three leaching solutions:

2.5 mM $CaCl_2$, 2.5 mM $CaSO_4$ and 2.5 mM $Ca(NO_3)_2$. This is perhaps surprising given that there are considerable differences in the stability constants for the various complex ions (Table 6.1). Moreover, previous workers have found both NO_3^- and SO_4^{2-} to be less effective in reducing Cd adsorption to soil than Cl^- (O'Connor *et al.*, 1984; Homann and Zasoski, 1987; Hirsch and Banin, 1990; Temminghoff *et al.*, 1995). However, at these low anion concentrations, it is possible that only a small percentage (values between 9 and 38% have been predicted) of Cd was complexed with Cl^-, the majority probably remained as Cd^{2+} (Hahne and Kroontje, 1973; Egozy, 1980; Bingham *et al.*, 1984; O'Connor *et al.*, 1984). Thus, it is more likely that the Cd redistribution seen in this experiment has resulted from the effect of ionic strength on the Cd sorption-desorption equilibria, and in particular competition between Cd^{2+} and Ca^{2+} for cation exchange sites. All leaching solutions had the same Ca^{2+} concentration and similar ionic strengths.

The movement of Cd seen in these columns was not extensive and may have been further restricted by increasing CEC as the pH of the soil rose. This was indicated by a rising leachate pH and a higher soil pH found at the completion of leaching. In all treatments, leachate pH began at around pH 5 - 5.5 and then climbed rapidly to over pH 6.5 within the first 100 mL (Figure 6.5). In the case of the deionized water treatment, this was followed by a continuing increase in leachate pH up to almost pH 8. Under these conditions Cd mobility is severely restricted (Brümmer and Herms, 1983;
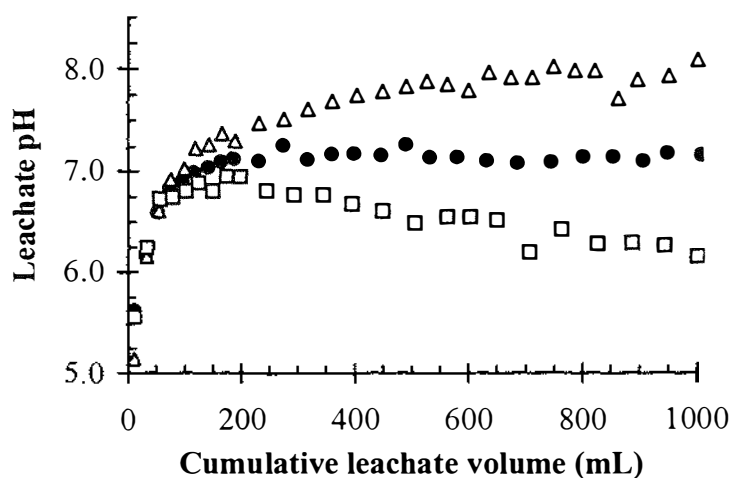
Figure 6.5. Trends in leachate pH for trial columns of Manawatu soil leached with 1000 mL of: deionized water (Δ); 2.5 mM $CaCl_2$ (□); and 2.5 mM $Ca(NO_3)_2$ (●).

Christensen, 1984a; Naidu *et al.*, 1994). This shift in pH could not be attributed to the leaching solutions whose pH values were around 5.6 (section 6.4.2, page 110), but may instead have resulted from ammonification occurring in the soil columns during leaching.

Effect of cation (Ca^{2+} and K^{+}) on cadmium movement

As was found for the leaching solutions containing Ca, discussed above, leaching of soil columns with KCl resulted in negligible recovery of Cd in the leachate (Table 6.6). However, whereas columns leached with 2.5 mM CaCl$_2$ showed Cd redistribution within the soil, this was not observed in any of the columns leached with KCl. A comparison between 2.5 mM CaCl$_2$ and 2.5 mM KCl is presented in Figure 6.6.

The results indicate that, as expected, Ca^{2+} has had a greater impact on Cd movement than K^{+}. This provides further evidence for the hypothesis that the Cl$^-$ concentrations used here were not high enough to increase Cd mobility through the formation of complexes. Thus it appears that Cd movement in these columns was induced predominantly through the presence of the competing cation, Ca^{2+}.
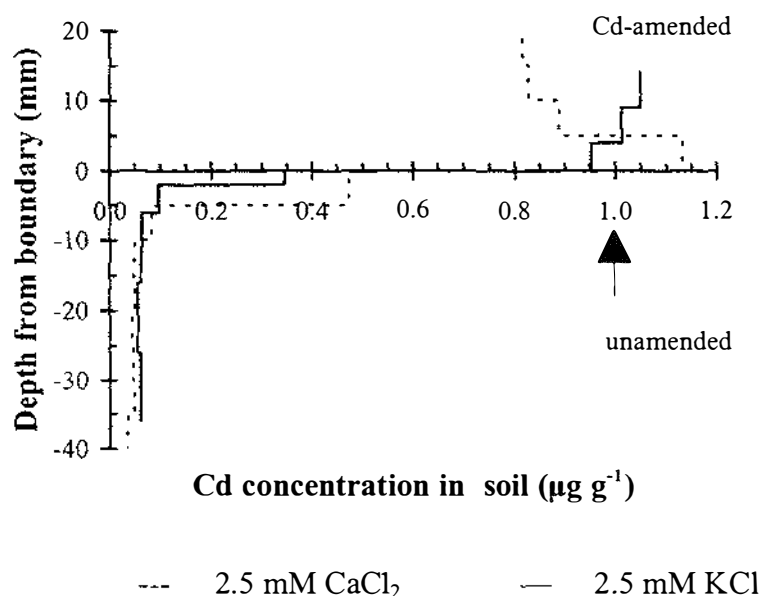
Figure 6.6. A comparison of the Cd distribution in trial columns of Manawatu soil leached with 1000 mL of: 2.5 mM CaCl$_2$ (dashed line) and 2.5 mM KCl (solid line). The top depth in the 2.5 mM KCl column has been omitted because of untraceable contamination. Arrow indicates initial Cd concentration in the Cd-amended soil of the top layer.

6.5.3 Experiment 2: Effect of increasing CaCl₂ concentration on cadmium movement in columns of Manawatu soil

Formation of the $CdCl^+$ complex has been calculated to begin at 1 mM Cl^- (Hahne and Kroontje, 1973), but a significant effect of Cl-Cd complexation on Cd sorption by clays has generally been found to begin only above 10 mM Cl^- (Egozy, 1980). An additional 50 mM $CaCl_2$ treatment was included with Experiment 1 (section 6.4.3) to verify these reports. As a result of the significant Cd mobility observed, it was decided to investigate closer this increase in Cd movement with increasing $CaCl_2$ concentration. Results from the 50 mM $CaCl_2$ treatment mentioned above are presented below.

A striking increase in Cd mobility occurred with increasing concentrations of $CaCl_2$ in the leaching solutions. This was demonstrated by both the increased loss of Cd to the

Table 6.7 Amount of Cd recovered in the leachate and that remaining in columns of Manawatu soil leached with 1000 mL (630 mm) of $CaCl_2$ solution.

Leaching solution	Cd collected in leachate		Cd loss from Cd-amended top soil layer	Cd recovery for treatment
	(µg)	(%)[†]	----------------(%)----------------	
Cd-amended Columns				
5 mM CaCl₂	0.26	0.7	20	105
10 mM CaCl₂	0.72	1.9	43	102
20 mM CaCl₂	5.23	14	72	104
35 mM CaCl₂	22.11	58	88	107
50 mM CaCl₂	32.76	87	93	105
Control Columns [‡]				
5 mM CaCl₂	0.23	4.5		154
10 mM CaCl₂	0.73	14		116
20 mM CaCl₂	1.67	33		127
35 mM CaCl₂	2.63	51		129
50 mM CaCl₂	2.66	52		119

[†] Expressed as % of the total Cd present in the soil column at the start of leaching (Table 6.4)

[‡] Recoveries for the control columns are greater than 100% due to the low Cd concentration in the unamended soil and accumulated inaccuracies in soil Cd determinations.

124
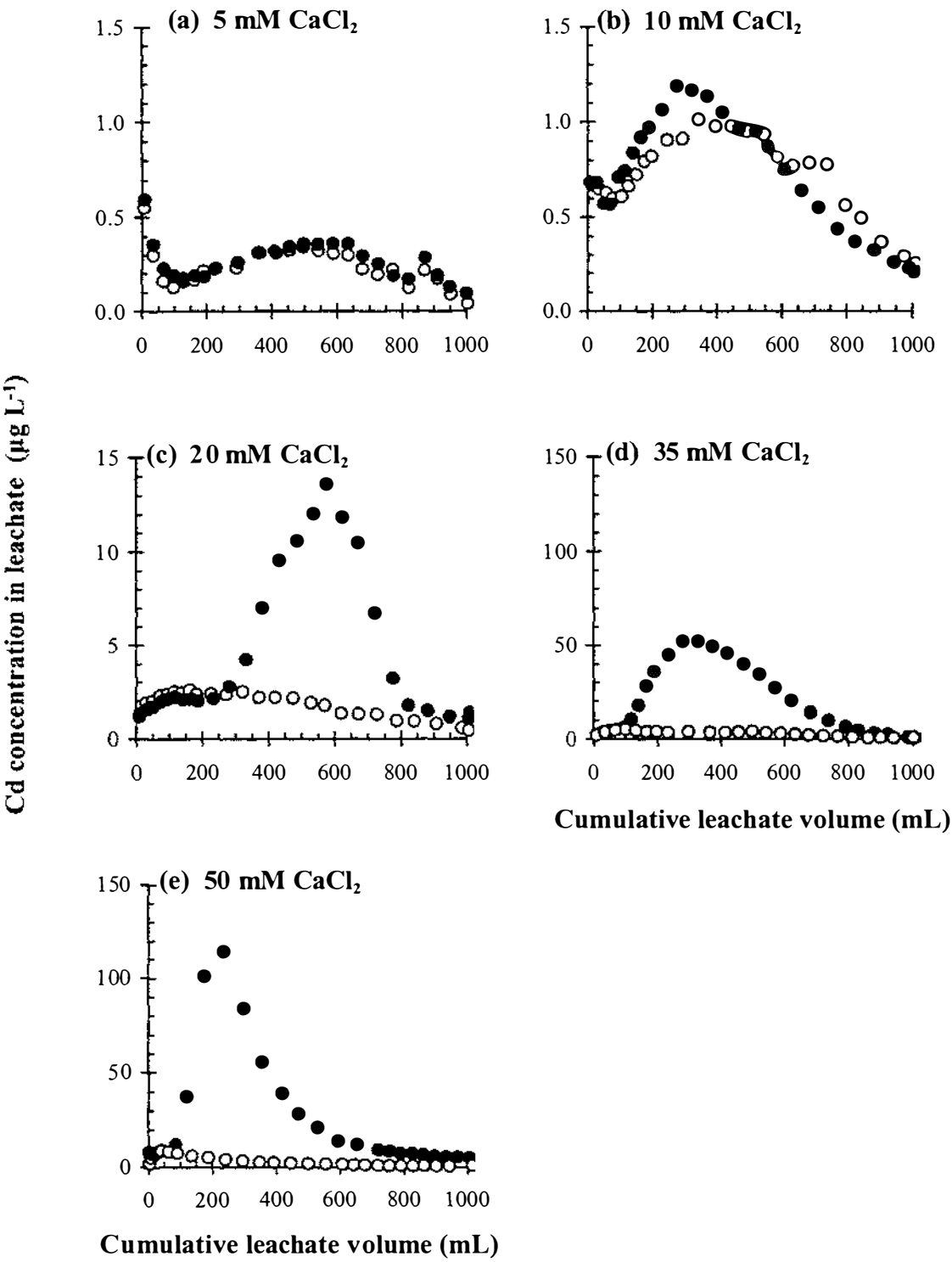
Figure 6.7   Concentrations of Cd in leachate from columns of Manawatu soil leached
with 1000 mL of: *(a)* 5 mM CaCl₂; *(b)* 10 mM CaCl₂; *(c)* 20 mM CaCl₂;
(d) 35 mM CaCl₂; and *(e)* 50 mM CaCl₂. Cd-amended columns which
contained added-Cd in the top soil layer are shown as closed symbols;
control columns are shown as open symbols. Note the change in scale of
one order of magnitude from *(a)-(b)* to *(c)*, and *(c)* to *(d)-(e)*.

leachate (Figure 6.7), and greater redistribution of added-Cd within the soil columns (Figure 6.8). However, it was not until the concentration reached 20 mM $CaCl_2$ that added-Cd from the top soil layer was found to have entered the leachate. Below this $CaCl_2$ concentration the same amount of Cd was lost from the Cd-amended and control columns of each treatment (Figure 6.7 and Table 6.7). This indicated that Cd in the leachate was derived solely from the bottom layer of unamended soil.

In the 50 mM $CaCl_2$ treatment, over 90% of Cd originally in the top soil layer had moved below the amended-unamended boundary (Table 6.7). This can be attributed to both the increasing predominance of Cd-Cl complexes and the increased competition by Ca^{2+} for exchange sites. At 100 mM Cl^- (50 mM $CaCl_2$), Cd speciation studies estimate that 80 % of the soluble Cd will probably exist as the highly mobile chloro complexes, $CdCl^+$ and $CdCl_2^0$; this is at least double that predicted to be complexed in 10 mM Cl^- (5 mM $CaCl_2$) (Hahne and Kroontje, 1973; O'Connor $et\ al.$, 1984). However, compared to the 5 mM $CaCl_2$ treatment, Ca^{2+} activity at 50 mM $CaCl_2$ is also greater (8.5 times) and therefore cation competition will continue to contribute substantially to enhanced Cd mobility (O'Connor $et\ al.$, 1984).

Soil pH appears to have played little part in the increasing mobility of Cd. Plots of leachate pH show the same rapid shift to higher pH values immediately after beginning
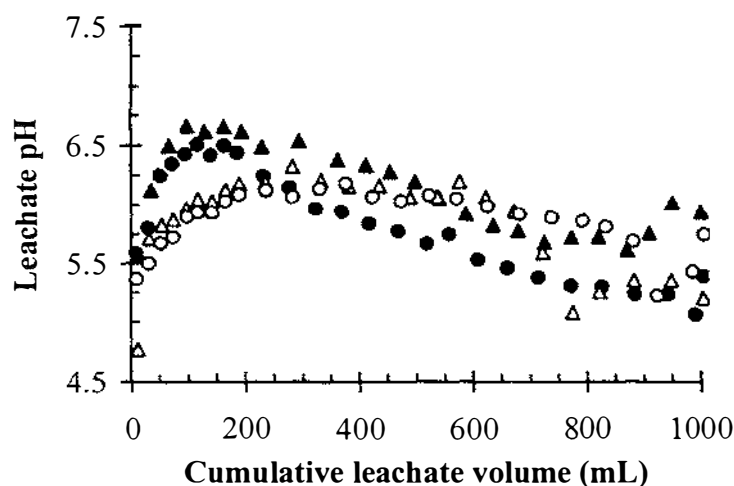
Figure 6.9. Trends in leachate pH for Cd-amended columns of Manawatu soil leached with 1000 mL of: 5 mM $CaCl_2$ (▲); 10 mM $CaCl_2$ (●); 20 mM $CaCl_2$ (Δ); and 35 mM $CaCl_2$ (O).

leaching, as was seen for the 2.5 mM CaCl₂ treatment in Experiment 1 (section 6.5.2). However, in all cases this was followed by a gradual decline back towards pH 5.5, the original pH of the soil (Figure 6.9). Leachate pH data from the 50 mM CaCl₂ treatment are not presented for reasons explained in section 6.4.3.

The changing mobility of Cd brought about by increases in CaCl₂ concentration can be expressed in terms of: 1) Cd loss from the Cd-amended top soil layer of the Cd-amended columns; and 2) Cd loss from the unamended soil of the control columns. A plot of these two variables against CaCl₂ concentration is shown in Figure 6.10. The data include results from the 2.5 mM CaCl₂ treatments presented previously in section 6.5.2.

From Figure 6.10 it appears that up to 50 % of the resident Cd in the unamended Manawatu soil has remained in an exchangeable form, this is despite its long-term exposure to the soil. Cadmium from the Cd-amended columns, and resident Cd from the
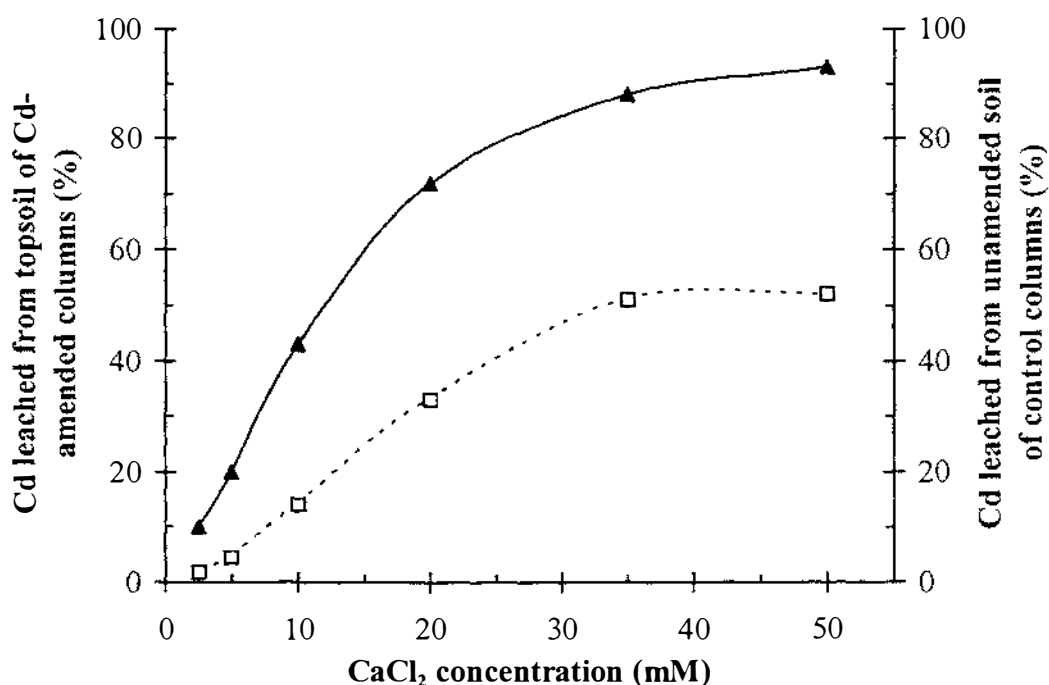
Figure 6.10. Comparison of Cd loss in columns of Manawatu soil with increasing concentrations of CaCl₂: *(a)* Cd loss from the Cd-amended top soil layer of Cd-amended columns (▲); *(b)* total Cd loss from control columns, i.e. percentage of Cd recovered in the leachate (□).

control columns show similar responses when leached with $CaCl_2$. In both cases there seems to be a linear relationship between Cd mobility and $CaCl_2$ concentration up to about 20 mM $CaCl_2$. There also appears to be no particular Cl^- concentration at which complexation begins to cause accelerated leaching of Cd. The steady increase in Cd movement shown by these results indicates a combined effect of Cl^- complexation of Cd^{2+} and competitive exchange by Ca^{2+} throughout the $CaCl_2$ concentration range.

Little additional loss of Cd occurs for $CaCl_2$ concentrations above 35 mM. In the case of the Cd-amended columns, this is because most of the available Cd has already been removed. In the unamended columns, however, nearly 50% of the Cd originally in the soil remains after leaching with 50 mM $CaCl_2$ (Figure 6.8 *(e)*). This Cd remaining in the soil is probably specifically sorbed to the solid phase – a phenomenon known to occur at low Cd concentrations (Garcia-Miragaya and Page, 1976; Tiller *et al.*, 1979; Tiller *et al.*, 1984a) – and therefore has a low availability.

Anomalies in the leaching results

Although Cd movement increased with increasing concentrations of $CaCl_2$, closer inspection of the leachate plots and soil column profiles revealed unexpected patterns in this movement. Normally a solute pulse travels through a repacked soil column as a single peak with some spreading due to dispersion effects. Leachate concentrations of the solute increase as the solute front approaches, and decrease once the peak has passed.

In the leaching results presented above, however, Cd concentrations in the leachate increased and then decreased (Figure 6.7 *(a)* - *(d)*) despite a significant proportion of the Cd remaining unleached (Table 6.7). In two of the columns (the 5 and 10 mM $CaCl_2$ treatments) the solute front clearly remains within the soil column and is positioned at the initial amended-unamended boundary for both treatments in spite of observed differences in overall Cd mobility (Figure 6.8 *(a)* and *(b)*). In the other two columns (20 and 35 mM $CaCl_2$ treatments), the majority of unleached Cd occurs as double peaks. One of these peaks is centred on the amended-unamended boundary – as also found in the 5 and 10 mM $CaCl_2$ treatments – while the other is positioned about 10 mm up from the base of the column (Figure 6.8 *(c)* and *(d)*). The satisfactory recovery of Cd in each

treatment (close to 100% of applied Cd and resident soil Cd, Table 6.7) indicated that these peaks were not caused by extraneous contamination. Instead an explanation for their presence must be found in the physical and chemical properties of the soil columns.

Several unusual observations therefore need to be accounted for in the leaching columns of this experiment. There is: 1) the formation of two Cd peaks within the soil column; 2) the premature decline in Cd leachate concentrations when much of the Cd remained unleached; and 3) the apparent immobility of the Cd solute front within the soil column despite clearly increasing Cd mobility with increasing $CaCl_2$ concentration. Anomalies of this type were not seen for any other soil studied (section 6.5.5).

One explanation for the anomalous behaviour described above begins with noting the positions of the double peaks seen in Figure 6.8 *(c)* and *(d)*. These can be viewed as defining areas of retarded Cd mobility, i.e. the filter paper marking the initial high Cd-low Cd boundary, and the base of the column. Analysis of soil from throughout the column did not reveal any unusual variations in soil pH or other element concentrations (e.g. Ca, Fe, Al, Zn) that could be associated with the Cd peaks. However, during sectioning of the soil columns, red-brown deposits consistent with the presence of iron oxides (McLaren and Cameron, 1990) were evident in soil at the base of the column, around the filter paper, and against the perspex column walls. These iron oxide deposits only appeared with leaching and were noticed in all experiments where this Manawatu soil was used.

This evidence of iron oxide precipitation lead me to consider the possibility that anaerobic and aerobic regions had developed in the soil columns during leaching. Such regions would be necessary for the reduction and oxidation of iron present in the Manawatu soil. There was no evidence of ponding in any of the columns studied – rather, preliminary work had indicated that flow rates twice that used, 0.05 mL min.$^{-1}$, were possible in this Manawatu soil. Consequently these columns should have been free draining and not subject to a rising saturation front. However, changes in redox conditions could still occur where distortions in hydraulic conductivity were

encountered – around the filter paper and at the base of the column (D. R. Scotter, pers. comm.).

If it is assumed that an amount of solution was held up at the filter paper and column base, then Cd immobility at these points could be explained by the changes which occur in a soil as a result of waterlogging. As noted in section 6.2.3, waterlogging can have several effects, including: a decrease in redox potential through the activity of micro-organisms; a rise in pH (this soil began as acidic but shifted towards neutral during the early stages of leaching); a predominance of hydrated forms of iron and manganese oxides; an increase in oxide surfaces and their decreased crystallinity; and a precipitation of ferrous and manganous ions where aerobic conditions are encountered (Iu *et al.*, 1981b). In addition, Cd present in solution can also be co-precipitated with the iron oxide. Hence, the highly adsorptive colloidal oxides possible under these conditions provide an efficacious explanation for the localized retardation of Cd.

Waterlogged conditions, however, take time to develop. Thus, Cd movement should be unhampered to begin with and will allow Cd migration at a rate determined by the ionic strength and composition of the leaching solution. For the weaker $CaCl_2$ treatments, leaching would be slow and therefore much of the Cd would remain accumulated above the filter paper. This accounts for the appearance of a stationary Cd solute front and the elevated Cd concentrations (above the initial 1 μg Cd g^{-1}) at this point in columns from both the 2.5 and 5 mM $CaCl_2$ treatments.

Where leaching solutions contain greater concentrations of $CaCl_2$, some Cd will pass beneath the amended-unamended boundary before conditions have developed to retard Cd movement significantly. This Cd would then be free to migrate further down the bottom soil layer. However, on reaching the base of the column, these Cd ions would encounter a second retarding zone and become immobilized there. This explains the double peaks seen in both the 20 mM and 35 mM $CaCl_2$ treatments. The development of this second zone would also affect Cd concentrations in the leachate. With Cd accumulating in the soil at the base of the column, Cd concentrations in the leachate would begin to decrease – irrespective of the amount of Cd remaining in the soil. This is

consistent with the observed behaviour of Cd in virtually all leachates collected from the Manawatu soil.

Implications for cadmium mobility under this experimental arrangement

With the above theory, most irregularities in data from the Manawatu soil columns can be accounted for. It seems likely that the fall in Cd concentrations in leachate from the 5 mM and 10 mM $CaCl_2$ columns, and the accumulation of Cd immediately above the amended-unamended [filter-paper marked] boundary in the 2.5 mM $CaCl_2$ and 2.5 mM $CaSO_4$ columns (Experiment 1, section 6.5.4), and the 5.0 mM $CaCl_2$ column, are also symptoms of these changes in soil chemistry.

In retrospect, the lack of any such Cd accumulation in the column leached with 2.5 mM $Ca(NO_3)_2$ (Figure 6.4) is now unusual. Perhaps waterlogging has not occurred to the same extent in these columns. This could be possible given the marked deterioration of the filter-paper noted in all columns treated with $Ca(NO_3)_2$. Attributed to microbial degradation, this disintegrated state of the filter paper might have provided less impedance to solution flow, and consequently lessened the severity of any waterlogging. As a result, these columns leached with $Ca(NO_3)_2$ may have been less affected by the chemical changes responsible for the anomalous Cd distributions observed in $CaCl_2$ and $CaSO_4$, and this might perhaps render the comparison between Cd movement in columns leached with $Ca(NO_3)_2$ and that in columns leached with $CaCl_2$ and $CaSO_4$ (section 6.5.2) less meaningful.

6.5.4   Experiment 3:   Response of leachate cadmium concentrations to wetting-drying cycles in columns of Manawatu soil

During a preliminary experiment in which Manawatu soil columns were leached with 2.5 mM $CaCl_2$, 2.5 mM $Ca(NO_3)_2$, 2.5 mM $CaSO_4$, and deionized water (data not presented), increased Cd concentrations (up to 3 and 5 µg Cd L^{-1}) were seen consistently in the leachate at the start of leaching. On the completion of leaching, most of the Cd leached from the soil columns in this preliminary experiment was found to be contained in the first 5 mL of leachate (0.2 pore volumes) – subsequent leachate generally contained concentrations of less than 0.1 µg Cd L^{-1}. Similar patterns are evident in other
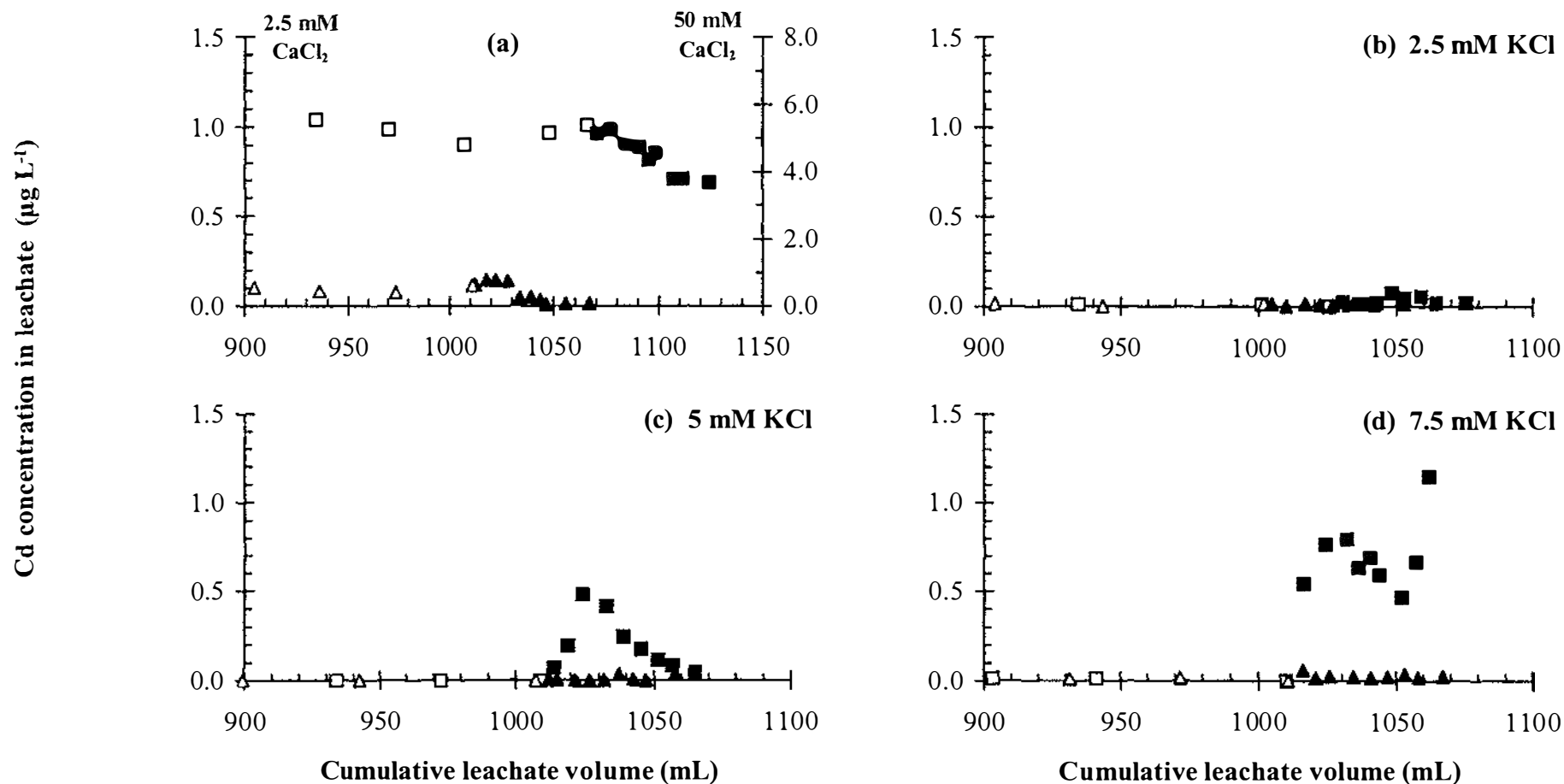
Figure 6.11. Concentrations of Cd in leachate during an initial leaching phase (open symbols) and during rewetting following a drying period (closed symbols) for: *(a)* Cd-amended columns of Manawatu soil leached with 2.5 mM CaCl₂ (Δ) and 50 mM CaCl₂ (□); and *(b)* - *(d)* Cd-amended (□) and control columns (Δ) of Manawatu soil leached with increasing concentrations of KCl.

leaching studies (Andersson, 1977; Smith, 1994), but an in-depth investigation of the cause has not been presented.

It is possible that these Cd peaks at the start of leaching are a result of Cd ions in the soil solution being carried by mass flow through the soil column with the invading solution front. If the rate of Cd desorption from soil is slow relative to the rate of water movement, then equilibrium between Cd ions in solution and Cd ions sorbed on to the soil will not re-establish. Thus, with continuous leaching, the Cd concentrations in the leachate following the solution front will fall away. If, however, a period of low solution flux was introduced to allow the solution-solid phase equilibrium to re-establish, at the next wetting event these Cd 'peaks' might re-appear. Should this be the case, cycles of wetting and drying might provide a significant mechanism for Cd loss from the soil system.

At the conclusion of Experiment 1 (section 6.4.3) the soil columns (replicate controls and treatments of: deionized water; 2.5 and 50 mM $CaCl_2$; 2.5 mM $CaSO_4$ and $Ca(NO_3)_2$; KCl at 2.5, 5.0 and 7.5 mM) were left to drain and partially dry at room temperature for 8 days (section 6.4.5). This period enabled some drying of the soil without shrinkage and cracking, thus preventing the development of flow paths which may have adversely affected the results, but the base of the column remained damp. A second leaching cycle was then begun.

Compared to the first leaching cycle (Figure 6.3 and Figure 6.7 *(e)*), the second leaching event produced no notable increases in leachate Cd concentration from any columns treated with Ca salts or deionized water. Examples from columns leached with 2.5 mM and 50 mM $CaCl_2$ are presented in Figure 6.11 *(a)*. In marked contrast, however, two columns leached with KCl did show increased concentrations of Cd in the leachate immediately following re-wetting (Figure 6.11 *(b) - (d)*). Since this increase in Cd concentration was restricted to columns containing added Cd, it is most likely that the Cd entering the leachate had originated from the Cd-amended top soil layer. However, as Ca, a stronger competitor for sorption sites than K, did not induce a similar effect at either at 2.5 mM or 50 mM $CaCl_2$, the mechanism causing this release of Cd in solutions of KCl is unlikely to be simply cation exchange.
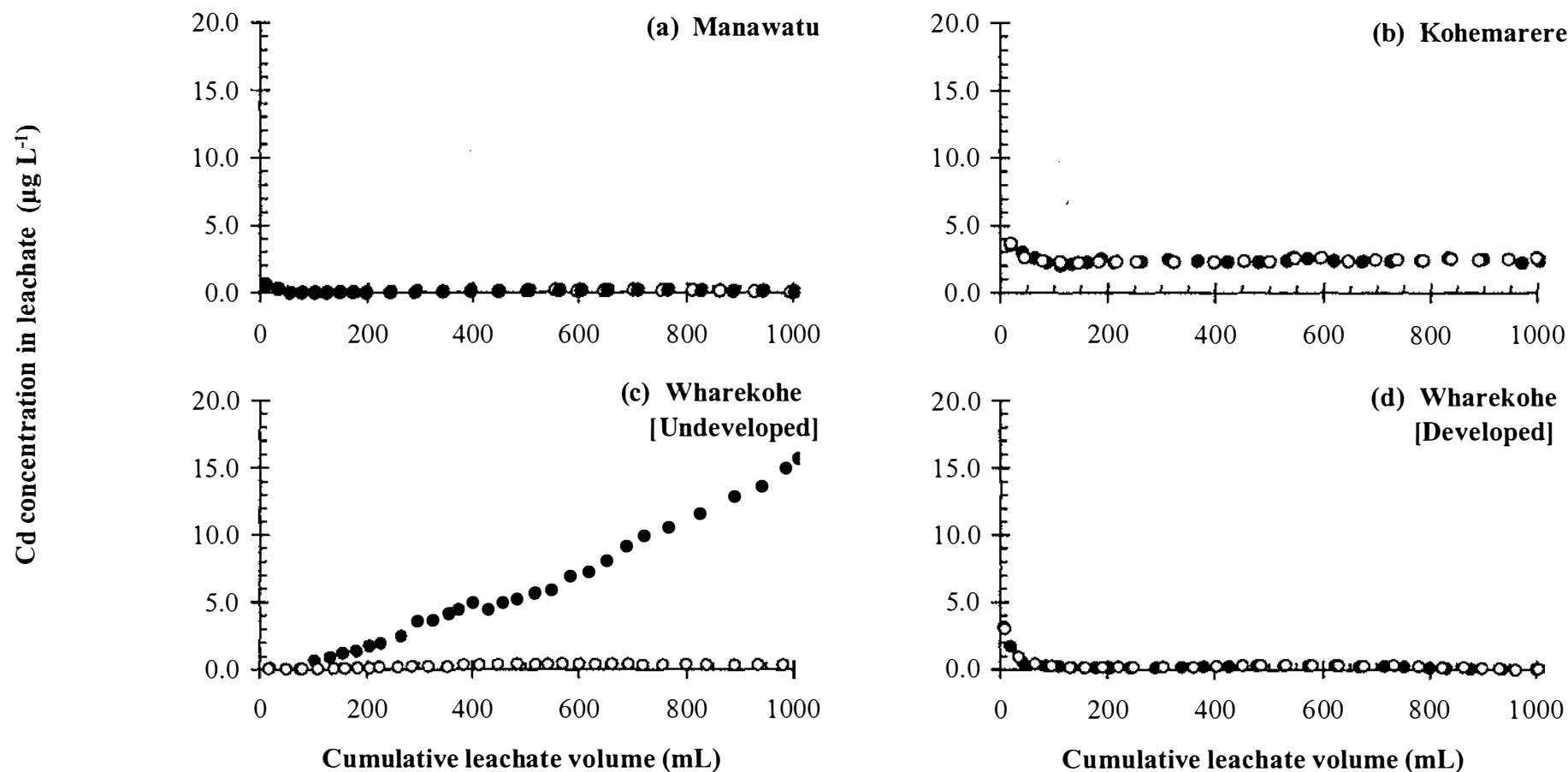
Figure 6.12. Concentrations of Cd in leachate from columns of soil leached with 1000 mL of 2.5 mM $CaCl_2$: *(a)* Manawatu; *(b)* Kohemarere; *(c)* Wharekohe [Undeveloped]; *(d)* Wharekohe [Developed]. Cd-amended columns which contained added-Cd in the top soil layer are indicated by closed symbols; control columns are indicated by open symbols.
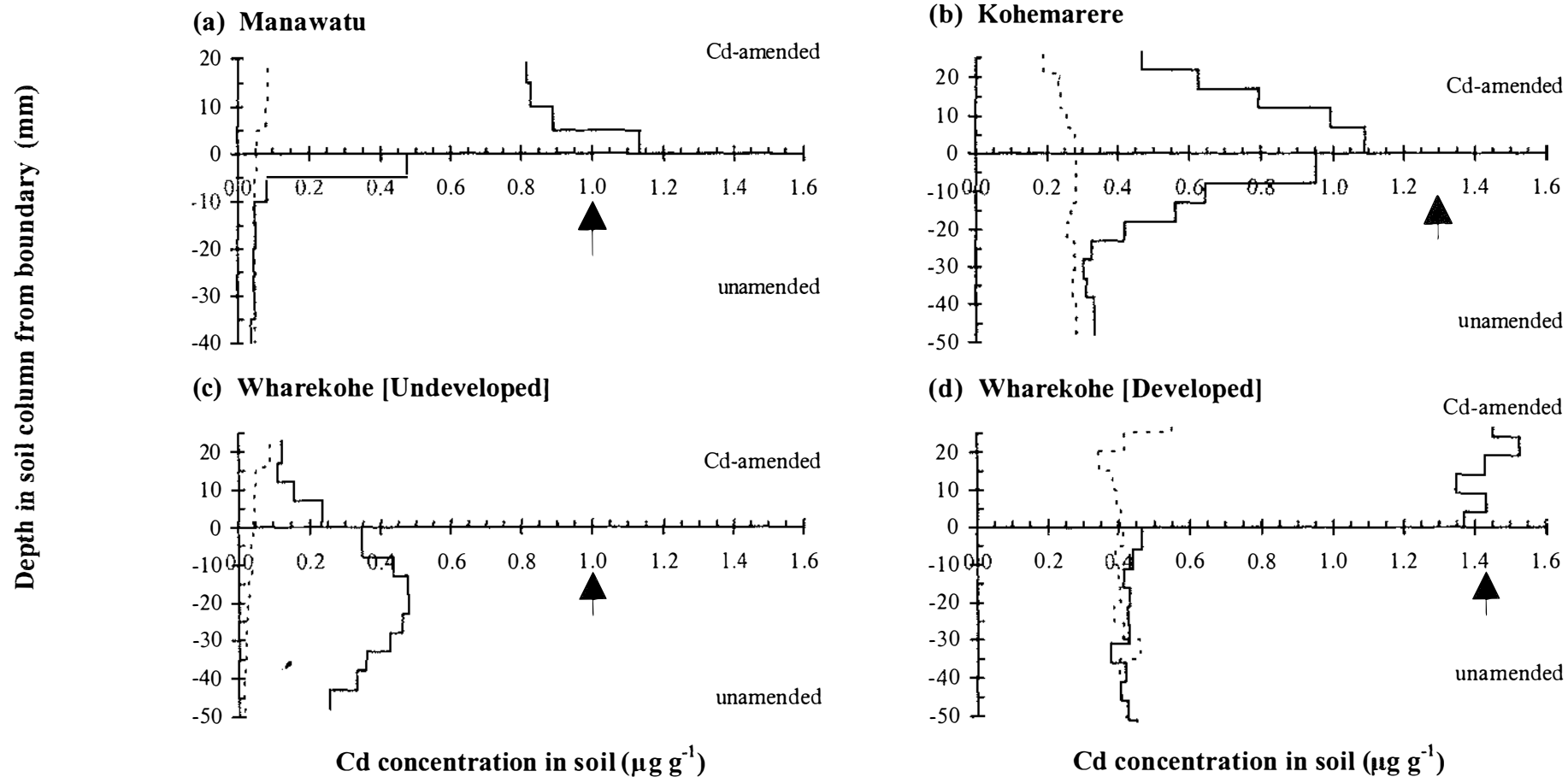
Figure 6.13. Distribution of Cd in columns of soil after leaching with 1000 mL of 2.5 mM CaCl₂: *(a)* Manawatu; *(b)* Kohemarere; *(c)* Wharekohe [Undeveloped]; *(d)* Wharekohe [Developed]. Cd-amended columns which contained added-Cd in the top soil layer are shown as a solid line; control columns are shown as a dashed line. Arrow indicates initial Cd concentration in the Cd-amended soil of the top layer.

The Cd peaks which appeared when the columns were first leached (Experiment 1) can possibly be attributed to fine soil particles and colloidal material washing through the permeameter mesh and carrying the Cd with them. Korentajer *et al.* (1993) and Keller and Domergue (1996) have both found that the association of elements such as Cd with clay particulate matter provides an important means of transport. As a reduced mesh size was used for the permeameter base in these experiments compared to that used in the preliminary study, the lower maxima of the Cd peaks (generally < 1.0 µg L^{-1}) might be explained by a reduction in sediment loss from the columns. Removal of extraneous soil particles from the column base after packing may also have contributed.

It is possible that the difference seen between columns leached with Ca solutions and those leached with K solutions could also be attributed to particulate transport of Cd. As noted in section 6.4.3, Ca^{2+} causes clay particles to flocculate, stabilizing the soil structure and making it less susceptible to sediment loss. Soils leached with K^{+}, however, may possibly have been less well flocculated, allowing the physical movement of clay particles. It seems, therefore, that Cd loss from the soil column as a result of some sorption equilibrium re-establishing between leaching events is not an important mechanism in this Manawatu soil under these conditions. And though physical transport in association with colloid material may be an important route for Cd loss from soils, it is outside the scope of this study.

6.5.5 Experiment 4: Cadmium movement in soils of differing chemical and physical properties when leached with 2.5 mM CaCl$_2$

Many of the physical, chemical and biological properties affecting Cd mobility are themselves interrelated in a complex manner. This makes the influences of various soil properties and conditions on Cd movement difficult to isolate. One means of gaining a quantitative understanding of how Cd behaviour changes under different conditions is to compare its movement in soils of differing properties.

When leached with 2.5 mM CaCl$_2$, a large variation in Cd mobility was found across the four soils studied here (Figures 6.12 and 6.13, previous pages). This movement ranged from very little in the columns of Wharekohe [Developed] soil, to extensive

Table 6.8 Amount of Cd recovered in the leachate and that remaining in the soil column when four different soils were leached with 1000 mL (630 mm) of 2.5 mM $CaCl_2$ solution.

Soil column	Cd collected in leachate		Cd loss from Cd-amended top soil layer	Cd recovery for treatment
	(μg)	(%)[†]	--------------(%)--------------	
Cd-amended Columns				
Manawatu	0.10	0.27	10	103
Kohemarere	2.5	4	37	103
Wharekohe [Undeveloped]	6.5	18	85	109
Wharekohe [Developed]	0.23	0.29	2	98
Control Columns				
Manawatu	0.10	1.9		116
Kohemarere	2.9	10		111
Wharekohe [Undeveloped] [‡]	0.24	18		236 [‡]
Wharekohe [Developed]	0.23	0.53		101

[†] Expressed as % of the total Cd present in the soil column at the start of leaching (Table 6.4)

[‡] From a mass balance it appears that the Wharekohe [Undeveloped] control columns (both duplicates) received additional Cd (1.6 μg) through contamination. This suggests that 4.5% of the Cd recovered from the Cd-amended columns is also due to contamination.

redistribution within, and rapid loss of added-Cd from the columns of its related soil, the Wharekohe [Undeveloped] (Table 6.8).

Compared to these extremes, the Kohemarere soil showed moderate Cd movement – 37% of Cd was lost from the top soil layer – while the Manawatu soil showed somewhat more restricted redistribution as described previously (section 6.5.2 - 2.5 mM $CaCl_2$ treatment).

Using the percentage of Cd lost from the top soil layer as a measure, Cd mobility in these soils increased in the order: Wharekohe [Developed] < Manawatu < Kohemarere < Wharekohe [Undeveloped]. This order is the same as that recorded for leachate pH and soil pH (Figure 6.14, Table 6.3) as most clearly demonstrated by the two Wharekohe

soils. These soils, though almost identical in mineralogy, differed markedly in pH and exchange acidity (Table 6.3). Whereas the Wharekohe [Undeveloped] soil was very acidic (pH 4.95) and had a CEC dominated by H^+, the CEC of the Wharekohe [Developed] soil was dominated by Ca^{2+} with an associated soil pH of 6.02 – features consistent with a history of liming and active soil management. These soil characteristics were clearly reflected in the significantly different leachate pH recorded for each soil (Figure 6.14) and provide the most plausible explanation for their striking contrast in Cd movement.

Similar results on the impact of pH have been reported in other studies. McBride (1994), for example, found greatly enhanced retention of Cd in a soil column when liming raised the soil pH to 6.5. Likewise, in a study of 15 different European soils, Holm *et al.* (1995) (as cited by Folke and Landner, 1996) found that the two soils which differed only in pH (5.1 and 7.8) produced the greatest and least leaching losses of Cd respectively. Indications are, therefore, that soil pH may have played an important part in determining the mobility of Cd in these soils under these leaching conditions – a finding consistent with the overwhelming evidence presented in literature.
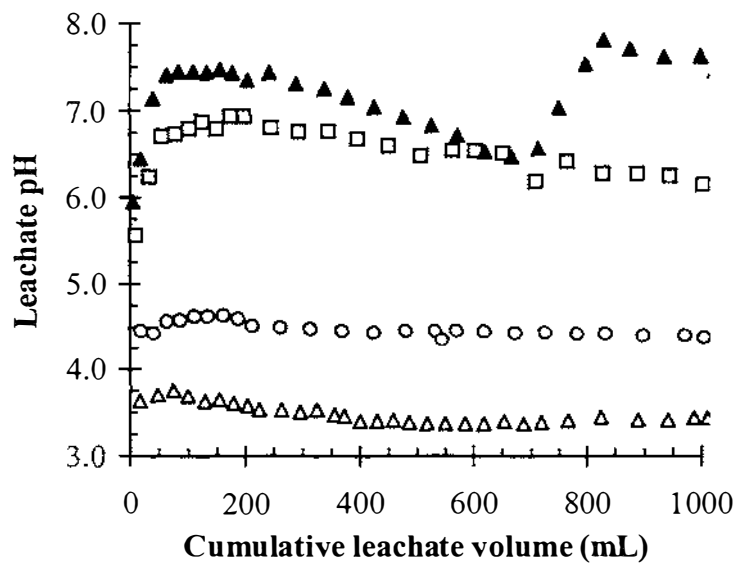
Figure 6.14. Trends in pH of leachate collected from Cd-amended columns of Manawatu (□); Kohemarere (O); Wharekohe [Undeveloped] (Δ); and Wharekohe [Developed] (▲) soil when leached with 2.5 mM $CaCl_2$.

In addition to the clear movement of added-Cd from the top soil layer of most soils, the Kohemarere soil also showed leaching of resident Cd. This was evident both from the concentration of Cd in the leachate of the control columns (Figure 6.12 *(b)*) and also the loss of Cd from the surface layer of these same columns (Figure 6.13 *(b)*).

With the possible exception of the Wharekohe [Developed] soil, none of the other soils appeared to show the distortions in Cd mobility which were so evident in the Manawatu soil. Features such as declining Cd concentrations in the leachate; the restriction of Cd redistribution to within the top soil layer; and accumulation of Cd above the boundary point are largely absent from Figures 6.12 *(b)* - *(d)* and 6.13 *(b)* - *(d)*. The fluctuations in leachate pH from the Wharekohe [Developed] columns (Figure 6.14) are, however, similar to that of the Manawatu soil and may indicate the development of anaerobic conditions in this soil. Certainly, nearing the completion of the experiment, columns of both the Wharekohe [Developed] and Wharekohe [Undeveloped] soils became fully saturated, and experienced severe surface ponding and declining leachate flow rates. In the case of the Wharekohe [Developed] soil this phase was accompanied by a second, sharp rise in leachate pH (Figure 6.14). The low pH of the Wharekohe [Undeveloped] soil probably inhibited the development of any anaerobic state, in spite of the waterlogged conditions. However, liming is known to increase the rate of development of anaerobic conditions (Iu *et al.*, 1981a) and may have made the Wharekohe [Developed] columns susceptible to these conditions. Nonetheless, the anomalous behaviour of Cd reported in section 6.5.3 was not observed in columns of either of these Wharekohe soils.

6.6 SUMMARY

Before the final conclusions and implications of this leaching work are presented, the major findings from each experimental section are briefly summarized.

Preliminary studies

- A predominance of Cl⁻ over other anions was found in the soil solution of soils on the coastal property of Limestone Downs.

140

Experiment 1

- In columns of Manawatu soil leached with $Ca(NO_3)_2$, $CaSO_4$ and $CaCl_2$, Cd showed a similar, but limited, degree of redistribution.

- Anomalous accumulation of Cd at one point in the soil profile was observed in columns leached with $CaCl_2$ and $CaSO_4$.

- Compared to leaching solutions containing $CaCl_2$, KCl caused little Cd movement.

Experiment 2

- Increasing $CaCl_2$ concentrations caused increased redistribution of both native Cd and added Cd in columns of Manawatu soil.

- The relationship between $CaCl_2$ concentration and Cd redistribution appeared linear up to 20 mM $CaCl_2$. In soil columns leached with 50 mM $CaCl_2$, nearly all added Cd appeared to have been removed.

- Anomalous behaviour by Cd was clearly apparent in several columns. This was attributed to the formation of anaerobic conditions at two points in the soil column

In the two experiments above, leachate pH appeared to have no bearing on the magnitude of Cd movement.

Experiment 3

- No evidence for significant Cd loss from soil on rewetting was found.

- Increased concentrations of Cd in the leachate at the beginning of each leaching study were therefore attributed to transport of Cd with displaced particulate matter.

Experiment 4

- A wide range of Cd movement was seen in four New Zealand pastoral soils.

- Two soils of identical mineralogy but markedly different pH, encompassed this range.

- The greatest impact on Cd mobility was concluded to be from soil and leachate pH.

6.7   Concluding discussion

The common observation is that Cd entering soil has a tendency to accumulate at the surface and this is interpreted to mean that Cd is essentially an immobile element. However a review of its chemical properties suggests that this is not necessarily the case under conditions which are aerobic and either acidic or neutral, or in the presence of high salinity, especially Cl^-.

In investigating the likelihood of inorganic complexation of Cd in soils on Limestone Downs, it was found that the coastal location had lead to the anion balance in the soil solution being dominated by Cl^-. Although Cl^- has been found to complex readily with Cd and thereby enhance Cd mobility in soils, the concentrations of Cl^- found in these soils (0.94 - 1.81 mM) were generally lower than those normally observed to cause accelerated leaching of Cd (section 6.2.4). Leaching experiments with varying concentrations of Cl^- in solution (as $CaCl_2$ and KCl) supported this opinion. At one extreme, very high concentrations of Cl^- (100 mM) caused virtually complete removal of Cd from the soil column. But at the other extreme under conditions more applicable to field soils (5 mM Cl^-), movement was restricted to redistribution over several centimetres. A similar degree of movement was seen with both 2.5 mM $CaSO_4$ and 2.5 mM $Ca(NO_3)_2$ solutions and this suggested that cation competition effects rather than chloride-complexation are the most probable mechanism for Cd redistribution in the soils of Limestone Downs.

Whereas small-scale movement is ineffective in removing Cd completely from the soil-plant system, it may still be important in bringing about changes in Cd availability in the top few centimetres of soil. In moving from a zone where accumulated organic material provides abundant sites for adsorption through cation exchange, and soil pH is high from regular lime application to several centimetres deeper where lower pH and less CEC means lower adsorption, the plant availability of Cd may change, increasing its potential risk to the farming system. However, though this study attempted to replicate certain aspects of Cd behaviour in soils, for example, the presence of pre-adsorbed Cd and its surface accumulation, it could not reproduce the changes in soil pH and CEC which occur with depth. More work is required in this area to assess the

importance of accumulated organic matter in the topsoil to Cd mobility and the influence of plant induced changes in the rhizosphere on its availability.

Studies on soils differing in chemical and physical characteristics indicated that changes in pH may be an important consideration in Cd movement. Thus the impact of farm management practices, for instance, liming and fertilizer application, may be highly influential in determining the Cd cycle within grazed pasture systems.

This work also revealed that a substantial proportion (50%) of the fertilizer and native Cd already resident in soil can remain in an exchangeable state and may therefore become mobile should the ionic strength of the soil solution increase – for example with the application of fertilizer salts or sheep and cattle urine. The latter situation is especially likely as urine also contains high concentrations of Cl^- (10 - 20 mM Cl^-) which may further increase Cd mobility through chloride-complexation. Evaporation of soil moisture is another means of increasing ionic strength and this may consequently lead to increasing Cd concentrations in solution. However, results from this study also suggested that such changes in soil conditions as the development of localized anaerobic zones and zones of iron oxide precipitation, may severely retard Cd movement irrespective of the potential for cation exchange or Cl^- complexation.

CHAPTER 7
CADMIUM REDISTRIBUTION IN SOIL – MODELLING

7.1   INTRODUCTION

In the previous chapter, evidence of measurable Cd movement in several New Zealand soil materials was presented. This movement occurred when both the soil Cd concentration and the ionic strength of the percolating solution were within the range likely to be encountered under field conditions. Though leaching losses are often dismissed as insignificant when constructing Cd mass balances for the field, the results of Chapter 6 indicate that Cd loss from field soils by leaching could be important and should be investigated further.

In this chapter, an elementary solute transport model was developed to test whether the variation in Cd movement between soils could be explained by simple, independent measures of Cd sorption. When the model proved successful in this regard, it was used to validate the possible importance of leaching as a mechanism of Cd loss in field soils.

7.2   THE SOLUTE TRANSPORT MODEL

Most modelling of heavy metal movement has been centred around the convection-dispersion equation (Schmitt and Sticher, 1986; Selim *et al.*, 1992; Hinz and Selim, 1994; Kookana *et al.*, 1994; Bajracharya *et al.*, 1996). This approach relies on describing the water flow within a volume of soil and incorporating mathematically, any physical or chemical transformations the solute experiences during transport. Because of the complexity of the system being represented, such a model only provides an approximation to reality. For example, assumptions used in deriving flow equations for water and solute transport in porous media are not necessarily satisfied in the field. This is freely acknowledged as being the case here.

The following sections briefly describe the basic elements of the convection-dispersion equation (CDE) and its translation into a computational model.

7.2.1   Theory behind the convection-dispersion equation

A full explanation of the CDE derivation can be found in Jury *et al.* (1991). The equations presented in this section have direct relevance to the computational model contained in Appendix 5.

The CDE is derived by considering the transport processes operating in an individual soil pore: diffusion and convection.

Molecular diffusion results from the random motion of molecules in a liquid or gas. For non-gaseous solutes in soil it is a slow process which occurs only through tortuous, interconnecting, liquid filled pores. For solute in the soil solution, molecular diffusion can be described by:

$$q_s = -\theta D_s \frac{dC}{dz} \qquad (7.1)$$

where q_s is the solute flux density (M L^{-2} T^{-1}), C is the solute concentration (M L^{-3}), z is the diffusion distance (L), θ is the volumetric water content (L^3 L^{-3}) and D_s is the molecular diffusion coefficient in soil (L^2 T^{-1}).

Convection causes solute to be carried conveyor-belt style by moving soil water. In reality this is a non-uniform process with fluid-flow fastest at the centre of each pore and near-zero at the walls. Convection is described mathematically by:

$$q_s = q_w C \qquad (7.2)$$

where q_s and C have the definitions given above and q_w is the Darcy flux density, i.e. the flow rate across unit cross-sectional area, (L T^{-1}).

With both molecular diffusion and convection acting, the solute flux density, q_s, becomes:

$$q_s = q_w C - \theta D_s \frac{dC}{dz} \qquad (7.3)$$

Interaction of convection with molecular diffusion at the local scale causes hydrodynamic dispersion which is roughly accounted for by replacing the molecular diffusion coefficient (D_s) with D, the dispersion coefficient ($L^2 T^{-1}$). Where a solute is not moving too slowly, hydrodynamic dispersion dominates over molecular diffusion. This allows D to be expressed as a function V, the average pore water velocity ($L T^{-1}$), equations 7.4 and 7.5. The proportionality constant, λ (L), is called the dispersivity.

$$V = \frac{q_w}{\theta} \qquad \text{(i.e. } q_w = \theta \ V) \qquad (7.4)$$

$$D = \lambda \ V \qquad (7.5)$$

Over a small time interval, dt, there is a change in the amount of solute contained within a volume of soil. Using the mass balance: change in amount of solute = solute entering - solute leaving, this change can be expressed as:

$$\frac{\partial C_{tot}}{\partial t} = \frac{\partial q_s}{\partial z} \qquad (7.6)$$

where C_{tot} is the total concentration of solute in unit soil volume ($M L^{-3}$), t is time (T) and ∂q_s ($M L^{-2} T^{-1}$) is the difference between solute flux in and solute flux out.

The final form of the convection-dispersion equation (7.7) is:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - V\frac{\partial C}{\partial z} \qquad (7.7)$$

where the R term is a dimensionless retardation coefficient included to account for reversible reactions between the solution and solid matrix. This is a mathematical description for one-dimensional steady-state transport of a conservative, reactive solute through a homogeneous soil of uniform water content. The form which R takes is discussed in the next section.

7.2.2   The retardation coefficient

Processes regulating the concentration of a solute in the soil solution, and thereby regulating its movement through the soil system include adsorption, desorption, precipitation, dissolution, abiotic degradation, biodegradation, volatilization and oxidation-reduction reactions (Travis and Etnier, 1981). In order to model the transport of a solute through soil these processes need to be described mathematically and incorporated into the CDE equation (7.7). For Cd at low concentrations (where precipitation processes are negligible) the main interest is in sorption reactions and these are expressed through the R term.

The means by which sorption processes are described mathematically has been thoroughly reviewed by Travis and Etnier (1981). The approach need not be mechanistically correct. A satisfactory approximation can be achieved by fitting sorption data to a particular equilibrium sorption isotherm with no implication as to the specific sorptive mechanism (Travis and Etnier, 1981). Predominantly, Cd reactions in soil have been modelled using either of two approaches: (a) equilibrium sorption isotherms, linear or curvilinear that assume fast sorption in comparison to the rate of soil water flux (Poelstra $et\ al.$, 1979; Christensen, 1985; Bajracharya $et\ al.$, 1996), or (b) an equilibrium sorption isotherm in conjunction with a kinetic sorption model which accommodates time dependent reactions (Selim $et\ al.$, 1992; Hinz and Selim, 1994; Kookana $et\ al.$, 1994).

A linear adsorption isotherm assumes that the amount of solute adsorbed by the soil matrix, S (mass of solute/mass of soil, M M^{-1}), and the concentration of solute in the soil solution at equilibrium, C (mass of solute/volume of solution, M L^{-3}), are linearly related by:

$$S = K_d\ C \tag{7.8}$$

where the proportionality constant, K_d (L^3 M^{-1}), is referred to as the distribution coefficient – a measure of the affinity a soil has for the solute. Though this isotherm has the limitation of not setting a maximum quantity of adsorbed solute (Travis and Etnier, 1981), at low concentrations, the Cd sorption isotherm is essentially linear (Kim and

Fergusson, 1992; Tjell and Christensen, 1992; Boekhold *et al.*, 1993) and hence linear isotherms were assumed here. The K_d value for a soil is found by plotting *S versus C*.

Incorporating this isotherm into the CDE is done by noting that the total solute concentration in a volume of soil, C_{tot}, is equal to the solute in solution plus that on the soil:

$$C_{tot} = \theta C + \rho_b S \qquad (7.9)$$

where ρ_b is the soil bulk density ($M\ L^{-3}$).

Substituting equation 7.8 for *S* in equation 7.9 and defining a retardation coefficient, *R*, as:

$$R = 1 + \frac{\rho_b K_d}{\theta} \qquad (7.10)$$

gives
$$C_{tot} = R\theta C \qquad (7.11)$$

where *R* is the same coefficient as that in equation 7.7.

7.2.3   Translating the theoretical CDE into a computational model

The equations given above to derive the CDE can be written in a programming language, for example BASIC or Pascal, to create a computer program capable of solving the CDE numerically. For this study, Turbo Pascal was used. A copy of the programme, definitions of the variables and an explanation of the calculations are contained in Appendix 5.

7.2.4   Estimating parameters in the CDE

Values for physical parameters in the CDE model were obtained from data recorded during Experiment 4 in section 6.5.5. These data are summarized in Table 7.1 for each of the four soils: Manawatu, Kohemarere, Wharekohe [Undeveloped] and Wharekohe [Developed].

148

Table 7.1 Physical parameters measured from the experimental soil columns studied in section 6.5.5 which acted as input data for the CDE model (Appendix 5) used to predict Cd movement in columns of each soil.

Parameters	Manawatu	Kohemarere	Wharekohe [Undeveloped]	Wharekohe [Developed]
Soil column height, l (m)	60×10^{-3}	75×10^{-3}	72×10^{-3}	91×10^{-3}
Height of Cd-amended top layer (m)	20×10^{-3}	27×10^{-3}	24×10^{-3}	30×10^{-3}
Soil volume, $vol. = \pi r^2 l$ (m^3) [†]	0.095×10^{-3}	0.119×10^{-3}	0.115×10^{-3}	0.145×10^{-3}
Mass of soil in column, m_s (kg) [§]	0.102	0.102	0.102	0.102
Packed bulk density, $\rho_b = m_s/vol.$ $(kg\ m^{-3})$ [§]	1070	855.0	890.7	704.8
Mass of water in column, m_w (kg) [‡]	0.0651	0.0662	0.0786	0.1946
Gravimetric water content, $w = m_w/m_s$ $(kg\ kg^{-1})$	0.638	0.649	0.771	1.908
Volumetric water content, $\theta = w*\rho_b/\rho_{water}$ $(m^3\ m^{-3})$	0.683	0.555	0.686	1.345
Average leachate flow rate, Q $(m^3\ h^{-1})$	2.1×10^{-6}	2.1×10^{-6}	1.62×10^{-6}	1.62×10^{-6}
Darcy flux density, $q = Q/area$ $(m\ h^{-1})$ [†]	1.32×10^{-3}	1.32×10^{-3}	1.02×10^{-3}	1.02×10^{-3}

Cd concentrations in top (Cd-amended) and bottom (unamended) soil layers prior to leaching:

	Manawatu	Kohemarere	Wharekohe [Undeveloped]	Wharekohe [Developed]
Cd-amended soil, C_{add} $(mg\ kg^{-1})$ [§]	1.014	1.290	1.019	1.435
Unamended soil, $C_{resident}$ $(mg\ kg^{-1})$ [§]	0.050	0.272	0.013	0.430
Influent Cd $(mg\ m^{-3})$	0.60	0.60	0.60	0.60

[†] r is radius of column, 22.5×10^{-3} m; *area* is cross-sectional area of column, $\pi r^2 = 1.59 \times 10^{-3}$ m^2.

[‡] m_w is mass of water remaining in the experimental soil columns after completion of leaching.

[§]   Data involving soil weights are given for oven dry (105 °C) soil.

An influent Cd concentration of 0.6 mg m^{-3} was included after analysis of the 2.5 mM CaCl$_2$ leaching solution indicated some low-level Cd contamination. The only parameters to be determined independently of the soil column leaching experiment were the distribution coefficient, K_d, and the (effective) dispersivity. A dispersivity of 3 mm was selected as a reasonable estimate (D. R. Scotter, pers. comm.). Higher values than this generally apply to structured soils with a range of pore sizes as opposed to the sieved and repacked soil columns used in Chapter 6.

The distribution coefficients for each soil were initially calculated from simple adsorption isotherms. However, some discrepancy was seen between the Cd movement predicted by the model and that observed in the experimental soil columns. Because initial movement in the soil columns of Chapter 6 was a result of desorption rather than adsorption mechanisms, a difference between the sorption and desorption isotherms (hysteresis) may cause adsorption data to inaccurately represent Cd movement. As a consequence, distribution coefficients from desorption isotherms were also considered in an attempt to improve the agreement between the model and the Cd redistribution observed in the leaching studies. The methodology for obtaining these sorption isotherms is detailed below. The procedure was carried out for each of the four soils, Manawatu, Kohemarere, Wharekohe [Undeveloped] and Wharekohe [Developed].

Batch equilibrium adsorption isotherms

Solutions of 2.5 mM CaCl$_2$ with Cd concentrations ranging from 0 to 150 µg L^{-1} (0 to 1.34 µM) were prepared from standard Cd(NO$_3$)$_2$. A 0.5 g sample of air-dry soil was suspended in 5 mL of solution at each Cd concentration. Blanks without soil were included for each of the Cd solutions to account for any extraneous adsorption on to the walls of the plastic centrifuge tubes. Each adsorption isotherm comprised 12 points representing 6 duplicated Cd concentrations of 0, 30, 60, 90, 120 and 150 µg Cd L^{-1}.

The soil suspensions and blanks were shaken for 20 hours on an end-over-end shaker at room temperature. After centrifuging at 4000 rpm for 10 minutes, a small aliquot of the supernatant solution was taken for measuring solution pH. The remaining solution was analyzed for (equilibrium) Cd concentration by GFAAS using an oxalic acid modifier

150

(section 3.5). The difference between the initial and equilibrium concentrations was used to calculate the amount of Cd adsorbed by the soil.

An equilibration period of 20 hours was chosen. This time was indicated by a review of the literature (Christensen, 1984a; Boekhold *et al.*, 1993; Hinz and Selim, 1994). In general, Cd adsorption occurs rapidly. Christensen (1984a), for example, reported 95% adsorption within 10 minutes and equilibration after one hour. Other equilibration periods have been used, e.g. 24 hours (Kookana *et al.*, 1994) and 48 hours (Kim and Fergusson, 1992).

Batch equilibrium sorption-desorption isotherms
There are several methods of conducting desorption experiments. The variation between methods comes from a difficulty in maintaining the same equilibrium conditions at each stage of the desorption isotherm, e.g. variations in soil:solution volume, equilibrium solution pH and ionic composition. Each method has advantages and disadvantages in this respect, however for this investigation the following procedure was chosen.

Five-mL aliquots of 2.5 mM $CaCl_2$ solution containing 150 μg Cd/L were placed in weighed centrifuge tubes. Eight samples of 0.5 g air dry soil were suspended in these solutions and shaken for 20 hours at 25 °C. These 8 samples represented 4 sets of duplicates. After centrifuging at 4000 rpm (10 minutes), the solution phase was decanted and analyzed for both pH and Cd concentration as done for the adsorption isotherms above.

After weighing, the duplicate centrifuge tubes containing the retained soil and entrained solution received either 5, 10, 20 or 40 mL [the Manawatu soil had an extra pair of samples with a desorption volume of 100 mL] of Cd-free 2.5 mM $CaCl_2$ solution. Following stirring on a vortex mixer to redisperse the soil particles, the soil and solution were shaken for a further 20 hours at 25 °C. After separation of the phases by centrifuging at 4000 rpm (10 minutes), the equilibrated solution was decanted and analyzed for both pH and Cd.
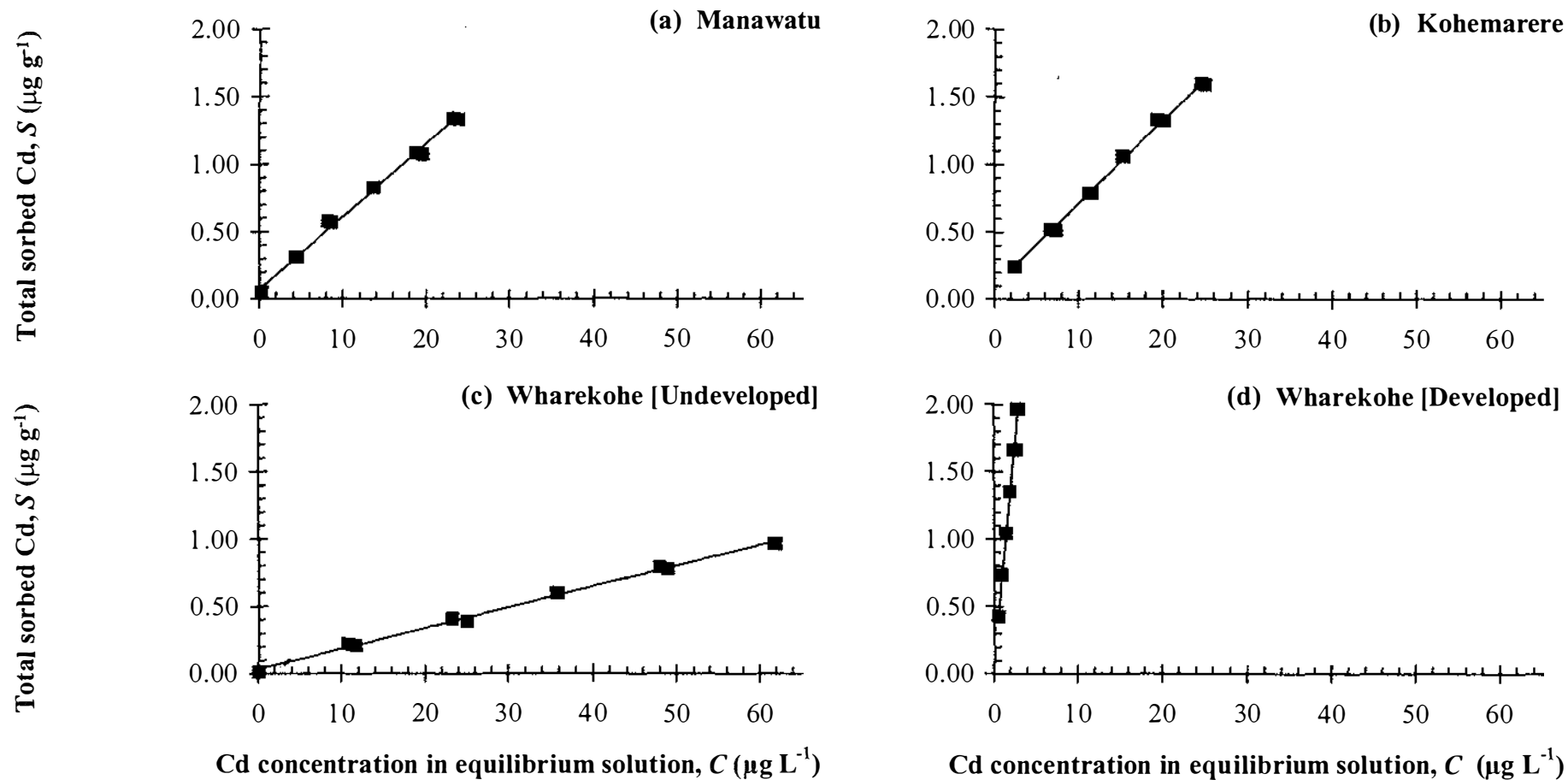
Figure 7.1. Adsorption isotherms for each soil determined in a background matrix of 2.5 mM $CaCl_2$ and at the soil's natural pH. Solution pH values and equations for the fitted linear isotherms are presented in Table 7.2.

7.3 RESULTS AND DISCUSSION

Adsorption isotherm data for each of the four soils are presented in Figure 7.1 and Table 7.2. With the possible exception of the Wharekohe [Undeveloped] soil – which shows some curvilinear behaviour – fitting a linear isotherm appears to describe each of the data sets satisfactorily.

Ranking the soils according to their K_d value (determined from the slope of the linear isotherms, Table 7.2) gives the same order as that obtained for Cd movement from the experimental soil columns. The soils which showed the least (Wharekohe [Developed]) and greatest (Wharekohe [Undeveloped]) Cd movement have the highest and lowest K_d values respectively.

All isotherms had a positive intercept on the solid-phase axis; this indicates a high affinity of the soil for Cd at low Cd concentrations. The value of the intercept (given in Table 7.2) can be taken as an estimate of Cd specifically, or irreversibly, adsorbed on to the solid phase (Garcia-Miragaya and Page, 1976), and it was subsequently incorporated into the CDE model (Appendix 5) as a measure of non-desorbable or 'fixed' Cd in each soil.

By inserting the value for K_d, obtained from the adsorption isotherm, and the data contained in Table 7.1, Cd movement in each of the four soil columns was simulated. Results are presented in Figures 7.2 and 7.3.

Overall, a fairly accurate prediction of Cd movement, in terms of the solute concentration in the leachate and the position of the solute peak within the soil column, is achieved for all four soils using the simple CDE model and linear adsorption isotherm. There is, however, some variation in the agreement between modelled results and experimental data. This is discussed briefly below.

The best agreement between predicted and observed movement is seen in the case of the Kohemarere soil. Here both the Cd profile in the soil column and the Cd concentrations in the leachate agree closely with the experimental results (Figure 7.2 *(b)* and Figure 7.3 *(b)*). This was helped by the incorporation of a value for non-desorbable Cd on the solid

Table 7.2 Adsorption isotherm equations for sorption of Cd on four soils in 2.5 mM $CaCl_2$.

Soil	Manawatu	Kohemarere	Wharekohe [Undeveloped]	Wharekohe [Developed]
Equation of linear isotherm[†]	$S = 0.0539C + 0.070$ (0.995)	$S = 0.0611C + 0.099$ (0.997)	$S = 0.0154C + 0.031$ (0.997)	$S = 0.624C + 0.158$ (0.985)
K_d (L g^{-1})	0.0539	0.0611	0.0154	0.624
Non-desorbable Cd (μg g^{-1})	0.070	0.099	0.031	0.158
pH of equilibrium solution from adsorption isotherms	4.97 - 5.04	4.44 - 4.53	3.57 - 3.64	5.99 - 6.38
Leachate pH from experimental columns[‡]	5.56 - 7.03 (6.58 ± 0.33)	4.35 - 4.64 (4.48 ± 0.07)	3.36 - 3.76 (3.49 ± 0.11)	5.77 - 7.80 (7.16 ± 0.42)

[†] R^2 values for the linear isotherm equation are given in parentheses.
[‡] The average leachate pH over the duration of leaching is given in parentheses.
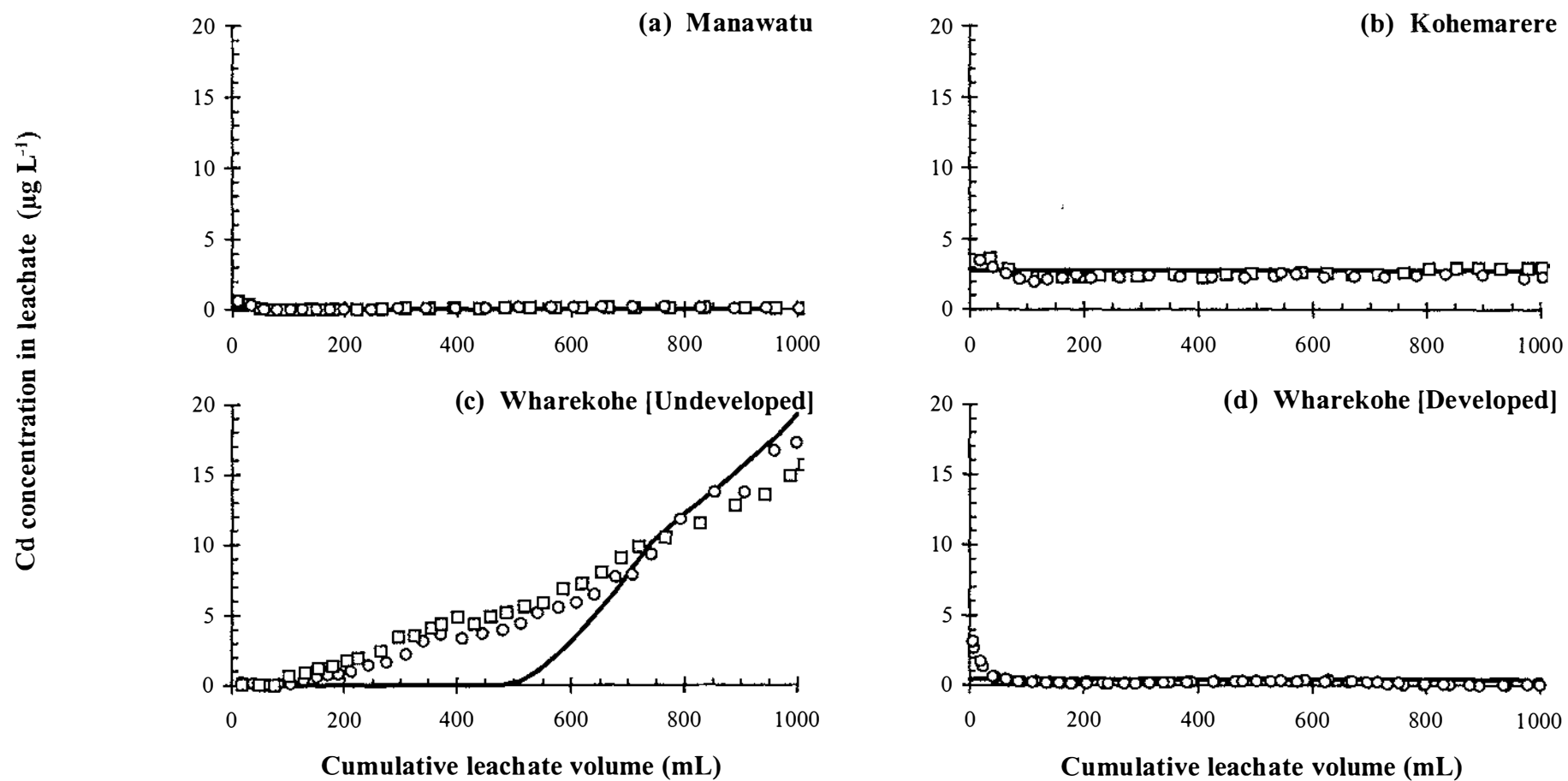
Figure 7.2. Concentrations of Cd in leachate from columns of soil leached with 2.5 mM CaCl$_2$: measured (symbols) from experimental soil columns; and predicted (—) using a simple convection-dispersion equation and assuming sorption equilibrium. Model constants are given in Table 7.1 and 7.2.
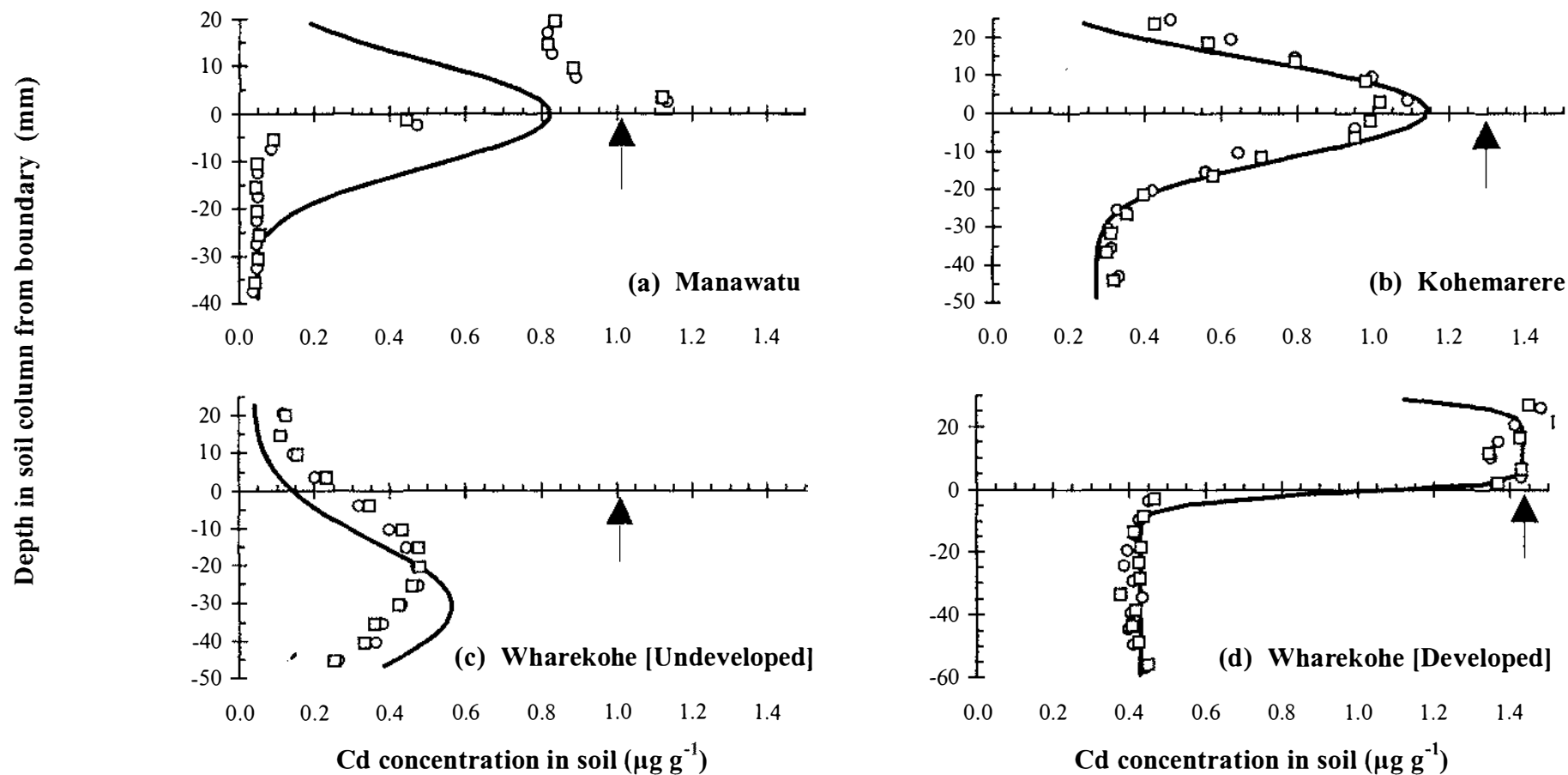
Figure 7.3. Concentrations of Cd in soil columns after leaching with 1000 mL of 2.5 mM CaCl$_2$: measured (symbols) from experimental soil columns; and predicted (—) using a simple convection-dispersion equation and assuming sorption equilibrium. Model constants are given in Table 7.1 and 7.2. Arrow indicates starting Cd concentration for the high-Cd, top layer.

phase, particularly in bringing the predicted Cd concentrations in the leachate close to those of the experimental data (Figure 7.2 *(b)*). Without the inclusion of this non-desorbable value, the loss of Cd to the leachate would have been over predicted by about 1.5 times.

Similarly, the simple CDE model has satisfactorily predicted Cd movement in the Wharekohe [Developed] soil – despite the lower pH of the adsorption isotherm solutions compared to the leachate from the experimental soil columns (Table 7.2) . The high K_d calculated from the adsorption isotherm reflects well the severe retardation of Cd mobility found experimentally in this soil (Figure 7.3 *(d)*).

Cadmium redistribution in the Wharekohe [Undeveloped] soil is also reasonably well modelled. However, while the model slightly over predicts Cd movement in the soil column (with respect to the position of the Cd peak), it fails to replicate the rapidity with which Cd actually appeared in the leachate. Two factors in the model may be responsible for these contradictory observations. Firstly, the inclusion of a non-desorbable Cd concentration in the model, which delays the predicted appearance of Cd in the leachate (Figure 7.2 *(c)*). And secondly, the assumption in the model that the soil column is already saturated at the start of the experiment. In contrast to the saturated state of the theoretical column, the experimental columns all began in an unsaturated state. Hence, all leachate collected from the experimental columns had passed through the high-Cd topsoil. Where Cd mobility is high, such as in the Wharekohe [Undeveloped] soil, even initial collections of this leachate could contain added-Cd.

The close agreement obtained between the modelled and observed redistribution of Cd is illustrated further by comparing the predicted and observed loss of Cd from the top, Cd-amended layer. Data for this comparison are presented in Table 7.3. With one exception, the predicted and observed loss agree within 10%. In the Manawatu soil, however, it is evident that the model has seriously over predicted the degree of Cd redistribution. This is despite having predicted well the final position of the Cd peak within the soil profile (Figure 7.3 *(a)*).

Table 7.3 Comparison of Cd loss from the Cd-amended topsoil predicted using the CDE model with a distribution coefficient determined from adsorption isotherms, and measured Cd loss from the experimental soil columns.

Soil	Proportion of Cd lost from top soil layer	
	--- Predicted by model ---	-- Found experimentally --
Kohemarere	47 %	37 %
Manawatu	50 %	10 %
Wharekohe [Undeveloped]	93 %	85 %
Wharekohe [Developed]	3 %	2 %

Recalling the anomalous behaviour shown by Cd in the Manawatu soil (section 6.5.3), the discrepancy between the modelled and experimental data, described here probably should not be unexpected. Changes in soil chemistry, such as those proposed to have occurred in the columns of Manawatu soil during leaching, can not be accommodated by a retardation coefficient determined from an adsorption isotherm. Consequently, differences in the chemical properties of the leached soil (experimental columns) and unleached soil (adsorption isotherm) may account for some of the gross model error.

In general, some poorness-of-fit between the experimental and predicted data is evident for each soil. There has also been no allowance in the model for the dependence of Cd movement on desorption processes (section 6.3). In basing the leaching model solely on adsorption data, one is implicitly assuming that the adsorption and desorption isotherms are similar. This may not be the case. In some soils, under some conditions, *desorption* and time-dependent changes in Cd speciation may be the regulating factors in Cd movement (Mann and Ritchie, 1994). The possibility that the model predictions (particularly in the case of the Manawatu soil) could be improved by considering Cd desorption rather than adsorption was, therefore, investigated.

Sorption-desorption isotherms

Cadmium sorption on to soil shows both total reversibility and partial irreversibility, depending on the soil in question and solution conditions (Pickering, 1980; Christensen,

1985; Gray *et al.*, 1998). This is evident as a divergence between the adsorption and desorption isotherms. In some cases the divergence is such that a given Cd concentration in the solution is associated with a much higher Cd concentration on the soil surface in the desorption phase than is found at equilibrium in the adsorption phase – an indication that time-dependent immobilization processes are operating.

Desorption isotherms for all four soils are shown in Figure 7.4. Because very little desorption occurred from the high sorbing Wharekohe [Developed] soil, the data points for this soil's isotherm were closely grouped and could not be satisfactorily delineated (Figure 7.4 *(d)*). In the other three soils (Kohemarere, Manawatu and Wharekohe [Undeveloped]) functional desorption isotherms were obtained. A comparison of these isotherms with those obtained by adsorption seems to indicate some degree of hysteresis (or time-dependent sorption) in each soil. Closer inspection of the data reveal, however, that this hysteresis may be superficial. In two of the soils (Kohemarere and Wharekohe [Undeveloped]) the initial sorption point in the desorption experiment does not coincide exactly with the equivalent point in the adsorption isotherm. Thus the lines of the isotherms may simply be displaced as a result of analytical error or day-to-day variation in the experimental conditions (for example, temperature) rather than as a result of some time-dependent reaction.

It is only in the Manawatu soil that there is some clear evidence of hysteresis. However, use of these desorption data in the CDE model did not greatly assist in improving the prediction of Cd movement in this soil. Ideally, more work would be required before the usefulness of desorption isotherms could be fully established.

Predicting cadmium movement over time under pasture conditions

Having established that the simple CDE model can describe Cd movement in three out the four soils studied, the model can then be used to estimate potential leaching rates of Cd from these soils under field conditions. In doing this, however, there are no pretensions to accuracy. Extrapolating laboratory findings to the field is difficult as assumptions used to model laboratory data may not be applicable in the field (Bond and Smiles, 1988). Water infiltration, for example, is often represented as piston flow (or displacement) – a suitable description for simulating repacked soil columns, but it does
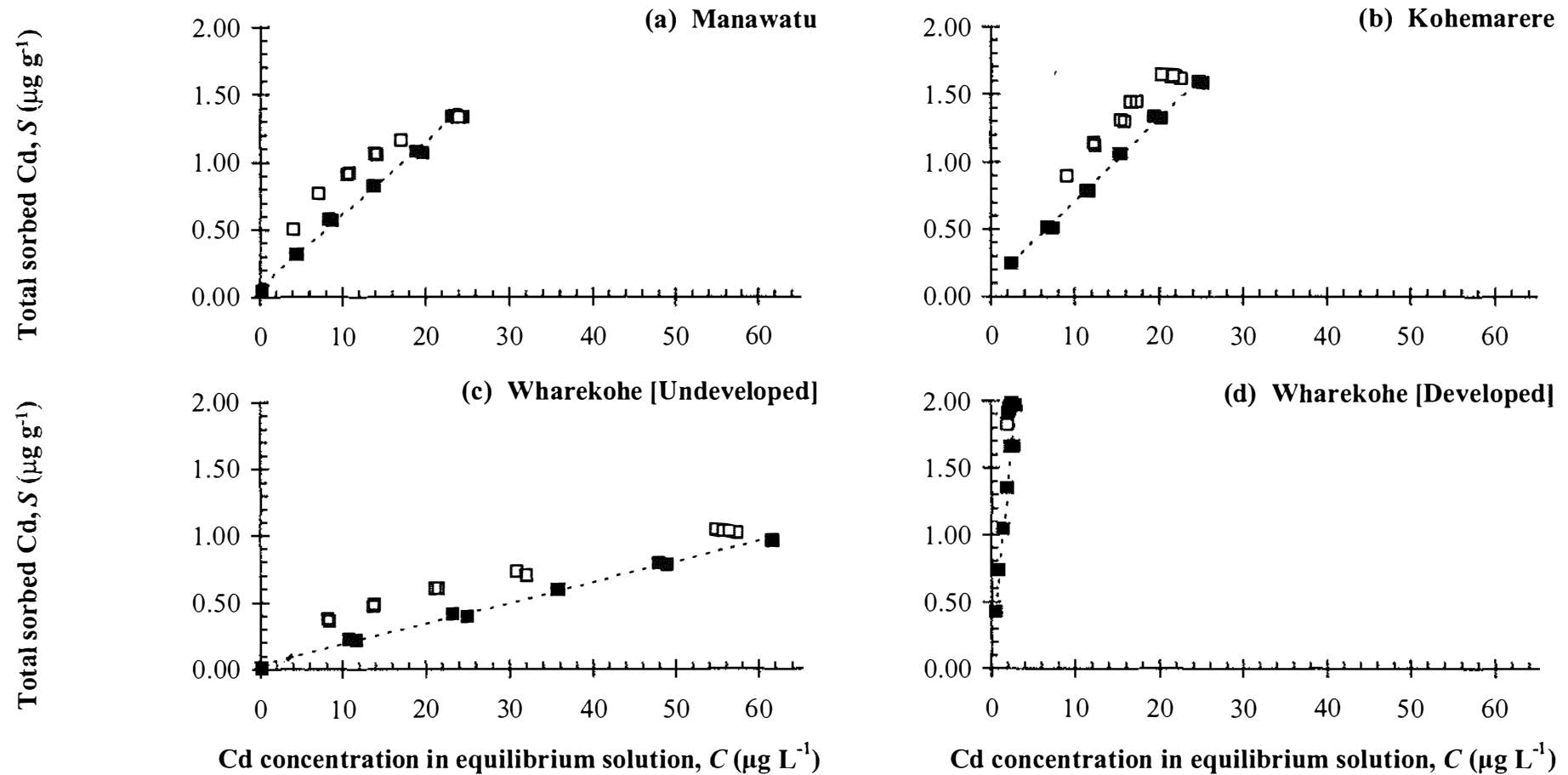
Figure 7.4. Sorption-desorption isotherms ($\square$) and the adsorption isotherms ($\blacksquare$) from Figure 7.1 determined for each soil in a background matrix of 2.5 mM $CaCl_2$ and at the soil's natural pH.

not represent the field situation quite so well (Thomas and Phillips, 1979). Rather, this section is an exploration of possible leaching scenarios and their potential impact on Cd accumulation rates.

In order to estimate the potential leaching rates of Cd from each of the four soils, the following assumptions were made:

1)   That solute flow and behaviour in the field would be similar to that seen in the experimental soil columns.

2)   All Cd present in the soil, with the exception of non-desorbable Cd determined from the adsorption isotherms, is available for exchange. This may not apply in the immediate topsoil where a proportion of the Cd will have been returned to the soil as decaying plant material and dung (i.e. in an organically complexed form) and where an accumulation of organic matter may improve the soil's ability to bind Cd.

3)   Physical properties of the field soils are similar to those existing in the repacked soil columns. Bulk densities for the Wharekohe soils in the field were not dissimilar, over the depth 0 - 3 cm, to those of the repacked soil columns – the Wharekohe [Developed] averaged 714 kg m^{-3} while the Wharekohe [Undeveloped] averaged 898 kg m^{-3} (J. Edwards, pers. comm.).

4)   The field sites have a Cd concentration of 0.44 mg kg^{-1} – the average soil Cd concentration reported by Roberts *et al.* (1994) – and experience an annual average drainage of 300 mm down through the soil profile.

5)   Soil solution ionic strengths and salt concentrations can be approximated by 2.5 mM CaCl$_2$, making the distribution coefficients determined for each soil in this matrix applicable to the field situation.

6)   Cd losses through plant uptake and assimilation by stock were estimated using pasture production and pasture utilization figures of 10 000 kg dry matter yr^{-1}

Table 7.4 Estimated Cd loss from topsoil through grazing and leaching (predicted using the CDE model and parameters discussed previously). [†]

		Estimated annual Cd losses	Cd store in soil
		(g ha^{-1})	(g ha^{-1})
Removal via grazing and animal products:		0.016	
Loss via leaching:	Kohemarere	17	132
	Manawatu	20	165
	Wharekohe [Undeveloped]	75	137
	Wharekohe [Developed]	1.4	109

[†] Estimated for an average concentration of 0.44 mg Cd kg^{-1} soil, a soil bulk density of that given in Table 7.1 for the repacked soil columns, and a soil depth of 3.5 cm – the depth of most interest regarding Cd accumulation in pastoral soils.

and 80 % respectively, a pasture concentration of 0.2 mg Cd kg^{-1} dry matter, and a Cd retention by the animal of 1% (Lee et al., 1996).

Estimates for Cd removal from the top 3.5 cm of soil using these simple calculations are presented in Table 7.4. The outstanding feature of the data contained in Table 7.4 is the magnitude of the estimated Cd leaching losses compared to annual Cd loss by plant and animal uptake. Even if these leaching rates were overestimated several fold by the model, the data suggest that leaching will still be the more important mechanism for Cd movement from the immediate surface soil.

Leaching losses of a similar magnitude have been reported in studies overseas and this lends support to the possible importance of leaching as a loss mechanism for Cd from soil. As examples, leaching rates of between 0.5 and 17 g Cd ha^{-1} per 100 mm net infiltration have been found in a range of European soils (Holm et al., 1995, as cited by Folke and Landner, 1996) and, though lower than the values given in Table 7.4, Nicholson et al. (1996) calculated losses of between 0.7 and 4.9 g Cd ha^{-1} yr^{-1} for the humus-rich permanent grassland soils of Rothamsted, England. But, whereas data presented, both in Chapter 6 of this study and in the study of Holm et al. (cited in Folke and Landner, 1996), indicate a strong dependence of leaching rate on soil pH, the work

by Nicholson *et al.* (1996) found Cd loss to be independent of this variable – similar losses were recorded for limed (pH 6.5) and unlimed (pH 4.9) plots.

The potential for Cd loss by leaching can now be viewed in the context of the broader Cd cycle on a pastoral farm. According to estimates by Bramley (1990) the Cd input to soil from fertilizer is likely to be of the order of 8.9 g Cd ha^{-1} yr^{-1}. This is within the region of the Cd losses predicted by the model for three of the soils at concentrations of around 0.44 mg Cd kg^{-1} soil. There is therefore, a possibility that Cd may reach a steady state concentration in the topsoil whereby this element is lost through leaching at a rate equal to that at which it is being applied. In view of the potential leaching rates discussed above, this steady state concentration may be quite low for some soils.

7.4   CONCLUDING DISCUSSION

A simple convection-dispersion equation using retardation coefficients obtained from linear adsorption isotherms, was tested for its ability to describe Cd movement in columns of repacked soil. It did this successfully for three of the four soils. In the case of the Manawatu soil, marked discrepancies between observed and predicted redistribution were found. Although this soil showed some degree of hysteresis between adsorption and desorption of Cd, this was insufficient to remove the discrepancies. It is considered that the anomalous experimental conditions described with respect to this soil in Chapter 6 were largely responsible for the disagreement.

In the remaining three soils, the model closely predicted the Cd concentrations in the leachate and the final position of the Cd peak in the soil column. The model was therefore used to explore the possible potential for Cd leaching from these soils in the field. A comparison of possible leaching rates with probable losses through plant and animal uptake – the other main means of Cd removal from topsoil – highlighted the potential importance of Cd loss from pastoral soils by leaching. Even on such a highly sorbing soil as the developed Wharekohe fine silt loam, leaching provides the greatest opportunity for Cd loss. Losses by plant and animal uptake are clearly several orders of magnitude lower than what may occur through leaching. A further comparison with the likely input rates of Cd from fertilizer, indicated that the rates of leaching loss may be

sufficiently high to have a significant impact on its accumulation in soil. Several of the soils studied here demonstrate the potential to reach a comparatively low steady state concentration of Cd. Though this may be beneficial to agriculture it could shift the concern to Cd concentrations in water reservoirs.

The possibility of significant leaching rates suggested in this preliminary study support the comments by Rothbaum *et al*. (1986) regarding the loss of fertilizer-applied Cd as a result of leaching. Though Cd loss by leaching has often been dismissed as insignificant (section 6.2), on some soils under certain conditions (such as low pH and low organic matter) leaching may provide the major means of regulating Cd accumulation in soils.

While not quantifying accurately the loss of Cd from field soils by leaching, the data presented here do justify further work in investigating Cd leaching from New Zealand soils. However, this should be undertaken in a way, and under conditions, that render the results more applicable to a practical assessment of the field situation.

CHAPTER 8

FATE OF CADMIUM IN A WHAREKOHE SILT LOAM CHRONOSEQUENCE

8.1 INTRODUCTION

This thesis has presented evidence for the dominant role that phosphatic fertilizer has played in elevating Cd concentrations in New Zealand farming soils. Additional work was able to show that, under certain soil conditions, Cd has the potential to be relatively mobile and could be leached through soil columns with weak electrolyte solutions. This suggested that some of the Cd entering the soil with phosphatic fertilizer additions may be lost from some soil profiles over time.

Both Cd accumulation and Cd movement are time dependent. The fate of Cd in soils over time is therefore of primary interest. But, to investigate this requires a soil chronosequence where sites have received known fertilizer applications, and hence have known Cd application rates, for varying periods of time. Such a chronosequence exists on the Wharekohe fine silt loam, a Northern podzol, at the AgResearch Grasslands research station in Kaikohe, New Zealand.

The development of pastoral land at this research station over many years has provided sites ranging in development age from zero years (undeveloped land under manuka scrub) to 32 years (under permanent pasture and regularly fertilized with superphosphate). Work investigating the accumulation of P at this site has already been done and results indicate that up to 30% of applied P, generally considered an immobile anion, can not be accounted for in mass balances (Edwards *et al.* 1994). Laboratory-based leaching experiments, on intact soil cores, and field work both showed P movement through leaching and surface and subsurface water runoff. In view of the strong relationship found between P and Cd in pastoral soils in general, it appeared that this soil could provide an ideal opportunity to study leaching losses of Cd.

The objectives of this Chapter were, therefore, to: 1) construct mass balances for sites of varying pasture development age in order to evaluate the magnitude of Cd accumulation and Cd loss from the Wharekohe silt loam, and 2) interpret and explain

166

the results from these mass balances in terms of the knowledge gathered in the preceding Chapters of this study on Cd behaviour in soils.

Acknowledgment

Samples of soil and herbage from the chronosequence, and additional data (e.g. soil pH, bulk density, fertilizer histories) were kindly provided by Dr. Jenni Edwards. I would like to take this opportunity to thank Jenni and her supervisor, Dr. Paul Gregg, for the opportunity that this co-operative research provided.

8.2   BACKGROUND

Site selection, soil and herbage sampling procedures, and methods of analysis for soil pH and total P in the soil samples are detailed in Edwards (1997), section 3.3. The following briefly covers information relevant to this case study.

The dominant soil type in the field area at Kaikohe is the Wharekohe silt loam variant. This soil is characterized by a dense, pale, eluvial horizon (denoted as the E horizon) and very low P retention in the surface horizons compared to other soils (NZ Soil Bureau, 1968b; Edwards, 1997).
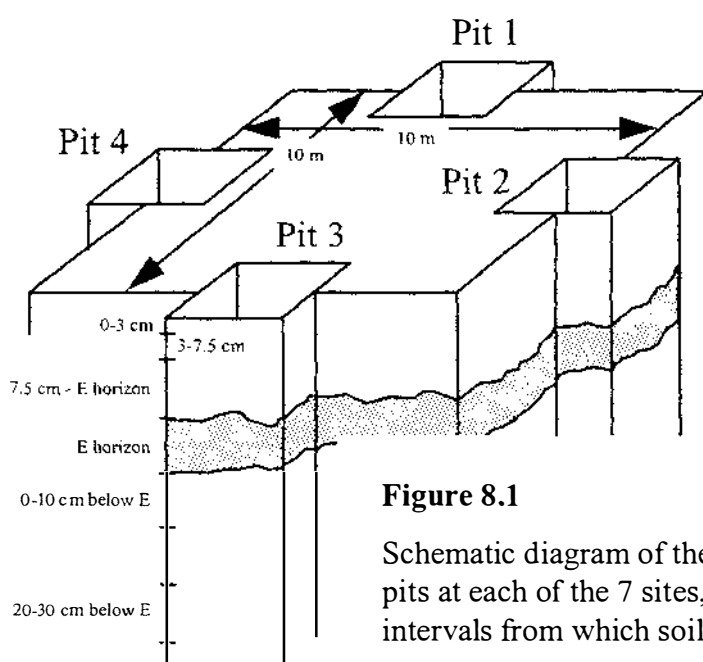
Figure 8.1

Schematic diagram of the position of the four pits at each of the 7 sites, and the depth intervals from which soil was sampled.

Soil samples were taken from sites that had been under pasture for 0, 8, 23, 25, 30 and 32 years. A 10 m by 10 m area not subject to stock-camping was located for each site. Four pits were dug on each side as shown in Figure 8.1, and soil sampled from 6 depths. The sampling intervals were: 0 - 3 cm; 3 - 7.5 cm; 7.5 - top of E horizon; E horizon; 0-10 cm below the E horizon; and 20-30 cm below the E horizon. Soil sampling took place during the spring of 1990, while pasture samples from each site were collected on 11 February, 1992, from beneath animal exclusion cages (Edwards, 1997).

Variability in the depth to the E horizon resulted in varying depths for the profiles, both between sites and between pits at the same site. Average depths to the top of the E horizon and bulk density data for each site are presented in Table 8.1. With the exception of the 0 year site, these values are averaged over the 4 pits. The 0 year data are averages over 8 pits from two separate sampling sites, undeveloped 1 and undeveloped 2.

Detailed fertilizer histories for each pasture development age were available (J. Edwards, pers. com.), these are reproduced in Appendix 6. Lime was also applied throughout the pasture development period; data for tonnage applied at the beginning of the development period and several years prior to soil sampling are presented in Table 8.2. Recorded soil pH values are shown in Table 8.2.

Table 8.1 Age, profile depth and bulk density data for soil sampling sites in the Wharekohe chronosequence. [†]

Site	Development age (years)	Depth to top of E horizon (cm)	Soil bulk density (kg m^{-3})		
			0 - 3 cm	3 - 7.5 cm	7.5 cm - E
Undeveloped	0	13.4	898	1125	1264
Pa 1	8	17.5	822	1146	1179
M Farm	23	10.1	945	1092	1245
L Block	25	13.0	714	926	1060
College 4	30	14.4	831	958	1200
Pylon 2	32	23.8	626	836	1311

[†] Average of at least 4 pits, Edwards (1997).

Table 8.2 Soil pH at the time of sampling and recorded lime applications for each site following initial pasture development and over the 10 years prior to soil sampling. [†]

Site	Development age (years)	Lime application (tonne ha^{-1})		Soil pH at time of sampling (spring 1990) [‡]		
		first 7 years	1981 - 1990	0 - 3 cm	3 - 7.5 cm	7.5 cm - E horizon
Undeveloped	0			4.0	4.0	4.1
Pa 1	8	9.1	11.1	6.0	6.0	5.4
M Farm	23	unknown	5.0	5.6	5.6	5.7
L Block	25	10.6	7.2	5.6	5.5	5.3
College 4	30	4.5	5.0	5.5	5.4	5.4
Pylon 2	32	15.3	5.0	5.6	5.5	5.2

[†] Reproduced from Edwards (1997).
[‡] Mean value determined from at least 4 pits.

8.3   MATERIALS AND METHODS

8.3.1   Chemical analyses

Soil samples were obtained in a 2 mm-sieved state. To determine total Cd and total Zn, subsamples were taken and ground using a ceramic mortar and pestle as described in section 3.3. *Total* Cd and *total* Zn were determined using the $HF:HNO_3$ digestion procedure outlined in section 3.3.2 and section 3.6.2 respectively.

Pasture samples from each site were provided ready for analysis and only required drying at $70^\circ C$ before digestion in concentrated HNO_3 to determine total Cd (section 3.4).

8.3.2   Cadmium mass balance calculations

A detailed fertilizer history was needed to estimate the amount of Cd applied to each site coincident with the application of phosphatic fertilizer (Appendix 6). Unfortunately, the Cd contents of the fertilizers used had not been regularly determined. Thus, in order to estimate the likely Cd concentrations in the single superphosphate (SSP) product, P:Cd ratios in the raw phosphate rocks used in the manufacture of the fertilizer at that time have been used (section 2.4.2). Over the period 1958 to 1990, the source of phosphate rock changed several times. In the absence of more specific information, it was assumed for this study that Northland fertilizer manufacturers used a similar mix of phosphate rock to that reportedly used at Ballantrae, Woodville (Loganathan *et al.* 1995). The proposed fertilizer mixes and their Cd content, assuming a final SSP P

Table 8.3   Proposed phosphate rock mixes used to manufacture superphosphate in New Zealand from 1958 to 1990 and the estimated Cd contents of the resulting SSP.

Years	Phosphate rock sources to make SSP	Fertilizer P/Cd SSP	Cd in fertilizer (mg kg^{-1})
1958 - 1970	50:50 Nauru/Ocean I.	1441	63
1971 - 1978	70:30 Nauru/Christmas I.	2208	41
1979 - 1986	50:50 Nauru/Christmas I.	2571	35
1986 - 1990	60:40 Nauru/N. Carolina	2174	42

content of 9.1% (J. Edwards, pers. comm.), are presented in Table 8.3. The P concentrations and P/Cd ratios used for these calculations are given in bold text in Table 2.3.

Although SSP made up the base of most P-fertilizers used on the Wharekohe sites, the application rate frequently included quantities of sulphur, potash, serpentine rock or RPR. With the exception of RPR, it was assumed that none of these additional components in the fertilizer contributed Cd. Estimates of the Cd and P additions made to each site with each fertilizer application (using the data in Table 8.3) are presented in Appendix 6 as part of the fertilizer histories and the Cd inputs for each site are summarized later in Table 8.4.

Aerial deposition and lime were also considered as potential sources of Cd. However, these could be discounted. Aerial deposition would be negligible in the lightly populated, predominantly rural inland area of Kaikohe, and additions from liming would be insignificant compared to that from SSP. Compared to phosphate rocks, the Cd content of limestone is very low (section 2.4.2). Other farm-based sources of Cd, such as anthelmintic drenches, can also be regarded as unimportant (Longhurst et al., 1994).

An estimate of Cd loss from the soil system by plant uptake and removal through animal products was determined for each site over the period of fertilizer application. In this calculation it was assumed that net Cd loss via animal transfer of dung off the site was unimportant, and that Cd contained in plant roots can be treated as a part of the soil Cd store (and is unavailable for ingestion by stock).

To approximate the increasing concentration of Cd in the herbage with increasing top-soil Cd concentrations over the development period, Cd uptakes by pasture at the sites were calculated incrementally using Cd concentrations in the herbage samples of successive development ages. Pasture production of around 10,000 kg dry matter (DM) ha^{-1} yr^{-1} was assumed over the development period for each site. This value falls within the range of dry matter yields reported for 1991 and 1992 by Edwards (1997). Cadmium stored in the pasture at time of soil sampling was estimated by assuming a standing pasture mass of 1000 kg DM ha^{-1}.

The removal of Cd from the soil-plant-animal system via animal products was estimated using an average stocking rate of 15.6 stock units (SU) (J. Edwards, pers. comm.) – where 1 SU consumes 550 kg DM ha^{-1} yr^{-1}. On this basis the figure for pasture utilization would be about 86%. Due to the poor structural nature of the Wharekohe soil (J. Edwards, pers. comm.), soil ingestion by the stock (sheep) was included at a rate of 75 kg soil animal^{-1} yr^{-1} (PEH Gregg, pers. comm.). Predominantly topsoil (0 - 3 cm) would be ingested and because Cd concentrations would be increasing each year, the amounts of Cd ingested were calculated incrementally using topsoil concentrations from each development age. Of the Cd ingested by stock, approximately 1% is retained in the animal (Lee *et al.* 1996); 99% is returned to the soil pool. A breakdown of these Cd loss estimates is given in Appendix 7.

Results from the mass balance calculations for each site are presented later in Table 8.4.

8.4   RESULTS AND DISCUSSION

8.4.1   Cadmium accumulation in the Wharekohe silt loam

The impact of fertilizer use on Cd concentrations in these Wharekohe soils is plainly evident. The difference in soil Cd concentrations between the unfertilized soil (year 0) and sites which have been subject to phosphatic fertilizer applications is far greater than the small variability in Cd concentrations between replicate pits at the same site, Figure 8.2. Thus, all soils developed under pasture are clearly showing an accumulation of Cd at the surface. Furthermore, the distribution of Cd with depth (Figure 8.2) suggests that Cd may be accumulating at depth down the soil profile as pasture development continues. Negligible amounts of Cd were found, however, within the E horizon or below. Accordingly, only the top three depths (0 - 3 cm, 3 - 7.5 cm and 7.5 cm - E horizon) are considered in the following discussion.

These results are in close agreement with those of a similar study presented in Chapter 5 that investigated the accumulation of Cd in soils under bush (unfertilized) and pasture (fertilized) on the hill-country station of Limestone Downs.
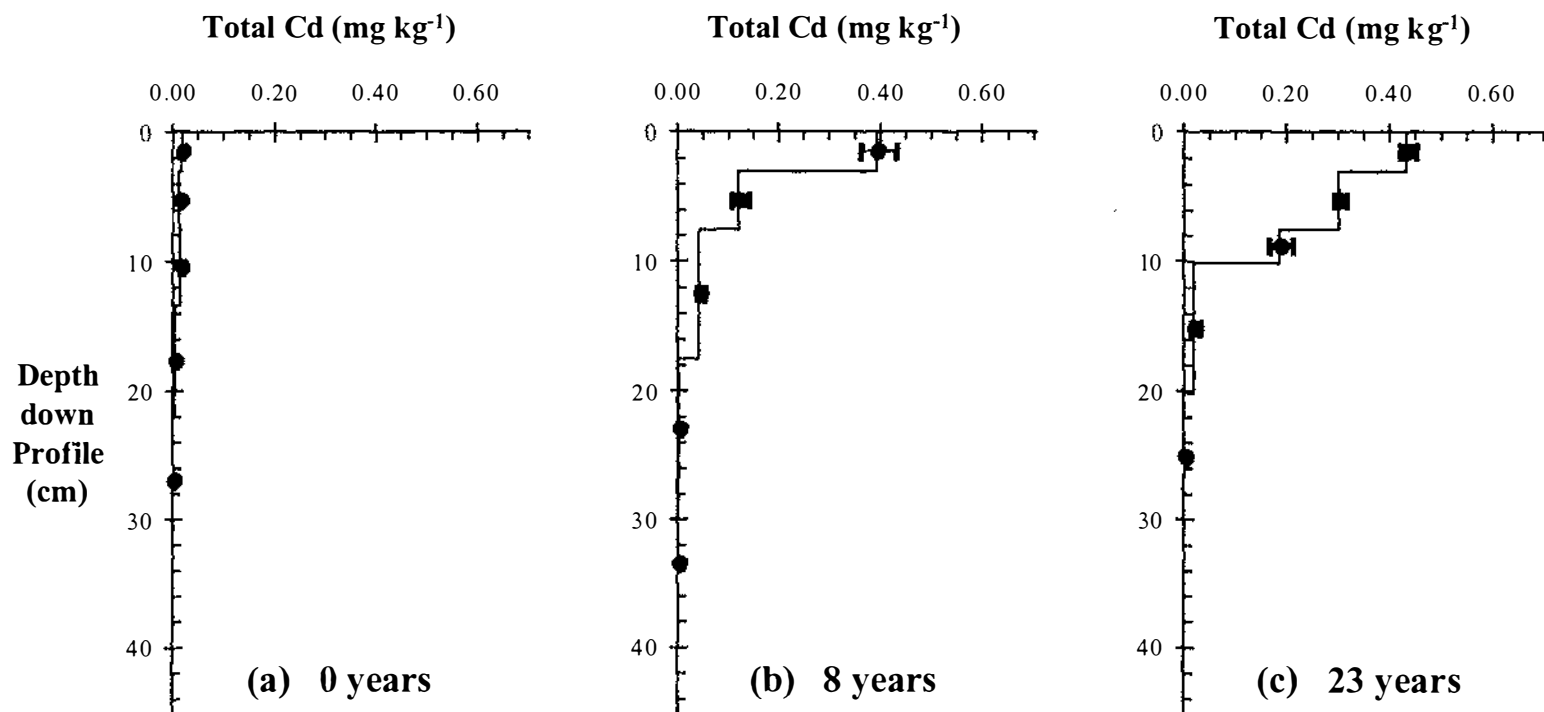
Figure 8.2 Distribution profiles of Cd in soil for each development age as determined from an average of, in most cases, four pits. Error bars denote the standard error of the mean value. Continued next page.
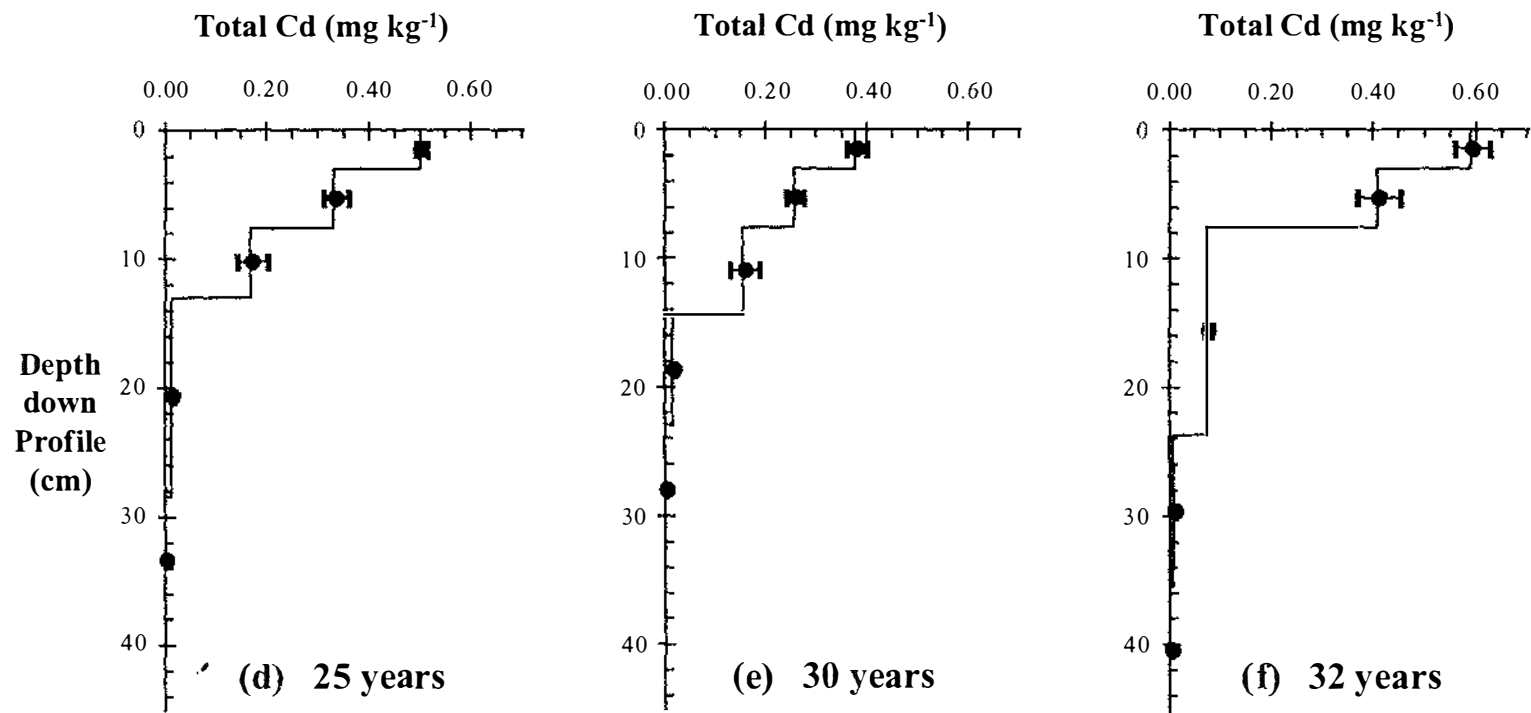
Figure 8.2　Continued from previous page. Distribution profiles of Cd in soil for each development age as determined from an average of, in most cases, four pits. Error bars denote the standard error of the mean value.

174

Inspection of the relationship between Cd and P concentrations in the soil at each site (Figure 8.3) shows that, as seen in other pastoral soils that have received fertilizer (Chapter 4 and 5), these two elements are again strongly related. The ratio of Zn/Cd concentrations in the soil also follow the common trend for phosphate fertilized soils (section 2.4.2 and Chapter 5) and are narrower at the fertilized sites (under pasture) than the unfertilized sites, Figure 8.4. Though there is perhaps one exception. The Zn/Cd ratios in the 8 years site at the 7.5 - E horizon depth are similar to those found in unfertilized soils (the 0 year sites) – the data are not shown explicitly in Figure 8.4 as depths are not differentiated. This may indicate that little fertilizer has penetrated below 7.5 cm in this recently developed soil, an observation consistent with the low Cd concentration seen in the 7.5 - E horizon interval (Figure 8.2 *(b)*).

The 8 year site further differs from the other older sites with respect to the P-Cd relationship, Figure 8.3. There is a suggestion that soil samples taken from this site have, on average, a marginally greater P:Cd ratio than that of the other sites. The trend in recent years towards lower-Cd fertilizers may account for this observation – the 8
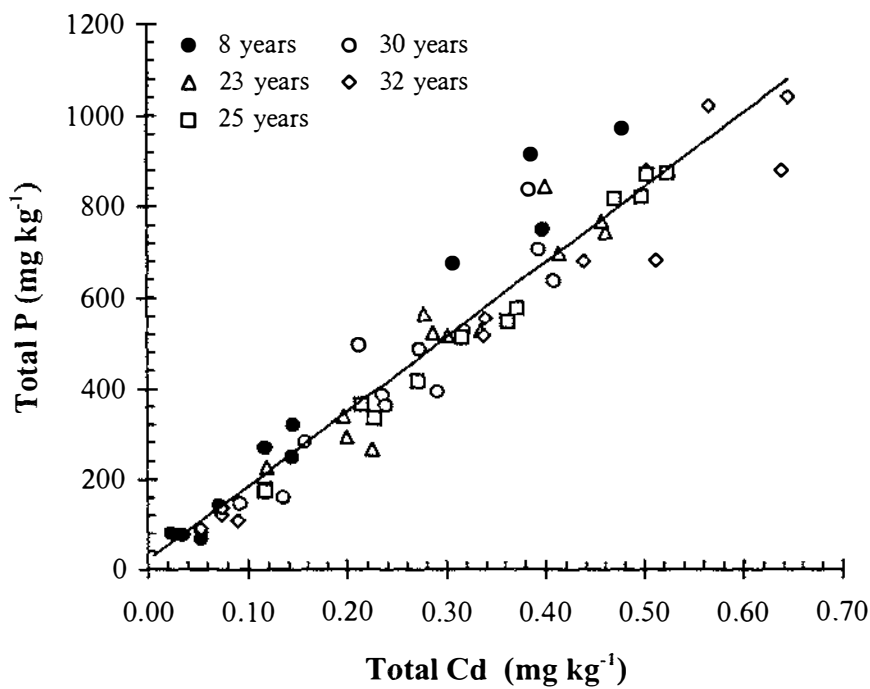
Figure 8.3   Total P and total Cd concentrations in soil samples from depths of 0 - 3 cm; 3 - 7.5 cm; and 7.5 cm - E horizon (r = 0.95, P < 0.001).
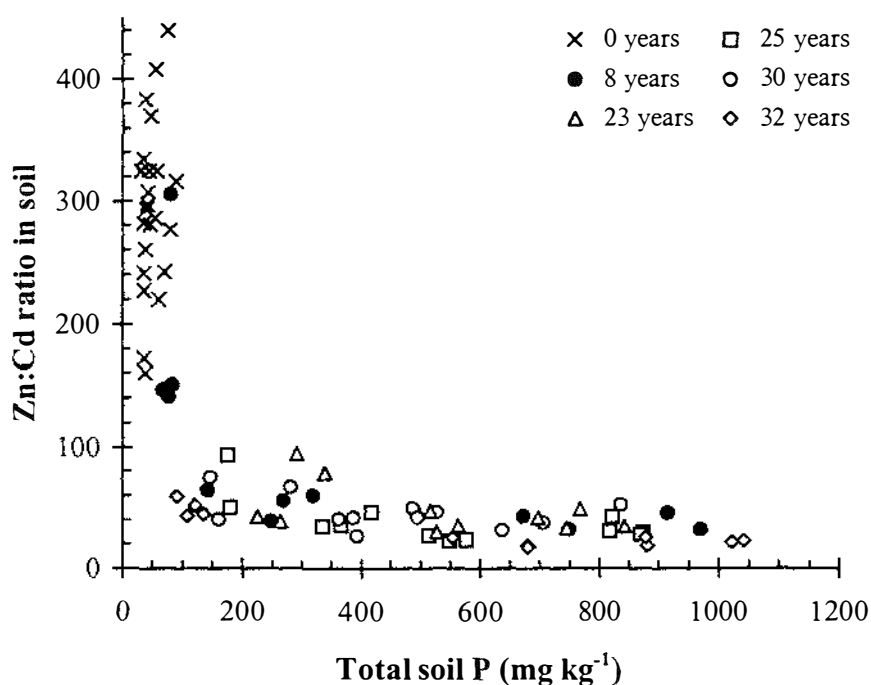
Figure 8.4   Ratios of Zn/Cd concentrations in the soil: 0 - 3 cm; 3 - 7.5 cm; and 7.5 cm - E horizon, plotted as a function of total P concentration (an indicator of phosphatic fertilizer input).

year site probably receiving most of its P with a lower input of Cd. But also there may be an effect from leaching losses. Edwards (1997) found a lower loss of P from the soil profile at this site compared to sites of a greater development age. Hence the difference in the P-Cd relation might be attributed to differences in the relative losses of P and Cd. The Cd mass balances constructed for each site are presented and discussed below.

8.4.2   Cadmium mass balance

Although the number of years of development ranged from 8 to 32 years, the total amounts of P and Cd added in fertilizer did not vary in direct proportion to the years of development. Thus, Cd accumulation in the soil does not increase linearly with increasing development age (Table 8.4). Results from the mass balance (Figure 8.5) further reveal that, with the exception of the youngest site (year 8), significant amounts of Cd thought to have been applied cannot be accounted for in the soil profile above the E horizon (Table 8.4). In the year 8 site, slightly more Cd was recovered from the soil profile above the E horizon than was estimated to have been added. Inaccuracies in input estimates, determination of soil Cd concentrations and natural variation in the field
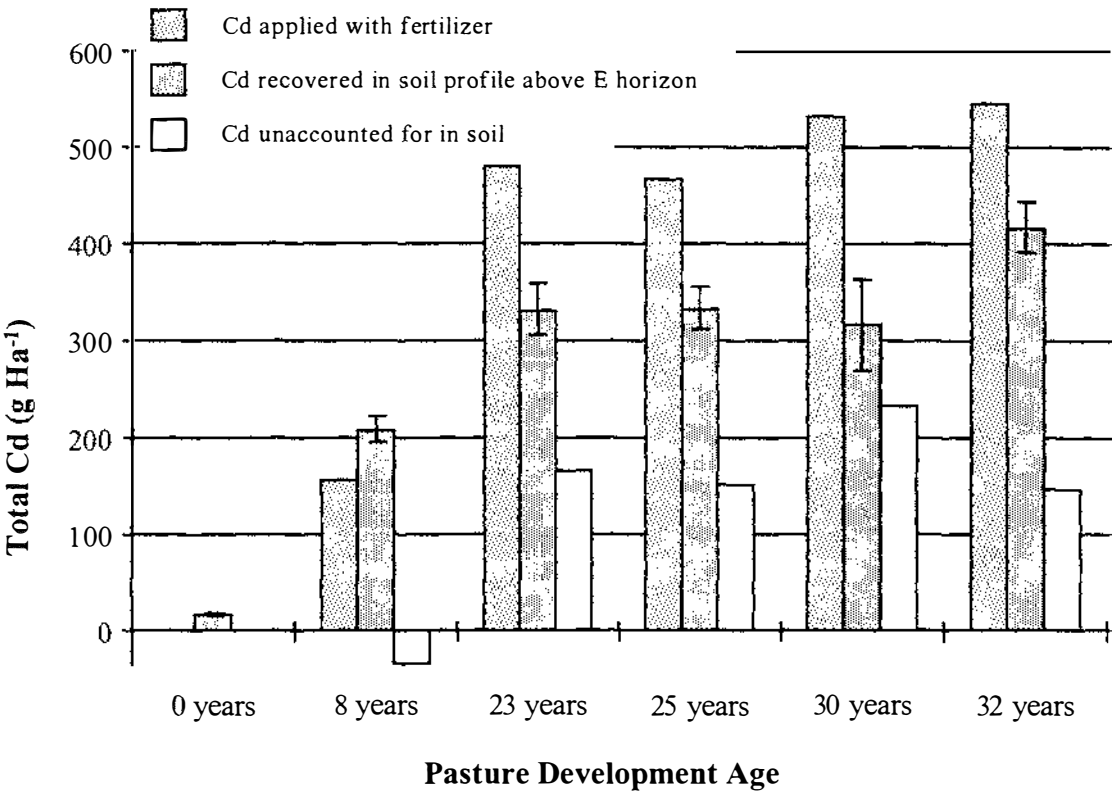
Figure 8.5   Diagrammatic representation of the Cd mass balance calculated for each site. Bars represent: total amount of Cd estimated to have been applied to each site with fertilizer; total amount of Cd accumulated in the soil above the E horizon at each site – error bars denote the standard error of the mean value for at least four pits; and the amount of Cd unaccounted for at each site. See also Table 8.4.

may be responsible, but, the total retention of applied Cd within the soil profile implied by the mass balance agrees well with indications of limited Cd movement into the 7.5 cm - E horizon depth.

Correction for losses through plant uptake and removal of animal product do not reconcile the mass balance figures. Instead it is apparent that, compared to the Cd inputs from fertilizer, losses through plant and animal are negligible (Table 8.4). This leaves between 27 and 44% of the Cd unaccounted for. Losses of a similar order of magnitude were also found at each site for P, but were generally lower in the older sites, ranging from 16 to 27%, with the 8 year site showing a 4% loss (Edwards, 1997). Thus, the close relationship between Cd and P anticipated when starting this study has been verified.

Table 8.4   Cadmium mass balance for each site showing the amount of Cd accumulated in the soil at time of sampling, likely additions from phosphatic fertilizer and estimated losses through leaching.

		0 years	8 years [†]	23 years	25 years	30 years	32 years
				Pasture development age			
Cd accumulated in soil (g ha^{-1}):		17	207	332	333	316	415
Estimated inputs (g ha^{-1}):	*Fertilizer*	●	156	480	464	532	546
Cd unaccounted for above E horizon (g ha^{-1}):		-	-34	165	147	232	147
Estimated losses (g ha^{-1}):	*Product removal*	-	0.08	0.30	0.34	0.46	0.60
	Standing herbage	-	0.07	0.11	0.17	0.22	0.39
Proportion of Cd estimated to have been applied with fertilizer which is unaccounted for (%):		-	0	34	32	44	27
Assuming Cd which is unaccounted for has been leached from soil profile:							
Estimated leaching rate of Cd (g Cd ha^{-1} yr^{-1}):			0	7.2	5.9	7.7	4.6

[†]   More Cd was recovered from the soil at this site than was estimated to have been added with the fertilizer, see discussion.

8.4.3 Cadmium loss through leaching

Assuming losses by erosion and lateral soil movement to be unimportant at these sites (land slopes ranged from 4 to 14° – Edwards, 1997), leaching provides the most probable explanation for the unaccounted Cd. To reconcile the mass balance figures, an annual leaching loss of between 4.6 g Cd ha^{-1} yr^{-1} (for the 32 year site) and 7.7 g Cd ha^{-1} yr^{-1} (for the 30 year site) would be required on the older sites (Table 8.4). These rates are not unreasonable given the range reported recently in literature (Holm *et al.*, 1995, as cited in Folke and Landner, 1996), however, they are several times greater than the 1.4 g Cd ha^{-1} yr^{-1} predicted in Chapter 7 using soil from the 25 year site (Table 7.4, Developed).

Edwards (1997) attributed the loss of P from the Wharekohe silt loam to a low P sorption capacity in the soil. For this reason she proposed that P loss from the soil would be low during the years following initial pasture development, and would become higher in later years. Despite the apparently close relationship between P and Cd, Cd loss from this Wharekohe soil is unlikely to follow a similar pattern. During the laboratory leaching studies of Chapter 6 it was found that Cd movement in the Wharekohe silt loam was greatest when the soil was undeveloped and reduced substantially in soil that had been developed for 25 years. Furthermore, adsorption isotherms (Chapter 7) for this developed soil showed a very high sorptive capacity for Cd up to at least 2 mg Cd kg^{-1} soil – a concentration which does not appear to have been exceeded at the sites sampled for this study.

Cadmium leaching losses are more likely than P leaching losses to be affected by changes in soil properties (such as pH, organic matter, and CEC) which occur with pasture development. In the undeveloped state these Wharekohe soils are very acidic (Table 8.2, year 0), and exhibit high Cd mobility (section 6.5.5). Therefore, the highly soluble Cd present in SSP fertilizer (Loganathan and Hedley, 1997) applied at the beginning of pasture development was probably susceptible to leaching. Following regular additions of lime and further SSP, however, both soil pH and organic matter would increase, resulting in decreased Cd mobility (section 6.2) and consequently reduced leaching rates. Thus, losses of Cd from the soil profile may have been high in

the initial years following pasture development and declined in later years. This is the reverse of that proposed by Edwards (1997) for P.

Just as the use of fertilizers containing reactive phosphate rock (RPR) probably reduced P losses on the Wharekohe silt loam (Edwards, 1997), so too would their use reduce the loss of Cd. Cadmium in the RPR fraction has extremely low solubility (Loganathan and Hedley, 1997) and would therefore be less available for leaching than Cd present in SSP. The low loss of Cd calculated for the year 8 site is most likely a consequence of this fact. Almost half of its Cd was applied in the form of 'Longlife-super', a fertilizer with a high RPR component. On the older sites, by comparison, most of the Cd was applied in a much more soluble form as SSP.

8.5   CONCLUDING DISCUSSION

The development chronosequence studied here shows clearly that the application of phosphatic fertilizer has had a huge impact on Cd concentrations in pastoral soils. However, a mass balance accounting for Cd inputs from fertilizer and losses by plant uptake and removal in animal products showed that up to 44% of Cd applied to the surface has been lost from the soil profile above the E horizon. Though these losses are consistent with the those of fertilizer-derived phosphorus, the stages when most rapid loss occurred and the reason for this loss may be quite different.

Cadmium loss from the soil profiles is most likely to have occurred during the early stages of pasture development when the soil was still relatively acidic and large quantities of the highly soluble SSP fertilizer had just been applied. The low soil pH and high solubility of the SSP-derived Cd could be expected to favour Cd mobility. This suggests that variability in Cd loss between sites can probably be attributed to differences in liming rates during the initial stages of pasture development, and differences in the proportion of Cd applied during this stage. The greatest loss, for example, was found to have occurred on the 30 year site (College 4) which coincidently had the lowest lime application rate during the first 7 years (Table 8.2). In contrast, Edwards (1997) proposed that most losses of P took place later in pasture development when the soil's sorptive capacity for P was exceeded. Nonetheless, removal of the

soluble P and Cd from the surface soil probably occurred in the same manner – through lateral movement of soil water above the impermeable E horizon.

With all the Wharekohe sites now showing high soil pH and soil organic matter – both of which influence Cd mobility – future additions of Cd can probably be expected to accumulate in the topsoil with little movement to depth. The estimated leaching rates for these sites over their development period (between 0 and 7.7 g ha^{-1} yr^{-1}) are therefore likely to over predict future Cd losses. This will be further exacerbated by the use of fertilizers containing RPR, since Cd present in such material is relatively insoluble and would be more resistant to leaching.

CHAPTER 9
SUMMARY AND SUGGESTIONS FOR FUTURE RESEARCH

9.1   INTRODUCTION

Cadmium is recognised as a threat to the health of the human population through the consumption of agricultural products. Much work has demonstrated that addition of Cd, and its subsequent accumulation in soil, is an almost irreversible process. Consequently, the exposure of soil to phosphatic fertilizer, sewage sludge and atmospheric pollution has lead to increasing Cd concentrations in topsoils world-wide. Policies are therefore being instituted globally to control both Cd additions to soils and the exposure of the human population to Cd from foodstuffs. Included in these is a push to restrict the application of soil amendments containing Cd, and a reduction of the Cd concentrations of these amendments where possible. Further control policies are focusing on limiting the exposure of the human population to Cd through the exclusion of products from sale where these products exceed a threshold Cd concentration. Both of these measures are currently affecting New Zealand agriculture.

Phosphatic fertilizer has been used extensively for many decades in New Zealand agriculture. It has played an important part in sustaining the productivity of much of our pastoral land. With the knowledge that phosphatic fertilizers can contain significant concentrations of Cd, this history of widespread use is now causing concern as to the extent of Cd accumulation that has taken place unknowingly in New Zealand soils. Currently, New Zealand soils exhibit Cd concentrations on a par with that shown by most countries active in the Cd debate. And, in line with the international trend, we have instituted control measures to protect the consumer from excessive exposure to Cd. The export of animal offal, for example, has been limited to product containing less than 1 ppm Cd fresh weight. Meanwhile, New Zealand fertilizer companies are coming under increasing pressure to provide low-Cd fertilizers.

There is an economic cost to these measures; particularly the production of low Cd fertilizer. As a result, there has been some understandable reluctance on the part of fertilizer companies to make major changes until all potential inputs of Cd to New Zealand soils have been investigated. Biocycling (not studied in the current work) could

cause accumulation of Cd in topsoils through root uptake of Cd from depth down the soil profile, and its deposition on to the surface as leaf litter. The impact of this process on surface Cd concentrations depends largely on the concentration of Cd in the subsoil and parent material. With a lack of published data on the Cd contents of New Zealand parent rock, the importance of parent material as a contributor of Cd to New Zealand soils has been open to some debate.

Should it be proven that phosphatic fertilizer is the major source of Cd, then the acceptable Cd concentration in this product will need to reviewed. The permissible level will depend on the current status of Cd in New Zealand soils, the likely rates of Cd accumulation and the maximum concentration at which damage to the environment or human health is perceived to begin.

Several studies have reported on the range and average concentration of Cd in New Zealand soils. However, these data do not convey the high variability of Cd concentrations in soil, even within the limited area of a paddock. The Cd concentration of a soil sample is highly dependent on factors such as the physical and chemical properties of the soil, the soil parent material, the local topography and variations in Cd inputs from non-lithogenic sources, e.g. animal transfer and fertilizer. A poor understanding of this variation reduces our ability to effectively manage the Cd accumulation in stock that is raised on Cd contaminated land.

Currently we are searching for a balance between the economic costs of protecting the environment and the health of the human population and the advantages gained by permitting the application of Cd-containing material to the soil. This requires a thorough understanding of the sources of Cd, its behaviour and redistribution within the soil-plant-animal system and its potential for entry into the human food chain.

9.2 AIMS OF THE STUDY

This work centred on the study farm, Limestone Downs. The diversity of soil types and soil parent materials on this farm permitted a study of potential Cd sources to pastoral

soils, and enabled the development of a better understanding of the spatial distribution and variability of Cd in the landscape.

While investigating the Cd distribution and origin in the above soils, significant quantities of Cd were found at depth in the soil profile. Having concluded that this Cd was predominantly fertilizer-derived, and had therefore resided in the surface soil at some point, there appeared to be strong evidence for Cd redistribution in soil. Though leaching of Cd from soil is generally considered to be negligible; in some soils, under some conditions, significant leaching has been reported. There is a paucity of data on Cd leaching in New Zealand soils and this was considered an important gap in our understanding of Cd. The ability of Cd to migrate through soil was therefore investigated with the aid of laboratory-based leaching experiments and modelling.

9.3   CADMIUM DISTRIBUTION AND ORIGIN IN PASTORAL SOILS

A large variation in Cd concentration was found for the topsoils of a regularly fertilized hill-country farm. The range was 0.07 to 0.91 mg Cd kg^{-1} with an arithmetic mean of 0.36 mg Cd kg^{-1}. These values were typical of those reported elsewhere for New Zealand agricultural soils.

The Cd contribution from parent material was studied for pedologically described and sampled soil profiles. In most cases, digestion with HF acid (to break down all minerals including acid-resistant silicates) failed to recover any Cd from depth in the B and C horizons or from parent rock. This indicated that parent material was, in general, unlikely to be responsible for the high Cd content of most topsoils.

Four exceptions to the above observation were found. In two cases, Cd in the parent material (between 0.1 and 0.16 mg Cd kg^{-1}) could be related back to the presence of calcareous deposits in the rock. In another instance, Cd in the parent material (0.13 mg Cd kg^{-1}) was concluded to be predominantly from iron sand deposits. These ironsands represented a potential source of Cd not only to topsoils developed *in situ*, but also to topsoils some distance away through aeolian deposits derived from local ironsand dunes. However, the Cd from this source was soluble only in HF acid. It would

therefore be of very low plant availability, and consequently of no threat to plants and animals. In the fourth parent material, an excessively large concentration of Cd (0.76 mg Cd kg^{-1}) was found. The origin of this Cd was unknown, but could possibly be from marine detritus.

Overall, grouping topsoils according to their parent material was unable to explain their variability in Cd concentrations. The only soil characteristics that were found to correlate significantly with Cd concentrations in topsoils across the whole farm were the P status (r = 0.84) and the total carbon content (r = 0.79) of the soil.

Cadmium spatial variability was investigated for its relationship to changes in topography and the resultant effect of animal transfer. In this localized study, P and Cd were also correlated, but the strength of this correlation was strongly dependent on topography. Soils from the steep slope showed a very strong, linear correlation between P and Cd (r = 0.86). This was interpreted as indicating that variation in the spread of fertilizer granules had caused the variation in soil Cd concentrations. In contrast, the Cd-P correlation on the low slope was much weaker (r = 0.46).

A small increase in Cd concentration was seen for soils on the low slope over that on the steep slope. However, the increase was only 1.1 times, and much less than the two-fold increase reported by another, similar study. The effect of slope on P concentrations was more marked – a 1.4 times increase on low slopes. These observations lead to the conclusion that, while animal transfer would always act to increase Cd concentrations on low slopes, the impact of this process would be highly dependent on the plant availability of Cd in the surrounding soil. The apparently greater impact of animal transfer on P than on Cd also suggested that this process could be responsible for the weakening correlation between Cd and P and the low slopes. Furthermore, some of the variability in Cd concentration between sample points on these low slopes could perhaps also be attributed to spatially-variable dung deposition.

The consistently strong correlation between Cd and P in topsoils on this regularly fertilized farm pointed clearly to P fertilizer history as a means of explaining both the magnitude of, and variability in Cd concentrations. This was confirmed by a study

comparing fertilized and unfertilized sites on the same farm. A mass balance for Cd and P showed that the Cd accumulated in the soil profile could reasonably be accounted for by inputs from phosphatic fertilizer over many decades. Other sources of Cd, such as atmospheric and sea spray were concluded to be negligible.

9.4 CADMIUM MOBILITY IN SOILS

Artificial columns of repacked soil were created with a layer of Cd-amended soil overlying unamended soil. This closely represented the field situation where soil high in Cd is frequently found at the surface. With the pre-adsorbed Cd and Cd-free leaching solutions, this arrangement also allowed the study of Cd movement as a pulse under typical field conditions.

Pertinent aspects of Cd behaviour in soil were reviewed and this revealed, in addition to the effect of pH, a significant impact of Cl^- concentrations on the mobility of Cd. The finding that Cl^- was the dominant anion in soil solution samples taken from the coastal study farm (Limestone Downs) lent importance to the effect of this anion on Cd behaviour in New Zealand soils.

Using columns of Manawatu soil, Cl^- was studied for its effect on Cd mobility. Only limited redistribution of Cd occurred when this soil was leached with 2.5 mM $CaCl_2$. A comparison with several other leaching solutions containing different anions and cations [$Ca(NO_3)_2$, $CaSO_4$ and KCl] indicated that, at the concentration used (2.5 mM $CaCl_2$), the primary cause of Cd redistribution was competition between Cd^{2+} and Ca^{2+} for cation exchange sites rather than Cl^- complexation. A concurrent study demonstrated, however, that almost complete removal of Cd from the soil columns could be achieved with 50 mM $CaCl_2$. This lead to an investigation of changing Cd mobility with increasing $CaCl_2$ concentration.

Increasing the concentration of $CaCl_2$ clearly increased the mobility of Cd, both native and added. This increase (measured as loss of Cd from the Cd-amended layer) was seen to be linearly related to the concentration of $CaCl_2$ up to about 20 mM. Above 35 mM $CaCl_2$ the extent of Cd movement increased only slightly, a result of much of the added

Cd (88%) having been already removed from the top layer of soil. At these $CaCl_2$ concentrations, significant complexation of Cd by Cl^- is reported frequently. Nonetheless, competition for cation exchange sites by Ca^{2+} will also be important. Thus it was concluded that cation competition and anion-complexation had operated together throughout the $CaCl_2$ concentration range to cause Cd redistribution.

Although the effect of $CaCl_2$ concentration on Cd movement was clear, anomalous behaviour in several of the columns lead to a discussion of factors that can enhance Cd adsorption in soil. The Manawatu soil demonstrated how physical changes in the soil can modify Cd mobility, and hence emphasized the sensitivity of this cation to its environment. Iron oxide precipitation in the soil column during leaching indicated waterlogging had occurred. Through its effect on the soil chemistry, this waterlogging was believed to be responsible for the observed immobility and accumulation of Cd at specific points in some columns – despite the high concentrations of $CaCl_2$. This was not seen in any other soil studied. These observations may have implications for the field where iron oxide precipitates are commonly found – around root channels, for example.

Three additional soils, with differing physical and chemical properties, were studied concurrently with the Manawatu soil. These soils were also leached with 2.5 mM $CaCl_2$, an electrolyte solution which reasonably approximates field soil solution concentrations. Under the approximated field conditions of these leaching columns, a broad range of Cd movement was seen. Movement varied from very limited to extensive. Interestingly, these extremes of Cd mobility were shown by two soils almost identical in mineralogy but markedly different in soil pH and carbon content. This difference had come about through the application of lime and superphosphate to one of the soils (Wharekohe [Developed]) during 25 years of pasture development and maintenance. This developed soil showed the smallest degree of Cd movement and therefore highlighted the effect of a high pH (6.0) and high carbon content (7.5%) on Cd mobility.

Using the convection-dispersion equation and adsorption isotherms, the Cd redistribution found in the above four soils (leached with 2.5 mM $CaCl_2$) was, in general, modelled satisfactorily. When this basic model was used to predict Cd loss

from pastoral soils, it was concluded that the process of leaching is likely to be significantly more important than losses through the removal of animal products. In some situations, the loss of Cd may even equal inputs from phosphatic fertilizer, thus mediating the threat of Cd accumulation. Such information is important if Cd levels in fertilizer are to be based on prospective Cd accumulation rates.

The above observations were instrumental in understanding and explaining the Cd distribution profiles at a second study site. The Wharekohe chronosequence investigated in Chapter 8 presented a unique opportunity to study the Cd balance in a pastoral soil. While the soils in this sequence showed marked Cd accumulation – attributable to phosphatic fertilizer application – data on their fertilizer history suggest that considerable loss of Cd from the soil profile (up to 44%) had also occurred. Changes in the soil properties with pasture development, and the effect of these changes on Cd mobility (demonstrated by the leaching experiments described above), indicated that most of this Cd loss probably occurred at the beginning of pasture development. During this period, soil pH would have been low and would have enabled rapid leaching of Cd contained in the highly soluble fertilizer, SSP.

9.5 CONCLUDING COMMENTS AND AREAS FOR FUTURE RESEARCH

Observations on the Cd content of pastoral soils on Limestone Downs indicate a general accumulation of Cd in topsoils across the property. The primary origin of this Cd would appear to be external, and most likely phosphatic fertilizer. Levels of Cd in subsoils and parent material are generally too low to account for this accumulation through biocycling. Fertilizer was confirmed as the predominant source by a comparison of fertilized and unfertilized soils.

Cadmium variability between soil samples was marked, even over small sampling distances. This variability could not be explained by variations in Cd concentration associated with parent material or soil group. The best explanation came from fertilizer application and, to a lesser extent, the grazing patterns of stock. Cadmium is transferred to stock camps in much the same way as P. However, in contrast to P, the extent of this animal transfer will vary markedly according to the properties of the surrounding soil –

for example, pH which has a major influence on herbage Cd concentrations and hence animal uptake.

Cadmium distributions down the soil profiles, mass balance calculations and laboratory leaching studies all indicated the potential for Cd loss from topsoil. Under some soil conditions model predictions suggest that the loss of Cd by leaching is likely to be much more important than loss of Cd from the farm system in animal products. Current information on leaching and movement of Cd under field conditions is sparse. There is, therefore, an urgent need for further research in this area.

If leaching is indeed the major loss mechanism for Cd from topsoils, then quantification of this process is critical to the development of models for the accumulation of Cd in soils. Such models are essential for the fertilizer industry and regulatory authorities to determine appropriate Cd loadings in fertilizer.

Further, with the regulation of Cd plant-availability by soil properties (e.g. pH and organic carbon content), and with changes in these properties over depth, even limited movement of Cd in the topsoil may significantly affect its plant availability. Understanding this process will be important if the management of Cd availability by surface application of lime is to be recommended.

Another area for further study is the aspect of Cd transfer to campsites by stock. This transfer results in high Cd concentrations on campsites, but the associated deposition of dung and urine also results in changes in many soil properties, for example, pH and organic carbon content. The implications of this to Cd availability and leaching are essentially unknown.

A final area of future study relates to the impact of increasing soil acidity – as a consequence of farming practices or changes in land use – on Cd availability and movement. Laboratory studies, described earlier in this work, clearly demonstrated the importance of soil pH to Cd movement. Ongoing acidification may therefore assist in removing accumulated Cd from topsoils, but the impact of the leached Cd on the wider environment would need careful consideration.

REFERENCES

Adeloju, S.B. and Bond, A.M. (1985). Influence of laboratory environment on the precision and accuracy of trace element analysis. *Analytical Chemistry* **57**: 1728 - 1733.

Adriano, D. C. (1986). Trace Elements in the Terrestrial Environment. Springer-Verlag, New York, 533 pp.

Adriano, D. C. [Ed] (1992). Biogeochemistry of Trace Metals. Lewis Publishers, Boca Raton, 513 pp.

Ainsworth, C. C., Pilon, J. L., Gassman, P. L., and Van Der Sluys, W. G. (1994). Cobalt, cadmium, and lead sorption to hydrous iron oxide: Residence time effect. *Soil Science Society of America Journal* **58**: 1615 - 1623.

Alesii, B. A., Fuller, W. H. and Boyle, M. V. (1980). Effect of leachate flow rate on metal migration through soil. *Journal of Environmental Quality* **9**: 119 - 126.

Alloway, B. J. (1995a). Cadmium. In: Heavy Metals in Soils [Ed. B. J. Alloway], 2nd ed., Blackie Academic and Professional, Glasgow, pp 122 - 151.

Alloway, B. J. [Ed] (1995b). Heavy Metals in Soils, 2nd ed., Blackie Academic and Professional, Glasgow, 368 pp.

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

Andersson, A. (1976). On the influence of manure and fertilizers on the distribution and amounts of plant-available Cd in soils. *Swedish Journal of Agricultural Research* **6**: 27 - 36.

Andersson, A. (1977). Heavy metals in Swedish soils: on their retention, distribution and amounts. *Swedish Journal of Agricultural Research* **7**: 7 - 20.

Andrewes, P., Town, R. M., Hedley, M. J. and Loganathan, P. (1996). Measurement of plant-available cadmium in New Zealand soils. *Australian Journal of Soil Research* **34**: 441 - 452.

Athanasopoulos, N. (year unknown). Flame Methods Manual for Atomic Absorption by GBC Scientific Equipment Pty Ltd.

Atteia, O., Dubois, J.-P. and Webster, R. (1994). Geostatistical analysis of soil contamination in the Swiss Jura. *Environmental Pollution* **86**: 315 - 327.

Baham, J., Ball, N.B. and Sposito, G. (1978). Gel filtration studies of trace metal-fulvic acid solutions extracted from sewage sludges. *Journal of Environmental Quality* **7**: 181 - 188.

Bajracharya, K., Tran, Y. T. and Barry, D. A. (1996). Cadmium adsorption at different pore water velocities. *Geoderma* **73**: 197 - 216.

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

Barrow, N.J. (1986). Testing a mechanistic model. II. The effects of time and temperature on the reaction of zinc with a soil. *Journal of Soil Science* **37**: 277 - 286.

Barrow, N.J. (1992). A brief discussion on the effect of temperature on the reaction of inorganic ions with soil. *Journal of Soil Science* **43**: 37 - 45.

Barrow, N. J. (1993). Mechanisms of reaction of zinc with soil and soil components. In: Zinc in Soils and Plants, Proceedings of the International Symposium on 'Zinc in Soils and Plants', University of Western Australia, 27 - 28 September 1993 [Ed. A. D. Robson], Kluwer Academic Publishers, Dordrecht/Boston/London. pp15 - 31.

Barrow, N. J. and Ellis, A. S. (1986). Testing a mechanistic model. V. The points of zero salt effect for phosphate retention, for zinc retention and for acid/alkali titration of a soil. *Journal of Soil Science* **37**: 303 - 310.

Baucells, M., Lacort, G. and Roura, M. (1985). Determination of cadmium and molybdenum in soil extracts by graphite furnace atomic-absorption and inductively coupled plasma spectrometry. *Analyst* **110**: 1423 - 1429.

Benjamin, M. M. and Leckie, J. O. (1981). Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. *Journal of Colloid and Interface Science* **79**: 209 - 221.

Benjamin, M.M. and Leckie, J.O. (1982). Effects of complexation by Cl, SO_4, and S_2O_3 on adsorption behaviour of Cd on oxide surfaces. *Environmental Science and Technology* **16**: 162 - 170.

Berggren, D. (1992). Speciation and mobilization of aluminium and cadmium in podzols and cambisols of S. Sweden. *Water, Air, and Soil Pollution* **62**: 125 - 156.

Bergkvist, B. (1987). Leaching of metals from forest soils as influenced by tree species and management. *Forest, Ecology and Management* **22**: 29 - 56.

Bergkvist, B., Folkeson, L. and Berggren, D. (1989). Fluxes of Cu, Zn, Pb, Cd, Cr, and Ni in temperate forest ecosystems. *Water, Air and Soil Pollution* **47**: 217 - 286.

Bernard, A. and Lauwerys, R. (1986). Cadmium in human population. In: Cadmium in the Environment (Experientia. Supplementum; vol. 50) [Eds. H. Mislin and O. Ravera], Birkhäuser Verlag, Basel, pp 114 - 123.

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

Bingham, F. T., Strong, J. E. and G. Sposito, G. (1983). Influence of chloride salinity on cadmium uptake by swiss chard. *Journal of Environmental Quality* **13**: 71 - 74.

Black, A. L. (1988). Toxic effects of cadmium in animals and man. In: Cadmium accumulation in Australian agriculture: National Symposium 1 - 2 March, 1988 [Ed. J. Simpson and W. Curnow]. Department of Primary Industries and Energy, Bureau of Rural Resources, Canberra, pp 161 - 166.

Blakemore, L. C., Searle, P. L. and Daly, B. K. (1987). Methods for chemical analysis of soils. *NZ Soil Bureau Scientific Report 80*, 103 pp.

Blaser, P. and Zimmermann, S. (1993). Analytical problems in the determination of inorganic soil contamination. In: Soil Monitoring; Early Detection and Surveying of Soil Contamination and Degradation [Eds. R. Schulin, A. Desaules, R. Webster, and B. von Steiger]. Birkhäuser Verlag, Basel, pp 201 - 217.

Bøckman, O. C., Kaarstad, O., Lie, O. H. and Richards, I. (1990). Agriculture and Fertilizers, Fertilizers in perspective. Agricultural Group, Norsk Hydro a.s, Oslo, Norway, 245 pp.

Boekhold, A. E. and Zee, S. E. A. T. M. van der (1992a). Significance of soil chemical heterogeneity for spatial behavior of cadmium in fields. *Soil Science Society of America Journal* **56**: 747 - 754.

Boekhold, A. E. and Zee, S. E. A. T. M. van der (1992b). A scaled sorption model validated at the column scale to predict cadmium contents in a spatially variable field soil. *Soil Science* **154**: 105 - 112.

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

Boekhold, A. E., Zee, S. E. A. T. M. van der, and Haan, F. A. M. de (1991). Spatial patterns of cadmium contents related to soil heterogeneity. *Water, Air and Soil Pollution* **57 - 58**: 479 - 488.

Bolan, N. and Hedley, M. J. (1987). Selected methods of analysis course: Analytical techniques. Fertiliser and Lime Research Centre, Massey University, Palmerston North.

Bolan, N. S., Hedley, M. J. and Loganathan, P. (1993). Preparation, forms and properties of controlled release phosphate fertilizers. *Fertilizer Research* 35, 13 - 24.

Bond, W. J. and Smiles, D. E. (1988). Predicting the average movement of reactive solutes in soil. *Soil Use and Management* 4: 115 - 120.

192

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

Bramley, R. G. V. (1990). Cadmium in New Zealand agriculture. *New Zealand Journal of Agricultural Research* **33**: 505 - 519.

Bramley, R. G. V. and Barrow, N. J. (1994). Differences in the cadmium content of some common Western Australian pasture plants grown in a soil amended with cadmium - describing the effects of level of Cd supply. *Fertilizer Research* **39**: 113 - 122.

Brehler, B. (1972) In: Handbook of Geochemistry [Ed. K. H. Wedepohl] *48-A*. Springer-Verlag Berlin-Heidelberg-New York.

Brown, P. H., Dunemann, L., Schulz, R. and Marschner, H. (1989). Influence of redox potential and plant species on the uptake of nickel and cadmium from soils. *Zeitschrift für Pflanzenernährung und Bodenkunde* **152**: 85 - 91.

Brümmer, G. W. and Herms, U. (1983). Influence of soil reaction and organic matter on solubility of heavy metals in soils. In: Effects of Accumulation of Air Pollutants in Forest Ecosystems [Eds. B. Ulrich and J. Pankrath]. D. Reidel Publishing Company, Dordrecht, Germany, pp 233 - 243.

Brümmer, G. W., Gerth, J. and Herms, U. (1986). Heavy metal species, mobility and availability in soils. *Zeitschrift für Pflanzenernährung und Bodenkunde* **149**: 382 - 398.

Brümmer, G. W., Gerth, J. and Tiller, K. G. (1988). Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals. *Journal of Soil Science* **39**: 37 - 52.

Buat-Ménard, P. and Arnold, M. (1978). The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano. *Geophysical Research Letters* **5**: 245 - 248.

Burrough, P. A. (1993). Soil Variability: a late 20th century view. *Soils and Fertilizers* **56**, 529 - 562.

Cabon, J. Y. and Le Bihan, A. (1992). Direct determination of cadmium in sea-water using electrothermal atomization atomic absorption spectrometry with Zeeman-effect background correction and oxalic acid as a chemical modifier. *Journal of Analytical Atomic Spectrometry* **7**: 383 - 388.

Campbell, G. S. (1985). Soil Physics with Basic: Transport models for soil-plant systems [Developments in Soil Science 14]. Elsevier, Amsterdam, 150 pp.

Carroll, J., Miller-Ihli, N.J., Harnly, J.M., O'Haver, T.C. and Littlejohn, D. (1992). Comparison of sodium chloride and magnesium chloride interferences in continuum source AAS with wall, platform and probe electrothermal atomization. *Journal of Analytical Atomic Spectrometry* **7**: 533 - 538.

Chaney, R. L. and Hornick, S. B. (1977). Accumulations and effects of cadmium on crops, In: Cadmium 77, Edited Proceedings of the First International Cadmium Conference, San Francisco, 31 January - 2 February 1977. Metal Bulletin Ltd, London.

Chapple, G. and Athanasopoulos, N. (1991). System 2000/3000 Graphite Furnace Methods manual (Edition: 1.1), Manual No. 01-0202-00. GBC Scientific equipment Pty Ltd.

Chen, J., Wei, F., Zheng, C., Wu, Y. and Adriano, D. (1991). Background concentrations of elements in soils of China. *Water, Air and Soil Pollution* **57 - 58**: 699 - 712.

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

Christensen, T. H. (1984b). Cadmium soil sorption at low concentrations: II. Reversibility, effect of changes in solute composition, and effect of soil aging. *Water, Air and Soil Pollution* **21**: 115 - 125.

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

Christensen, T. H. (1987a). Cadmium soil sorption at low concentrations: V. Evidence of competition by other heavy metals. *Water, Air and Soil Pollution* **34**: 293 - 303.

Christensen, T. H. (1987b). Cadmium soil sorption at low concentrations: VI. A model for zinc competition. *Water, Air and Soil Pollution* **34**: 305 - 314.

Christensen, T. H. (1989). Cadmium soil sorption at low concentrations: VIII. Correlation with soil parameters. *Water, Air and Soil Pollution* **44**: 71 - 82.

Cook, P. J. and Freney, J. R. (1988). Sources of cadmium in agriculture. In: Cadmium accumulation in Australian agriculture: National Symposium 1 - 2 March, 1988 [Ed. J. Simpson and W. Curnow]. Department of Primary Industries and Energy, Bureau of Rural Resources, Canberra, pp 4 - 19.

CRC Handbook of Chemistry and Physics, a ready-reference book of chemical and phsyical data (1997 - 1998), 78th ed., [Editor-in-chief D. R. Lide]. CRC Press, Cleveland, Ohio.

Creed, J., Martin, T., Lobring, L. and O'Dell, J. (1992). Minimizing chloride interferences produced by combination acid digestion using palladium and hydrogen as a matrix modifier in graphite furnace atomic absorption spectrometry. *Environmental Science and Technology* **26**: 102 - 106.

194

Crounse, R. G., Walter, J. P., Bray, J. T. and Mauger, R. L. (1983). Geochemistry and man: Health and disease, 2. Elements possibly essential, those toxic and others. In: Applied Environmental Geochemistry [Ed. I. Thornton]. Academic Press Geology Series, London, pp 309 - 333.

Davister, A. (1996). Studies and research on processes for the elimination of cadmium from phosphoric acid. In: Fertilizers as a Source of Cadmium - OECD Proceedings. OECD, Paris, pp 21 - 30.

De Temmerman, L. O., Hoenig, M. and Scokart, P. O. (1984). Determination of "normal" levels and upper limit values of trace elements in soils. *Zeitschrift für Pflanzenernährung und Bodenkunde* **147**: 687 - 694.

Department of Health (1992). Public health guidelines for the safe use of sewage effluent and sewage sludge on land. New Zealand.

Dudka, S. (1992). Factor analysis of total element concentrations in surface soils of Poland. *The Science of the Total Environment* **121**: 39 - 52.

During, C. (1984). Fertilisers and Soils in New Zealand Farming, 3rd rev. ed., Government Printer, Wellington, New Zealand, 354 pp.

Edmeades, D. C., Wheeler, D. M. and Clinton, O. E. (1985). The chemical composition and ionic strength of soil solutions from New Zealand topsoils. *Australian Journal of Soil Research* **23**: 151 - 165.

Edwards, J. K. (1997). The Fate of Fertiliser Phosphorus in Wharekohe Podzols. PhD Thesis, Massey University, New Zealand.

Edwards, J., Gregg, P. E. H., Mackay, A. D. and Richardson, M. A. (1994). Movement of phosphate on a Wharekohe podzol. In: The Efficient Use of Fertilizers in a Changing Environment: Reconciling productivity and sustainability. [Eds LD Currie and P Loganathan). Occassional Report No. 7. Fertilizer and Lime Research Centre, Massey University, Palmerston North, pp 318 - 325.

Egozy, Y. (1980). Adsorption of cadmium and cobalt on montmorillonite as a function of solution composition. *Clays and Clay Minerals* **28**: 311 - 318.

Elliot, H. A., Liberati, M. R. and Huang, C. P. (1986). Competitive adsorption of heavy metals by soils. *Journal of Environmental Quality* **15**: 214 - 219.

Eriksson, J. E. (1988). The effects of clay, organic matter and time on adsorption and plant uptake of cadmium added to the soil. *Water, Air and Soil Pollution* **40**: 359 - 373.

Eriksson, J. E. (1990). A field study on factors influencing Cd levels in soils and in grain of oats and winter wheat. *Water, Air and Soil Pollution* **53**: 69 - 81.

Fergusson, J. E. and Stewart, C. (1992). The transport of airborne trace elements copper, lead, cadmium, zinc and manganese from a city into rural areas. *The Science of the Total Environment* **121**: 247 - 269.

Filipinski, M. and Grupe, M. (1990). Distribution of lithogeneous, pedogeneous and anthropogeneous heavy metals in soils. *Zeitschrift für Pflanzenernährung und Bodenkunde* **153**: 69 - 73.

Filipinski, M. and Kuntze, H. (1990). Plant uptake and solubility of lithogeneous, pedogeneous and anthropogeneous cadmium of an Ap-horizon from Orthic Luvisol. *Zeitschrift für Pflanzenernährung und Bodenkunde* **153**: 403 - 407.

Fischer, W.R. (1986). Properties of and heavy metal complexation by aqueous humic extracts. *Zeitschrift für Pflanzenernährung und Bodenkunde* **149**: 399 - 410.

Fitzgerald, P. R., Peterson, J. and Lue-Hing, C. (1985). Heavy metals in tissues of cattle exposed to sludge-treated pastures for eight years. *American Journal of Veterinary Research* **46**: 703 - 707.

Folke, J. and Landner, L. (1996). Sustainable cadmium management in agriculture: balancing the cadmium fluxes in arable land and grassland. In: Fertilizers as a Source of Cadmium - OECD Proceedings. OECD, Paris, pp 113 - 118.

Förstner, U. (1980). Cadmium. In: Anthropogenic compounds. The Handbook of environmental chemistry; vol. 3, part A [Ed. O. Hutzinger] Springer-Verlag, Berlin Heidelberg, pp 59 - 107.

Frissel, M. J. and Reiniger, P. (1974). Simulation of Accumulation and Leaching in Soils. Centre for Agricultural Publishing and Documentation, Wageningen, 116 pp.

Furness, H. D. (1994). Cadmium research initiatives by the New Zealand Fertiliser Manufactures. In: *Third Cadmium Research Liaison Meeting, Agresearch Grasslands Research Centre* [Ed. J. Lee], Agresearch, Palmerston North, New Zealand.

Gambrell, R. P., Wiesepape, J. B., Patrick Jr., W. H. and Duff, M. C. (1991). The effects of pH, redox, and salinity on metal release from a contaminated sediment. *Water, Air, and Soil Pollution* **57 - 58**: 359 - 367.

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

Garcia-Miragaya, J. and Page, A. L. (1977). Influence of exchangeable cation on the sorption of trace amounts of Cd by montmorillonite. *Soil Science Society of America Journal* **41**: 718 - 721.

Garcia-Miragaya, J. and Page, A.L. (1978). Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition. *Water, Air and Soil Pollution* **9**: 289 - 299.

Gerth, J., Brümmer, G. W. and Tiller, K. G. (1993). Retention of Ni, Zn and Cd by Si-associated goethite. *Zeitschrift für Pflanzenernährung und Bodenkunde* **156**: 123 - 129.

Ghosheh, A., Bashir, S. and Dabbas, L. (1996). Managing the cadmium content of phosphate rock: a contribution to environmental impact mitigation. In: Fertilizers as a Source of Cadmium - OECD Proceedings. OECD, Paris, pp 13 - 20.

Gillingham, A. G., Syers, J. K., and Gregg, P. E. H. (1980). Phosphorus uptake and return in grazed, steep hill pastures. II. Above-ground components of the phosphorus cycle. *New Zealand Journal of Agricultural Research* **23**: 323 - 330.

Grant, C. A., Bailey, L. D., McLaughlin, M. J. and Singh, B. R. (1997). Management techniques to reduce cadmium transfer from soils to plants: A review. In: Cadmium in Soils and Plants. Developments in Plant and Soil Sciences [Eds. M. J. McLaughlin and B. R. Singh]. Kluwer Academic Publishers. (In Press).

Gray, C. W., McLaren, R. G, Roberts, A. H. C. and Condron, L. M. (1998). Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. *Australian Journal of Soil Research* **36**: 199 - 216.

Greene, R. S. B., Rengasamy, P., Ford, G. W., Chartres, C. J. and Millar, J. J. (1988). The effect of sodium and calcium on physical properties and micromorphology of two red-brown earth soils. *Journal of Soil Science* **39**: 639 - 648.

Grigal, D. F. and Ohmann, L. F. (1989). Spatial patterns in elemental concentrations of the forest floor across the North Central USA. *Journal of Environmental Quality* **18**: 368 - 373.

Grupe, M. and Kuntze, H. (1988). Investigations about the availability of heavy metals in soils with lithogen and anthropogen enrichment: I. Cd and Cu. *Zeitschrift für Pflanzenernährung und Bodenkunde* **150**: 319 - 324 (German).

Haan, F. A. M. de, Zee, S. E. A. T. M. van der, and Riemsdijk, W. H. van (1987). The role of soil chemistry and soil physics in protecting soil quality: variability of sorption and transport of cadmium as an example. *Netherlands Journal of Agricultural Science* **35**: 347 - 359.

Hahne, H. C. H. and Kroontje, W. (1973). Siginificance 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.

Hansen, L. G. and Schaeffer, D. J. (1995). Livestock and Domestic Animals. In: Soil Amendments - Impacts on Biotic Systems [Ed. J. E. Rechcigl]. Lewis Publishers, Boca Raton, pp 41 - 79.

Harmsen, K. (1992). Long-term behaviour of heavy metals in agricultural soils: a simple analytical model. In: Biogeochemistry of Trace Metals [Ed. D. C. Adriano]. Lewis Publishers, Boca Raton, pp 217 - 247.

Haygarth, P. M. and Jones, K. C. (1992). Atmospheric depostion of metals to agricultural surfaces. In: Biogeochemistry of Trace Metals [Ed. D. C. Adriano]. Lewis Publishers, Boca Raton, pp 249 - 276.

Haynes, R. J. and Williams, P. H. (1992). Changes in soil solution composition and pH in urine-affected areas of pasture. *Journal of Soil Science* **43**: 323 - 334.

He, Q. B. and Singh, B. R. (1993a). Plant availability of cadmium in soils. I. Extractable cadmium in newly and long-term cultivated soils. *Acta Agriculturæ Scandinavica, Section B, Soil and Plant Science* **43**: 134 - 141.

He, Q. B. and Singh, B. R. (1993b). Plant availability of cadmium in soils. II. Factors related to the extractability and plant uptake of cadmium in cultivated soils. *Acta Agriculturæ Scandinavica, Section B, Soil and Plant Science* **43**: 142 - 150.

He, Q.B. and Singh, B.R. (1993c). Effect of organic matter on the distribution, extractability and uptake of cadmium in soils. *Journal of Soil Science* **44**: 641 - 650.

Heinrichs, H. and Mayer, R. (1980). The role of forest vegetation in the biogeochemical cycle of heavy metals. *Journal of Environmental Quality* **9**: 111 - 118.

Hendrickson, L. L. and Corey, R. B. (1981). Effect of equilibrium metal concentrations on apparent selectivity coefficients of soil complexes. *Soil Science* **131**: 163 - 171.

Heng, L. K., White, R. E., Bolan, N. S. and Scotter, D. R. (1991). Leaching losses of major nutrients from a mole-drained soil under pasture. *New Zealand Journal of Agricultural Research* **34**: 325 - 334.

Herber, R. F. M. (1994). Cadmium. In: Handbook on Metals in Clinical and Analytical Chemistry [Eds. H. G. Seiler, A. Sigel and H. Sigel], Marcel Dekker, New York, pp 283 - 297.

Hermann, R. and Neumann-Mahlkau, P. (1985). The mobility of zinc, cadmium, copper, lead, iron and arsenic in ground water as a function of redox potential and pH. *The Science of the Total Environment* **43**: 1 - 12.

Hesse, P. R. (1971). A Textbook of Soil Chemical Analysis. John Murray (Publishers) LTd, London, 520 pp.

Hewitt, A. E. (1992). Soil Classification in New Zealand: Legacy and lessons. *Australian Journal of Soil Research* **30**: 843 - 854.

Hewitt, A. E. (1993). New Zealand Soil Classification. Landcare Research Science Series No. 1. Manaaki-Whenua Press, Lincoln, New Zealand.

Hilliard, E. P., Coffey, D. and Weston, B. (1988). Cadmium accumulation in the organic horizons of some soils under permanent pasture in Victoria. In: Cadmium accumulation in Australian agriculture: National Symposium 1 - 2 March, 1988 [Ed. J. Simpson and W. Curnow]. Department of Primary Industries and Energy, Bureau of Rural Resources, Canberra, pp 80 - 84.

Hinz, C. and Selim, H. M. (1994). Transport of zinc and cadmium in soils: Experimental evidence and modeling approaches. *Soil Science Society of America Journal* **58**: 1316 - 1327.

Hirsch, D. and Banin, A. (1990). Cadmium speciation in soil solution. *Journal of Envirnomental Quality* **19**: 366 - 372.

Holmgren, G. G. S., Meyer, M. W., Chaney. R. L. and Daniels, R. B. (1993). Cadmium, lead. zinc, copper, and nickel in agricultural soils of the United States of America. *Journal of Environmental Quality* **22**: 335 - 348.

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

Hornburg, V. and Brümmer, G. W. (1990). Heavy metal availability in soils and contents in wheat grain and other plants (German). [Schwermetall-Verfugbarkeit in Boden und Gehalte im Weizenkorn und anderen Pflanzen]. *Verband Deutscher Landwirtschaftlicher Untersuchungs und Forschungsanstalten, Reihe Kongressberichte* **No. 32**: 821 - 826. (From CAB Abstracts, Vol. 3A, 1990 - 1991. Accession No. S614863)

Hornburg, V. and Brümmer, G. W. (1993). Behaviour of heavy metals in soils. 1. Heavy metal mobility. *Zeitschrift für Pflanzenernährung und Bodenkunde* **156**: 467 - 477. (German)

Hulanicki, A., Bulska, E. and Wròbel, K. (1985). Effect of inorganic matrices on the determination of cadmium by atomic-absorption spectrometry with electrothermal atomization. *Analyst* **110**: 1141 - 1145.

Hutton, M. (1982). Cadmium in the European Community: a prospective assessment of sources, human exposure and environmental impact. The Monitoring and Assessment Research Centre, Chelsea College, University of London, 99 pp (MARC Report No. 26).

Inskeep, W.P. and Baham, J. (1983). Competitive complexation of Cd(II) and Cu(II) by water-soluble organic ligands and Na-montmorillonite. *Soil Science Society of America Journal* **47**: 1109 - 1115.

Iu, K. L., Pulford, I. D. and Duncan, H. J. (1981a). Influence of waterlogging and lime or organic matter additions on the distribution of trace metals in an acid soil: I. manganese and iron. *Plant and Soil* **59**: 317 - 326.

Iu, K. L., Pulford, I. D. and Duncan, H. J. (1981b). Influence of waterlogging and lime or organic matter additions on the distribution of trace metals in an acid soil: II. zinc and copper. *Plant and Soil* **59**: 327 - 333.

Jackson, A. P. and Alloway, B. J. (1992). The transfer of cadmium from agricultural soils to the human food chain. In: Biogeochemistry of Trace Metals [Ed. D. C. Adriano], Lewis Publishers, Boca Raton, pp 109 - 158.

Jensen, N. P. and Svensmark, B. (1989). Distribution and concentration of Pb and Cd in two adjacent Luvisols under grassland and forest in Denmark. *Zeitschrift für Pflanzenernährung und Bodenkunde* **152**: 121 - 124.

Jones, K. C., Symon, C. J. and Johnston, A. E. (1987). Retrospective analysis of an archived soil collection. II. Cadmium. *The Science of the Total Environment* **67**: 75 - 89

Jury, W., Gardner, W. and Gardner, W. (1991). Soil Physics. John Wiley and Sons inc., Fifth edition, 328 pp.

Kabata-Pendias, A. (1997). Factors influencing trace metal status in mineral soils developed under temperate humid climate. In: Proceedings of Extended Abstracts from the Fourth International Conference on the Biogeochemistry of Trace Elements. [Eds. I. K. Iskandar, S. E. Hardy, A. C. Chang and G. M. Pierzynski], June 23 - 26, Berkeley, California, USA, pp 33 - 34.

Kabata-Pendias, A. and Dudka, S. (1991). Baseline data for cadmium and lead in soils and some cereals of Poland. *Water, Air and Soil Pollution* **57 - 58**: 723 - 731.

Kabata-Pendias, A. and Pendias, H. (1992).Trace Elements in Soils and Plants, 2nd Ed. CRC Press, Boca Raton, Florida, 365 pp.

Keller, C. and Domergue, F. -L. (1996). Soluble and particulate transfers of Cu, Cd, Al, Fe and some major elements in gravitational waters of a Podzol. *Geoderma* **71**: 263 - 274.

Keller, C., Domergue, F. -L. and Védy, J. -C. (1992). Biogeochemistry of copper and cadmium in unpolluted forests In: Impact of Heavy Metal on the Environment [J.-P. Vernet Ed.]: Trace Metals in the Environment 2, pp 247 - 271.

Kim, N. (1990). Studies in the Concentration and Chemistry of Cadmium in the Environment. PhD Thesis, Canterbury University, New Zealand.

Kim, N. D. and Fergusson, J. E. (1992). Adsorption of cadmium by an Aquent New Zealand soil and its components. *Australian Journal of Soil Science* **30**: 159 - 167.

King, L. D. (1988). Retention of metals by several soils of the southeastern United Stated. *Journal of Environmental Quality* **17**: 239 - 246.

200

Kinniburgh, D. G. and Jackson, M. L. (1981). Cation adsorption by hydrous metal oxides and clay. In: Adsorption of Inorganics at Solid-Liquid Interfaces [Eds M. A. Anderson and A. J. Rubin]. Ann Arbor Science, Michigan, pp 91 - 160.

Koh, T-S. (1988). Cadmium in meat and meat products: An overview. In: Cadmium accumulation in Australian agriculture: National Symposium 1 - 2 March, 1988 [Ed. J. Simpson and W. Curnow]. Department of Primary Industries and Energy, Bureau of Rural Resources, Canberra, pp 89 - 112.

König, N., Baccini, P. and Ulrich, B. (1986). The influence of organic matter in the translocation of metals between soil and soil solution of an acid forest soil. *Zeitschrift für Pflanzenernährung und Bodenkunde* **149**: 68 - 82. (German)

Kookana, R. S., Naidu, R. and Tiller, K. G. (1994). Sorption non-equilibrium during cadmium transport through soils. *Australian Journal of Soil Research* **32**: 635 - 651.

Korentajer, L., Stern, R. and Aggasi, M. (1993). Slope effects on cadmium load of eroded sediments and runoff water. *Journal of Environmental Quality* **22**: 639 - 645.

Kossir, A. and Chik, A. (1996). Promoting the development and semi-industrial application of a potentially high performing process for cadmium removal from phosphate rock. In: Fertilizers as a Source of Cadmium - OECD Proceedings. OECD, Paris, pp 31 - 40.

Krishnamurti, G. S. R., Huang, P. M., Van Rees, K. C. J., Kozak, L. M. and Rostad, P. W. (1995). A new soil test method for the determination of plant-available cadmium in soils. *Communications in Soil Science and Plant Analysis* **26**: 2857 - 2867.

Kross, B. C., Olson, M. L., Ayebo, A. and Johnson, J. K. (1995). Humans. In: Soil Amendments - Impacts on Biotic Systems [Ed. J. E. Rechcigl]. Lewis Publishers, Boca Raton, pp 153 - 214.

Krosshavn, M., Steinnes, E. and Varskog, P. (1993). Binding of Cd, Cu, Pb and Zn in soil organic matter with different vegetational background. *Water, Air and Soil Pollution* **71**: 185 - 193.

Kuzel, S, Nýdl, V., Kolár, L. and Tichý, R. (1994). Spatial variability of cadmium, pH, organic matter in soil and its dependence on sampling scales. *Water, Air and Soil Pollution* **78**: 51 - 59.

Lee, J. Grace, N. D. and Rounce, J. R. (1994). Cadmium accumulation in liver and kidney of sheep grazing ryegrass/white clover pastures. *Proceedings of the New Zealand Society of Animal Production* **54**: 31 - 4.

Lee, J., Grace, N. D., Mackay, A. D., Hedley, M. J., and Rounce, J. R. (1993). Cadmium in soil, pasture and grazing ruminants. In: Proceedings of the XVII International Grassland Congress, 8 - 21 February 1993, Palmerston North, New Zealand, pp 817 - 818.

Lee, J., Rounce, J. R., Mackay, A. D. and Grace, N. D. (1996). Accumulation of cadmium with time in Romney sheep grazing ryegrass-white clover pasture: Effect of cadmium from pasture and soil intake. *Australian Journal of Agricultural Research* **47**: 877 - 894.

Levett, M. P., Adams, J. A., Walker, T. W. and Wilson, E. R. L. (1985). Weight and nutrient content of above-ground biomass and litter of a podocarp-hardwood forest in Westland, New Zealand. *New Zealand Journal of Forestry Science* **15 (1)**: 23-35.

Levi-Minzi, R., Soldatinin, G. F. and Riffaldi, R. (1976). Cadmium adsorption by soils. *Journal of Soil Science* **27**: 10 - 15.

Lindsay, W. L. (1979). Chemical Equilibria in Soils. Wiley-Interscience, New York, 449 pp.

Loganathan, P. and Hedley, M. J. (1993). Single superphosphate - reactive phosphate rock mixtures. 3. The use of concentration ratios of elements to identify the nature and amounts of unacidulated rock residues in the mixtures. *Fertilizer Research* **36**: 203 - 210.

Loganathan, P. and Hedley, M. J. (1997). Downward movement of cadmium and phosphorus from phosphatic fertilisers in a pasture soil in New Zealand. *Environmental Pollution* **95**: 319 - 324.

Loganathan, P., Hedley, M. J., Gregg, P. E. H. and Currie, L. D. (1997). Effect of phosphate fertiliser type on the accumulation and plant availability of cadmium in grassland soils. *Nutrient Cycling in Agroecosystems* **46**: 169 - 178.

Loganathan, P., Mackay, A. D., Lee, J. and Hedley, M. J. (1995). Cadmium distribution in hill pastures as influenced by 20 years of phosphate application and sheep grazing. *Australian Journal of Soil Science* **33**: 859 - 871.

Longhurst, R. D., Roberts, A. H. C., Brown, M. W. and Carlson, B. (1994). Cadmium cycling in sheep grazed hill country pastures. In: The Efficient Use of Fertilizers in a Changing Environment: Reconciling productivity and sustainability. [Eds LD Currie and P Loganathan). Occassional Report No. 7. Fertilizer and Lime Research Centre, Massey University, Palmerston North, pp 297 - 302.

Lorenz, S. E., Hamon, R. E., McGrath, S. P., Holm, P. E. and Christensen, T. H. (1994). Applications of fertilizer cations affect cadmium and zinc concentrations in soil solutions and uptake by plants. *European Journal of Soil Science* **45**: 159 - 165.

Lowe, K. (1992). Limestone Downs: Ten year history. C. Alma Baker Trust Series Publication No. 10.

202

Lund, L. J., Betty, E. E., Page, A. L. and Elliot, R. A. (1981). Occurrence of naturally high cadmium levels in soils and its accumulation by vegetation. *Journal of Environmental Quality* **10**: 551 - 556.

Mackay, A. D., Hedley, C. B., Neal, V. E. and Palmer, A. S. (1985). Reconnaissance Soil Map of Limestone Downs, Waikato. C. Alma Baker Trust Series Publication No. 2.

Mann, S. S. and Ritchie, G. S.P (1994). Changes in the forms of cadmium with time in some Western Australian soils. *Australian Journal of Soil Research* **32**: 241 - 250.

Manning, D. C. and Slavin, W. (1983). The determination of trace elements in natural waters using stabilized temperature platform furnace. *Applied Spectroscopy* **37**: 1 - 11.

Marro, N. (1996). The 1994 Australian Market Basket Survey [Ed. J. Cook]. Australian New Zealand Food Authority (ANZFA), Commonwealth of Australia, 141 pp.

Mattigod, S. V. and Page, A. L. (1983). Assessment of metal pollution in soils. In: Applied Environmental Geochemistry [Ed. I. Thornton]. Academic Press, London, pp 355 - 394.

McBride, M. B. (1980). Chemisorption of Cd^{2+} on calcite surfaces. *Soil Science Society of America Journal* **44**: 26 - 28

McBride, M. B. (1989). Reactions controlling heavy metal solubility in soils. In: Advances in Soil Science, Volume 10 [Ed. B. A. Stewart]. Springer-Verlag, New York, 200 pp.

McBride, M. B. (1994). Environmental Chemistry of Soils. Oxford University Press, New York, 406 pp.

McBride, M. B., Richards, B. K., Steenhuis, T., Russo, J. J. and Sauvé, S. (1997a). Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Science* **162**: 487 - 500.

McBride, M. B., Sauvé, S. and Hendershot, W. (1997b). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science* **48**: 337 - 346.

McGrath, S. P. (1987). Long-term studies of metal transfers following the application of sewage sludge. In: Pollutant Transport and Fate in Ecosystems [Eds. P. J. Coughtrey and M. H. Unsworth], Blackwell Scientific Publications, Oxford, pp 301 - 317.

McGrath, S. P. and Jarvis, S. C. (1993). Recent considerations of grassland "soil quality" in temperate regions. In: *Proceedings of the XVII International Grassland Congress*, pp 1409 - 1418.

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

McLaren, R. G. and Cameron, K. C. (1990). Soil Science: An introduction to the properties and management of New Zealand soils. Oxford University Press, Auckland, 294 pp.

McLaughlin, M. J. and Singh, B. R. [Eds] (1997). Cadmium in Soils and Plants. Developments in Plant and Soil Sciences. Kluwer Academic Publishers. (In Press).

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

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

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

Mennear, J. H. [Ed.] (1979). Cadmium Toxicity. Marcel Dekker, Inc., New York, 224 pp.

Merry, R. H. and Tiller, K. G. (1991). Distribution and budget of cadmium and lead in an agricultural region near Adelaide, South Australia. *Water, Air and Soil Pollution* **57 - 58**: 171 - 180.

Millward, C.G. and Kluckner, P.D. (1991). Determination of low levels of cadmium in marine and fresh water sediments by graphite furnace atomic absorption spectrometry employing a reduced palladium chloride modifier and by inductively coupled plasma atomic emission spectrometry. *Journal of Analytical Atomic Spectrometry* **6**: 37 - 40.

Milsin, H. and Ravera, O. [Eds] (1986). Cadmium in the Environment (Experientia. Supplementum; vol. 50), Birkhäuser Verlag, Basel, 144 pp.

Mitchell, G. E. (1981). Trace metal levels in Queensland dairy products. *Australian Journal of Dairy Technology* **36**: 70 - 73.

Mitchell, L. G., Grant, C. A. and Racz, G. J. (1997). Phytoavailability of cadmium in soils treated with nitrogen fertilizers. In: Proceedings of Extended Abstracts from the Fourth International Conference on the Biogeochemistry of Trace Elements. [Eds. I. K. Iskandar, S. E. Hardy, A. C. Chang and G. M. Pierzynski], June 23 - 26, Berkeley, California, USA, pp 131 - 132.

Moir, J. L., Hedley, M. J., Mackay, A. D. and Garland, C. B. (1995). Climate, soil fertility and pasture production in Wairarapa hill country. In: Fertilizer requirements of grazed pasture and field crops: Marco- and micro-nutrients. [Eds LD Currie and P Loganathan). Occassional Report No. 8. Fertilizer and Lime Research Centre, Massey University, Palmerston North, pp 254 - 260.

Morrison, I. K. and Hogan, G. D. (1986). Trace element distribution within the tree phytomass and forest floor of a tolerant hardwood stand, Algoma, Ontario. *Water, Air and Soil Pollution* **31**: 493 - 500.

Mortvedt, J. J. (1987). Cadmium levels in soils and plants from some long-term fertility experiments in the United States of America. *Journal of Environmental Quality* 16, 137 - 142.

Mortvedt, J. J. (1996). Heavy metal contaminants in inorganic and organic fertilizers. *Fertilizer Research* **43**: 55 - 61.

Mulla, D. J., Page, A. L. and Ganje, T. J. (1980). Cadmium accumulations and bioavailability in soils from long-term phosphorus fertilization. *Journal of Environmental Quality* **9**: 408 - 412.

Mullins, G. L. and Mitchell, C. C. (1995). Crops. In: Soil Amendments - Impacts on Biotic Systems [Ed. J. E. Rechcigl]. Lewis Publishers, Boca Raton, pp 1 - 40.

Mullins, G. L. and Sommers, L. E. (1986). Characterization of cadmium and zinc in four soils treated with sewage sludge. *Journal of Environmental Quality* **15**, 382 - 387.

Murphy J. and Riley J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* **27**: 31 - 36.

Naidu, R., Bolan, N. S., Kookana, R. S. and Tiller, K. G. (1994). Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science* **45**: 419 - 429.

Neal, R. H. and Sposito, G. (1986). Effects of soluble organic matter and sewage sludge amendments on cadmium sorption by soils at low cadmium concentrations. *Soil Science* **142**: 164 - 172.

Nelson, N. (1994). "Elusive and complex character", Manawatu Evening Standard, Saturday, February 12, p 10.

Neuhauser, E. F. and Hartenstein, R. (1980). Efficiencies of extractants used in analyses of heavy metals in sludges. *Journal of Environmental Quality* **9**: 21 - 22.

New Zealand Soil Bureau (1968a): Soils of New Zealand. Part 2. *New Zealand Soil Bureau Bulletin* **26** (2)

New Zealand Soil Bureau (1968b): Soils of New Zealand. Part 3. *New Zealand Soil Bureau Bulletin* **26** (3)

Nicholson, F. A.. Jones, K. C. and Johnston, A. E. (1996). Evidence for the leaching of surface deposited cadmium in agricultural soils. In: Fertilizers as a Source of Cadmium - OECD Proceedings. OECD, Paris, pp 218 - 231.

Nriagu, J. O. (1980a). Production, uses, and properties of cadmium. In: Cadmium in the Environment, Part I: Ecological Cycling [J. O. Nriagu]. John Wiley and Sons, New York, pp 35 - 70.

Nriagu, J. O. (1980b). Cadmium in the atmosphere and in precipitation. In: Cadmium in the Environment, Part I: Ecological Cycling [J. O. Nriagu]. John Wiley and Sons, New York, pp 71 - 114.

Nriagu, J. O. [Ed] (1980c). Cadmium in the Environment, Part I: Ecological Cycling. John Wiley and Sons, New York, 682 pp.

O'Connor, G. A., O'Connor, C. and Cline, G. R. (1984). Sorption of cadmium by calcareous soils: Influence of solution composition. *Soil Science Society of America Journal* **48**: 1244 - 1247.

Olsen, S.R., Cole, C.V., Watanabe, F.S. and Dean, L.A. (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular 939, 19 pp.

Orlov, D. S. (1992). Soil Chemistry. A. A. Balkema, Rotterdam, Brookfield, 390 pp.

Pacyna, J. M. (1986). Atmospheric trace elements from natural and anthropogenic sources. In: Toxic Metals in the Atmosphere [Eds. J. O. Nriagu and C. I. Davidson]. John Wiley and Sons, New York, pp 33 - 52.

Pacyna, J. M., Münch, J. and Axenfeld, F. (1991). European inventory of trace metal emissions to the atmosphere. In: Heavy Metals in the Environment. Trace Metals in the Environment 1 [Ed. J. -P. Vernet]. Elsevier, Amsterdam, pp 1 - 20.

Papadopoulos, P. and Rowell, D. L. (1988). The reactions of cadmium with calcium carbonate surfaces. *Journal of Soil Science* **39**: 23 - 26.

Peterson, P. J. and Alloway, B. J. (1979). Cadmium in soils and vegetation. In: The Chemistry, Biochemistry and Biology of Cadmium [Ed. M. Webb]. Elsevier/North-Holland Biomedical Press, pp 45 - 92.

Pickering, W. F. (1980). Cadmium retention by clays and other soil or sediment components. In: Cadmium in the Environment, Part 1: Ecological cycling [Ed. J. O. Nriagu], John Wiley and Sons, New York, pp 365 - 397.

Pierce, F. J., Dowdy, R. H. and Grigal, D. F. (1982). Concentrations of six trace metals in some major Minnesota soil series. *Journal of Environmental Quality* **11**: 416 - 422.

Plant, J. A. and Raiswell, R. (1983). Principles of environmental geochemistry. In: Applied Environmental Geochemistry [Ed. I. Thornton]. Academic Press, London, pp 1 - 39.

Poelstra, P., Frissel, M. J. and El-Bassam, N. (1979). Transport and accumulation of Cd ions in soils and plants. *Zeitschrift für Pflanzenernaerung und Bodenkunde* **142**: 848 - 864.

Pulford, I. D. (1986). Mechanisms controlling zinc solubility in soils. *Journal of Soil Science* **37**: 427 - 438.

Puls, R.W., Powell, R.M., Clark, D. and Eldred, C.J. (1991). Effects of pH, solid/solution ratio, ionic strength and organic acids on Pb and Cd sorption on kaolinite. *Water, Air and Soil Pollution* **57 - 58**: 423 - 430.

Pulsford, J. (1989). The Australian phosphorus fertilizer industry - some perspectives. *Agricultural Science* **2** (No. 5): 38 - 42.

Riffaldi, R. and Levi-Minzi, R. (1975). Adsorption and desorption of Cd on humic acid fraction of soil. *Water, Air and Pollution* **5**: 179 -184.

Riha, S., Senesac, G. and Pallant, E. (1986). Effects of forest vegetation on spatial variability of surface mineral soil pH, soluble aluminum and carbon. *Water, Air and Soil Pollution* **31**: 929 - 940.

Roberts, A. H. C., Longhurst, R. D. and Brown, M. W. (1993). Cadmium accumulation in New Zealand pastoral agriculture. *Proceedings of the XVII Internation Grassland Congress*, pp 1451 - 1452.

Roberts, A. H. C., Longhurst, R. D., and Brown, M. W. (1994). Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research* **37**: 119 - 129.

Roberts, T. L. and Stauffer, M. D. (1996). Agronomic implications of restricting cadmium content of phosphate rock. In: Fertilizers as a Source of Cadmium - OECD Proceedings. OECD, Paris, pp 70 - 78.

Roels, H., Buchet, J. P., Lauwerys, R., Bernard, A., Harvey, T., Chettle, D. and Al-Haddad, I. K. (1981). Critical concentrations of cadmium in liver and kidney in cadmium exposed workers. In: Heavy Metals in the Environment: International Conference, Amsterdam, September, 1981. CEP Consultants Ltd, Edinburgh, pp 518 - 521.

Ross, S. M. (1994a). Sources and forms of potentially toxic metals in soil-plant systems. In: Toxic Metals in Soil-Plant Systems [Ed. S. Ross]. John Wiley and sons Ltd. Chichester, pp 3 - 25.

Ross, S. M. (1994b). Retention, transformation and mobility of toxic metals in soils. In: Toxic Metals in Soil-Plant Systems [Ed. S. Ross]. John Wiley and sons Ltd. Chichester, pp 63 - 152.

Ross, S. M. (1994c). Toxic metals: Fate and distribution in contaminated ecosystems. In: Toxic Metals in Soil-Plant Systems [Ed. S. Ross]. John Wiley and sons Ltd. Chichester, pp 189 - 243.

Ross, S. M. [Ed] (1994d). Toxic metals in soil-plant systems. John Wiley and sons Ltd. Chichester, 469 pp.

Rothbaum, H. P., Goguel, R. L., Johnston, A. E., Mattingly, G. E. G. (1986). Cadmium accumulation in soils from long continued applications of superphosphate. *Journal of Soil Science* **37**: 99 - 107.

Rounce, J. R., Grace, N. D. and Lee, J. (1997). Accumulation of cadmium in kidney and liver tissue of the suckling Romney lamb from parturition to early weaning. *Proceedings of the New Zealand Society of Animal Production* **57**: 137 - 138.

Rounce, J. R., Lee, J. and Grace, N. D. (1995). Metabolic changes of cadmium and zinc in kidney and liver tissue during foetal development in Romney and Merino sheep. *Proceedings of the New Zealand Society of Animal Production* **55**: 176 - 178.

Roy, W. R., Krapac, I. G. and Steele, J. D. (1993). Sorption of Cadmium and Lead by Clays from Municipal Incinerator Ash-Water Suspensions. *Journal of Environmental Quality* **22**: 537 - 543.

Ryan, J. A., Pahren, H. R. and Lucas, J. B. (1982). Controlling cadmium in the human food chain: a review and rationale based on health effects. *Environmental Research* **28**: 251 - 302.

Saggar, S., Mackay, A. D., Hedley, M. J., Lambert, M. G. and Clark, D. A. (1990). A nutrient-transfer model to explain the fate of phosphorus and sulphur in a grazed hill-country pasture. *Agriculture, Ecosystems and Environment* **30**: 295 - 315.

Sánchez-Martín, M. J. and Sánchez-Camazano, M. (1993). Adsorption and mobility of cadmium in natural, uncultivated soils. *Journal of Environmental Quality* **22**: 737 -742.

Sauerbeck, D. R. and Styperek, P. (1985). Evaluation of chemical methods for assessing the Cd and Zn availability from different soils and sources. In: Chemical Methods for Assessing Bio-available Metals in Sludges and Soils [Eds. R. Leschber, R. D. Davis and P. L'Hermite]. Elsevier Applied Science Publishers, London, pp 49 - 66.

Schmidt, F. and Walter, B. (1988). Contents and distribution of heavy metals in greywacke and Devonian slate soils under forest and vineyard utilization. (German) [Schwermetallgehalte und Verteilung in Grauwacke- und Tonschieferboden unter Wald- und Weinbaulicher Nutzung].Abfallstoffe als Dunger Proceedings of the 99th VDLUFA congress, September 1987, Koblenz, German Federal Republic. VDLUFA-Schriftenreihe No. 23 1988, 355 - 365. (From CAB Abstracts, Vol. 2, 1987 - 1989, Accession No. 891934315)

Schmitt, H. W. and Sticher, H. (1986). Long-term trend analysis of heavy metal content and translocation in soils. *Geoderma* **38**: 195 - 207.

Seiler, H. G., Sigel, A. and Sigel, H. [Eds] (1994). Handbook on Metals in Clinical and Analytical Chemistry. Marcel Dekker, Inc., New York. 753 pp

Selim, H. M., Buchter, B., Hinz, C. and Ma, L. (1992). Modeling the transport and retention of cadmium in soils: Multireaction and multicomponent approaches. *Soil Science Society of America Journal* **56**: 1004 - 1015.

Senesi, N. (1992). Metal-humic substance complexes in the environment. Molecular and Mechanistic Aspects by multiple spectroscopic approach. In: Biogeochemistry of Trace Metals. [D. C. Adriano Ed.], Lewis Publishers, Boca Raton, pp 429 - 496.

Sharma, R. P., Street, J. C., Shupe, J. L. and Bourcier, D. R. (1982). Accumulation and depletion of cadmium and lead in tissues and milk of lactating cows fed small amounts o f these metals. *Journal of Dairy Science* **65**: 972 - 979.

Sherlock, J. C. (1986). Cadmium in foods and the diet. In: Cadmium in the Environment (Experientia. Supplementum; vol. 50) [Eds. H. Mislin and O. Ravera], Birkhäuser Verlag, Basel, pp 110 - 114.

Simpson, J. and Curnow, W. [Eds] (1988). Cadmium accumulation in Australian agriculture: National Symposium 1 - 2 March, 1988. Department of Primary Industries and Energy, Bureau of Rural Resources, Canberra, 226 pp.

Singer, M. J. and Munns, D. N. (1987). Soils, an introduction. New York, Macmillan, 492 pp.

Singh, B. and Gilkes, R.J. (1992). Properties and distribution of iron oxides and their association with minor elements in the soil of south-western Australia. *Journal of Soil Science* **43**: 77 - 98.

Slavek, J. and Pickering, W. F. (1986). Extraction of metal ions sorbed on hydrous oxides of iron (III). *Water, Air and Soil Pollution* **28**: 151 - 162.

Slavin, W. (1987). Letter to the Editor. *Spectrochimica Acta*, **42B**: 933 - 935.

Slavin, W. and Carnrick, G. R. (1986). Interferences in graphite furnace AAS continuum background correction: a survey. *Atomic Spectroscopy* **7**: 9 - 13.

Slavin, W. and Carnrick, G. R. (1988). Background correction in atomic absorption spectroscopy (AAS). *Critical Reviews in Analytical Chemistry* **19**: 95 - 134.

Slavin, W., Carnrick, G. R., Manning, D. C. and Pruszkowska, E. (1983). Recent experiences with the stabilized temperature platform furnace and zeeman background correction. *Atomic Spectroscopy* **4**: 69 - 86.

Smeyers-Verbeke, J., Yang, Q., Penninckx, W. and Vandervoort, F. (1990). Effectiveness of palladium chemical modification for the determination of cadmium by graphite furnace atomic absorption spectrometry. *Journal of Analytical Atomic Spectrometry* **5**: 393 - 398.

Smith, E. R. G. (1994). Long-term fate of heavy metals applied in sewage slugde to a sandy soil. BSc Honours Dissertation, Lincoln University, New Zealand.

Smith, G. (1993). Putting the Cadmium Issue in Perspective. Ravensdown Fertiliser, Feilding.

Sposito, G. (1983). The chemical forms of trace metals in soils. In: Applied Environmental Geochemistry [Ed. I. Thornton], Academic Press Geology Series, London, pp. 123 - 70.

Sposito, G. and Bingham, F. T. (1981). Computer modelling of trace metal speciation in soil solutions: correlation with trace metal uptake by higher plants. *Journal of Plant Nutrition* **3**: 35 - 49.

Stoeppler, M. and Piscator, M. [Eds] (1988). Cadmium: 3rd IUPAC Cadmium Workshop, Juelich, FRG, August 1985. Springer-Verlag, Berlin Heidelberg, 235 pp.

Syers, J. K., Mackay, A. D., Brown, M. W. and Currie, L. D. (1986). Chemical and physical characteristics of phosphate rock materials of varying reactivity. *Journal of the Science of Food and Agriculture* **37**: 1057 - 1064.

Taylor, M. D. and Percival, H. J. (1992). Interim report on contamination of New Zealand soils by cadmium and selected other heavy metals. DSIR Land Resources Technical Record 116.

Taylor, M.D. and Theng, B.K.G. (1995). Sorption of cadmium by complexes of kaolinite with humic acid. *Communications in Soil Science and Plant Analysis* **26**: 765 - 776.

Taylor, M. D. (1997). Accumulation of cadmium derived from fertilisers in New Zealand soils. *Science of the Total Environment* **208**: 123 - 126.

Temminghoff, E. J. M., Van Der Zee, S. E. A. T. M., and De Haan, F. A. M. (1995). Speciation and calcium competition effects on cadmium sorption by sandy soil at various pHs. *European Journal of Soil Science* **46**: 649 - 655.

Thomas, G. W. and Phillips, R. E. (1979). Consequences of water movement in macropores. *Journal of Environmental Quality* **8**: 149 - 152.

Thompson, M. (1983). Analytical methods in applied environmental geochemistry. In: Applied Environmental Geochemistry [Ed. I. Thornton]. Academic Press Geology Series, London, pp 75 - 101.

Thornton, I. (1983). Geochemistry applied to agriculture. In: Applied Environmental Geochemistry [Ed. I. Thornton]. Academic Press, London, pp 231 - 266.

Thornton, I. (1986). Geochemistry of cadmium. In: Cadmium in the Environment (Experientia. Supplementum; vol. 50) [Eds. H. Mislin and O. Ravera], Birkhäuser Verlag, Basel, pp 7 - 12.

Tiller, K. G. (1988).Cadmium accumulation in the soil-plant system: an overview in relation to possible transfers to agricultural products. In: Cadmium accumulation in Australian agriculture: National Symposium 1 - 2 March, 1988 [Ed. J. Simpson and W. Curnow]. Department of Primary Industries and Energy, Bureau of Rural Resources, Canberra, pp 20 - 47.

Tiller, K. G. (1989). Heavy metals in soils and their environmental significance. In: Advances in Soil Science [Ed. B. A. Stewart]. Vol. 9, Springer-Verlag, New York, pp 113 - 141.

Tiller, K. G., Gerth, J. and Brümmer, G. (1984). The relative affinities of Cd, Ni and Zn for different soil clay fractions and goethite. *Geoderma* **34**: 17 - 35.

Tiller, K. G., Nayyar, V. K. and Clayton, P. M. (1979). Specific and non-specific sorption of cadmium by soil clays as influenced by zinc and calcium. *Australian Journal of Soil Research* **17**: 17 - 28.

Tjell, J. C. and Christensen, T. H. (1992). Sustainable management of cadmium in Danish agriculture. In: Impact of Heavy metals on the Environment [Ed. J. -P. Vernet]. Elsevier Science Publishers, Amsterdam, pp 273 - 286.

Travis, C. C. and Etnier, E. L. (1981). A survey of sorption relationships for reactive solutes in soil. *Journal of Environmental Quality* **10**: 8 - 17.

U.S. Environmental Protection Agency (1994). Method 200.9, Revision 2.2, Determination of trace elements by stabilized temperature graphite furnace atomic absorption. [Eds. Creed, J. T., Martin, T. D. and O'Dell, J. W.], Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S.E.P.A., Cincinnati, Ohio, 41 pp.

Van Bruwaene, R., Kichmann, R. and Impens, R. (1986). Cadmium contamination in agriculture and zootechnology. In: Cadmium in the Environment (Experientia. Supplementum; vol. 50) [Eds. H. Mislin and O. Ravera], Birkhäuser Verlag, Basel, pp 87 - 96.

Vannoort, R. W., Hannah, M. L. and Pickston, L. (1995). 1990/1991 New Zealand Total Diet Survey, Part 2: Contaminant Elements. Institute of Environmental Science and Research Limited (ESR): Health, Wellington, New Zealand, 52 pp.

Verburg, K. and Baveye, P. (1995). Influence of quasi-crystal formation and intercrystalline swelling on cation exchange hysteresis in smectites. In: Clays Controlling the Environment [Eds. G. J. Churchman, R. W. Fitzpatrick and R. A. Eggleton]. Proc. 10th Int. Clay Conf., Adelaide, Australia, 1993. CSIRO Publishing, Melbourne, Australia, pp 173 - 177.

Vermeul, R. M. (1996). Cadmium removal from phosacid. In: Fertilizers as a Source of Cadmium - OECD Proceedings. OECD, Paris, pp 31 - 40.

Vernet, J. -P. [Ed] (1991). Heavy Metals in the Environment. Trace metals in the Environment 1. Elsevier, Amsterdam, 405 pp.

Versieck, J. and Vanballenberghe, L. (1994). Collection, transport, and storage of biological samples from the determination of trace metals. In: Handbook on Metals in Clinical and Analytical Chemistry [Eds. H. G. Seiler, A. Sigel and H. Sigel], Marcel Dekker, New York, pp 31 - 44.

Walkley, A. (1940). The zinc content of some Australian fertilizers. *Journal of the Council for Scientific and Industrial Research* **13**: 255 - 260.

Watanabe, F.S. and Olsen, S.R. (1965). Test of ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. *Soil Science Society of America Proceedings* **29**: 677 - 678.

Webb, M. [Ed] (1979). The Chemistry, Biochemistry and Biology of Cadmium. Elsevier/ North-Holland Biomedical Press, 465 pp.

Weiner, J. and Grodzinski, W. (1984). Energy, nutrient and pollutant budgets of the forest ecosystem. In: Forest Ecosystems in Industrial Regions: studies on the cycling of energy, nutrients, and pollutants in the Niepolomice Forest, southern Poland [Eds. W. Grodzinski, J. Weiner and P. F. Maycock]. Springer-Verlag, Berlin, pp 203 - 229.

Welz, B. (1994). Atomic absorption spectrometry. In: *Handbook on metals in clinical and analytical chemistry* [Eds H.G. Seiler, A. Sigel and H. Sigel], Marcel Dekker, New York, pp 85 - 106.

Werner, W., Venanzoni, R. and Wittig, R. (1987). Trunk base phenomena in Italian beech forests. A comparison with Central European conditions. *Acta Oecologica, Oecologia Plantarum* **8**: 359 - 374.

Whitton, J. S, and Churchman, G. J. (1987). Standard methods for mineral analysis of soil survey samples for characterisation and classification. In: NZ Soil Bureau Scientific Report **79**, 27 pp.

212

WHO (1992a). Cadmium: Environmental Health Criteria; 134. International Programme on Chemical Safety, World Health Organization, Geneva, 1992, 280 pp. (First draft Prepared by L. Friberg, C. G. Elinder and T. Kjellström)

WHO (1992b). Cadmium - Environmental Aspects: Environmental Health Criteria; 135. International Programme on Chemical Safety, World Health Organization, Geneva, 1992, 156 pp. (First draft Prepared by S. Dobson)

Wiklander, L. and Andersson, A. (1974). The composition of the soil solution as influenced by fertilization and nutrient uptake. *Geoderma* **11**: 157 - 166.

Williams, C. H. (1974). Heavy metals and other elements in fertilisers - environmental considerations. In: Fertilisers and the Environment. [Editor D. R Leece] Australian Institute of Agricultural Science, Sydney, pp 123 - 130.

Williams, C. H. (1977). Trace metals and superphosphate: toxicity problems. *Journal of the Australian Institute of Agricultural Science* **43**: 99 - 109.

Williams, C. H. and 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. and David, D. J. (1976). The accumulation in soil of cadmium residues from phosphate fertilizers and their effect on the cadmium content of plants. *Soil Science* **121**: 86 - 93.

Williams, C. H. and David, D. J. (1977). Some effects of the distribution of cadmium and phosphate in the root zone on the cadmium content of plants. *Australian Journal of Soil Research* **15**: 59 - 68.

Williams, C. R. and Harrison, R. M. (1986). Cadmium in the atmosphere. In: Cadmium in the Environment (Experientia. Supplementum; vol. 50) [Eds. H. Mislin and O. Ravera], Birkhäuser Verlag, Basel, pp 17 - 24.

Williams, D. E., Vlamis, J., Pukite, A. H. and Corey, J. E. (1987). Metal movement in sludge-amended soils: a nine year study. *Soil Science* **143**: 124 - 131.

Williams, P. H. and Haynes, R. J. (1994). Comparison of initial wetting pattern, nutrient concentrations in soil solution and the fate of ^{15}N-labelled urine in sheep and cattle urine patch areas of pasture soil. *Plant and Soil* **162**: 49 - 59.

Williams, R. M (1985). The Phosphateers: A history of the British Phosphate Commissioners and the Christmas Island Phosphate Commission. Carlton, Melbourne University Press, 586 pp.

Witter, E. (1996). Towards zero accumulation of heavy metals in soils. *Fertilizer Research* **43**: 225 - 233.

Wolff, E. W. and Peel, D. A. (1985). The record of global pollution in ppolar snow and ice. *Nature* (London) **313**: 535 - 540.

Wolt, J. D. (1994). Soil Solution Chemistry: Applications to Environmental Science and Agriculture. John Wiley and Sons, Inc., New York, 345 pp.

Wopereis, M. C., Gascuel-Odoux, C., Bourrie, G. and Soignet, G. (1988). Spatial variability of heavy metals in soil on a one-hectare scale. *Soil Science* **146**: 113 - 118.

Yao, T. and Hendrickx, J. M. H. (1996). Stability of wetting fronts in dry homogeneous soils under low infiltration rates. *Soil Science Society of America Journal* **60**: 20 - 28.

Yasumura, S., Vartsky, D., Ellis, K. J. and Cohn, S. H. (1980), Cadmium in human beings. In: Cadmium in the Environment, Part I: Ecological Cycling [Ed. J. O. Nriagu]. John Wiley and Sons, New York, pp 12 - 34.

Yin, X., Schlemmer, G. and Welz, B. (1987). Cadmium determination in biological materials using graphite furnace atomic absorption spectrometry with palladium nitrate-ammonium nitrate modifier. *Analytical Chemistry* **59**: 1462 - 1466.

Yost, K. J. (1979). Some aspects of the environmental flow of cadmium in the United States. In: Cadmium Toxicity [Ed. J. H. Mennear], Marcel Dekker, Inc., New York, pp 181 - 206.

APPENDIX 1

GFAAS furnace programmes used for the determination of Cd concentrations in acid-digested soil and plant samples and leachate samples from Chapters 4, 5, 6, 7 and 8.

For graphite tube with oxalic acid as a modifier.

Step number	Final temp. ($^{\circ}C$)	Ramp time (s)	Hold time (s)	Gas Type	Signal read
1	20	1	0	N_2	
2	95	20	20	N_2	
3	300	15	20	Ar	
4	300	0	1	None	
5	950	1.5	2	None	Peak Area
6	2000	3	2	N_2	

For graphite tube with Pd/Mg(NO_3)$_2$ modifier and using either ascorbic acid or H_2 in the Ar purge gas as a reducing agent.

Step number	Final temp. ($^{\circ}C$)	Ramp time (s)	Hold time (s)	Gas Type	Signal read
1	20	1	0	N_2	
2	120	10	50	Ar	
3	800	5	20	Ar	
4	800	0	1	None	
5	1600	0.5	3	None	Peak Area
6	2500	3	2	N_2	

For graphite tube with L'vov platform and Pd/Mg(NO_3)$_2$ modifier and using either ascorbic acid or H_2 in the Ar purge gas as a reducing agent.

Step number	Final temp. ($^{\circ}C$)	Ramp time (s)	Hold time (s)	Gas Type	Signal read
1	85	1	10	None	
2	120	5	5	N_2	
3	200	20	40	Ar	
4	250	15	0	Ar	
5	800	5	20	Ar	
6	800	0	1	None	
7	1500	1	3	None	Peak Area
8	2300	1	1	N_2	

APPENDIX 2

Descriptions of modal soil profiles from the hill country farm of Limestone Downs as recorded by F. W. Krieger (Department of Soil Science, Massey University, Palmerston North). The locations of these profile sites are indicated on Map 1 – the Reconnaissance Soil Map of Limestone Downs.

Key to Figures:

Soil Cd: —   Total Cd
                                 (determined using an HF-based digestion)

                            --- Extractable Cd
                                 (determined using a 0.1 M HCl extraction)

Soil pH: ●

Total soil carbon: ▲

Profile 1:   Whangape clay loam (Wg)
Profile 2:   Wairama Hill soils (WaH)
Profile 3:   Mangapiko clay (Mpc)
Profile 4:   Mangapiko humic clay loam (Mphcl)
Profile 5:   Kotare Hill soils (KtH)
Profile 6:   Kotare clay loam (Ktcl)
Profile 7:   Ruakiwi Hill soils (RwH)
Profile 8:   Dunmore silt loam (Du)
Profile 9:   Kotare fine sandy loam (Kfsl)
Profile 10:   Horea Hill soils (HoH)
Profile 11:   Horea fine sandy loam (Ho)
Profile 12:   Tuahu sandy loam (Tu)
Profile 13:   Akatea steepland soil (AkS)
Profile 14:   Waingaro steepland soil (WnS)
Profile 15:   Kapamahunga steepland soils (KpS)
Profile 16:   Kohemarere Hill soils (KeH)
Profile 17:   Tauterei humic fine sandy loam (Tt)

Profile 1:   Whangape clay loam (Wg)

Location: Limestone Downs
Topography/Relief: Terrace flat, 2 - 3° north slope
Vegetation: Rye-clover dominated, rushes
Parent material: Rhyolitic alluvium
Drainage: Imperfectly of somewhat poorly drained
Soil group: Yellow-brown earth

Horizon	Depth	Description
Ap	0 - 17 cm	Dark brown (10YR3/3) silt loam; very friable; moderately developed fine crumb structure; non-sticky, slightly plastic; many very fine to fine roots; diffuse, irregular boundary.
AB	17 - 32 cm	Yellowish brown (10YR5/4) silty clay loam; friable; moderately developed fine crumb to fine granular structure; slightly sticky, slightly plastic; common very fine roots; indistinct, wavy boundary.
Bt	32 - 55 cm	Yellowish brown (10YR5/6) silty clay; firm; moderately developed fine nut structure; sticky, plastic; few, fine, distinct manganese nodules; few very fine roots; indistinct, wavy boundary.
Btg	55 - 105 cm	Yellowish brown (10YR5/6) clay; firm; strongly developed fine nut to fine block structure; sticky, plastic; common, fine, distinct ochreous (10YR7/8, yellow) mottles; low chroma mottles (10YR8/1, white) begin at 75 cm; few, fine, distinct manganese nodules; distinct, smooth boundary.
Brg	105 + cm	Yellowish brown (10YR5/6) clay; firm; strongly developed fine nut to fine block structure; sticky, plastic; common, fine, distinct ochreous (10YR7/8, yellow) mottles; reduced low chroma mottles (10YR8/1, white); few, fine, distinct manganese nodules.
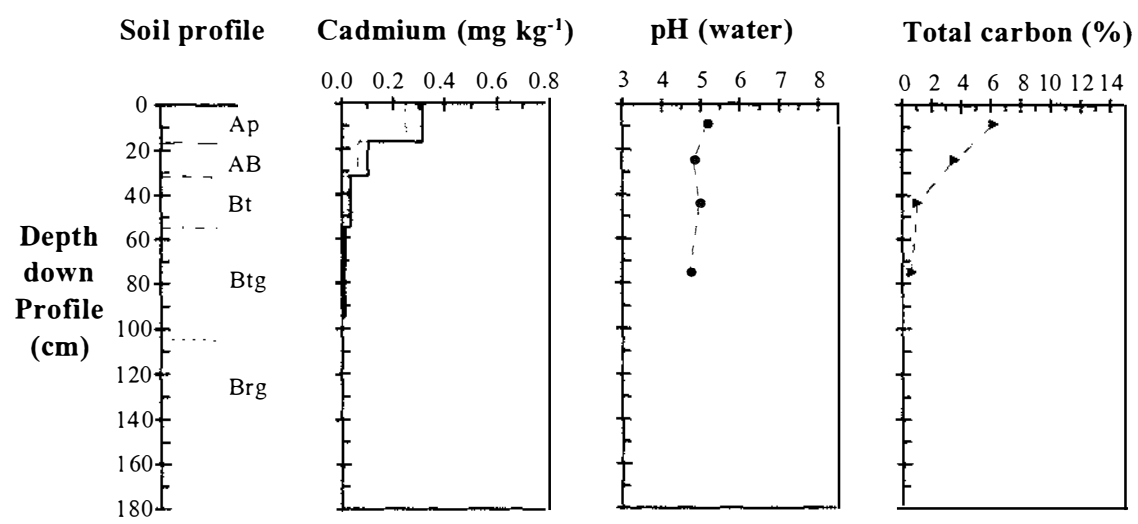
Profile 2: Wairama Hill soils (WaH)

Location:	Limestone Downs
Topography/Relief:	North-facing, 12 - 15° hill slope
Vegetation:	Rye-clover dominated
Parent material:	Calcareous siltstone, may also contain local bands of sandstone and low grade limestone
Drainage:	Moderately well drained
Soil group:	Yellow-brown earth

Horizon	Depth	Description
Ap	0 - 11 cm	Dark greyish brown (10YR4/2) silt loam; friable; moderately developed fine crumb to granular structure; slightly sticky, slightly plastic; many very fine to fine roots; distinct, irregular boundary.
AB	11 - 22 cm	Yellowish brown (10YR5/4) clay loam; firm; moderately developed fine nut structure; slightly sticky, slightly plastic; common very fine roots; indistinct, irregular boundary.
Bt	22 - 35 cm	Light yellowish brown (10YR6/4) clay; firm; strongly developed fine to medium nut, and fine to medium block structure; sticky, plastic; indistinct, wavy boundary.
Btg	35 - 100+ cm	Yellow (10YR7/8) clay; firm; strongly developed medium to coarse block structure; sticky, plastic; many, fine to medium, ochreous (7.5YR7/8, reddish yellow) mottles with distinct and clear boundary, decrease down profile; few, fine to medium distinct low chroma (7.5YR7/0, light grey) mottles with diffuse boundary, increase down profile.
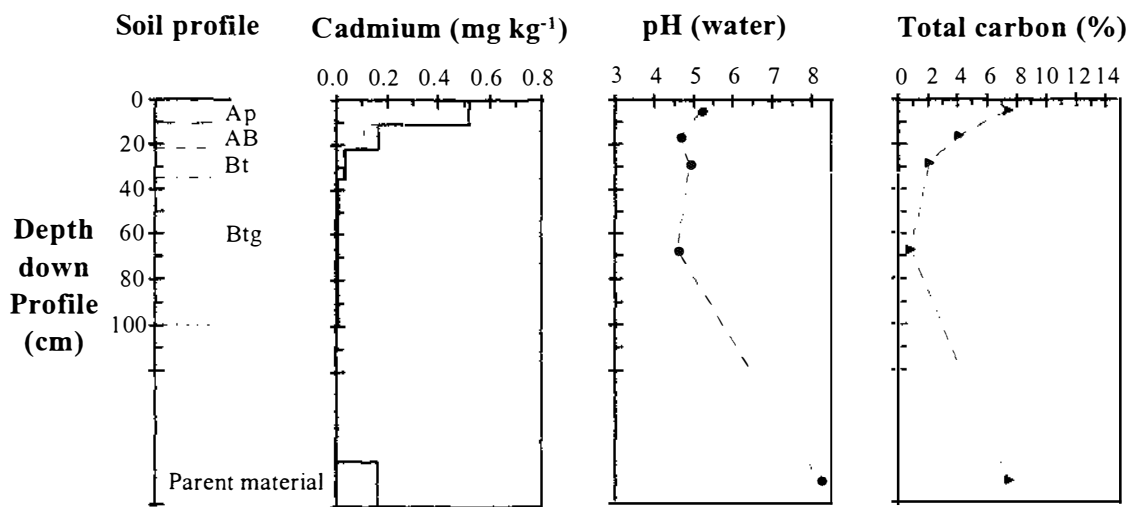
Profile 3:   Mangapiko clay (Mpc)

Location:	Limestone Downs
Topography/Relief:	Low-lying, swampy flats, humped and hollowed. Site on a hump
Vegetation:	Rye-clover dominated and many rushes
Parent material:	Alluvium of mixed origin
Drainage:	Poorly drained
Soil group:	Gley recent soils

Horizon	Depth	Description
Ap	0 - 4 cm	Greyish brown (10YR5/2) silty clay; very friable; weakly developed fine nut structure; sticky, plastic; common, fine, distinct ochreous (2.5YR5/8, red) mottles with clear boundaries along root channels; many very fine to fine roots (to 20 cm depth); indistinct, irregular boundary.
Btg	4 - 30 cm	Light yellowish brown (10YR6/4) clay loam; friable; weakly developed fine to medium nut structure; sticky, plastic; many fine to medium ochreous (2.5YR5/8, red) mottles, not only along root channels; few, fine, distinct manganese nodules.
	30 cm	Water Table

Soil profile   Cadmium (mg kg⁻¹)   pH (water)   Total carbon (%)
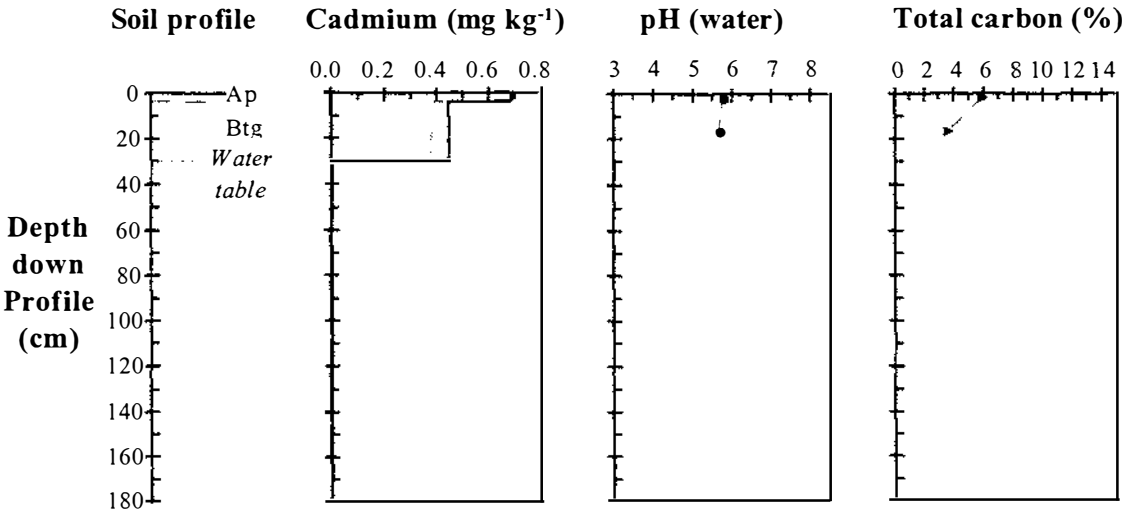
Profile 4:   Mangapiko humic clay loam (Mphcl)

Location: Limestone Downs
Topography/Relief: Low-lying, swampy flats, humped and hollowed. Site on a hump
Vegetation: Rye-clover with high percentage (10 - 20%) of rushes and
                      buttercup
Parent material: Alluvium of mixed origin
Drainage: Very poorly drained
Soil group: Gley recent soils

Horizon	Depth	Description
Ap/O	0 - 6 cm	Greyish brown (10YR5/2) silty clay; friable; weakly developed fine nut structure; sticky, plastic; common, fine, distinct ochreous (2.5YR5/8, red) mottles with clear boundaries along root channels; many very fine to fine roots (to 20 cm depth); indistinct, irregular boundary.
Bgt	6 - 30 cm	Light yellowish brown (10YR6/4) clay loam; friable; weakly developed fine to medium nut structure; sticky, plastic; many fine to medium ochreous (2.5YR5/8, red) mottles, not only along root channels; few, fine, distinct manganese nodules; distinct, wavy boundary.
Br	30 - 50 cm	Light brownish grey (2.5Y6/2) clay; very friable; lacking apparent structure, possibly due to high water content at time of mapping; very sticky, plastic.
Br	50 cm	Water Table

222
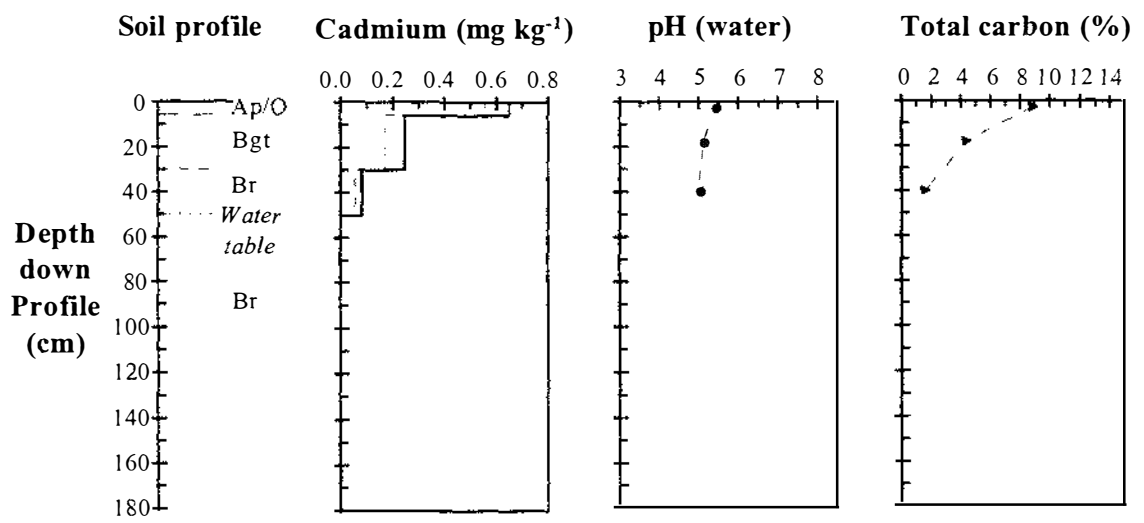
Profile 5:   Kotare Hill soils (KtH)

Location: Limestone Downs
Topography/Relief: North-facing, 10 - 12°, hill slope
Vegetation: Rye-clover dominated but poor pasture, some rushes
Parent material: Hamilton ash
Drainage: Imperfectly or somewhat poorly drained
Soil group: Brown granular loam

Horizon	Depth	Description
Ah	0 - 7 cm	Very dark greyish brown (10YR3/2) sandy clay loam; friable; moderately developed fine nut and fine to medium granular structure; non-sticky, slightly plastic; common, very fine to medium roots; sharp, irregular boundary.
Btg$_1$	7 - 30 cm	Pale brown (10YR6/3) sandy clay; firm; moderately developed fine to medium block and nut structure; slightly sticky, slightly plastic; many medium to coarse, prominent, sharp, ochreous (10YR6/8, brownish yellow) mottles; indistinct, wavy boundary.
Btg$_2$	30 - 60 cm	Yellowish brown (10YR5/8) sandy clay (slightly sandier than Btg$_1$); firm; moderately developed fine to medium block and nut structure; slightly sticky, slightly plastic; many medium to coarse, prominent, sharp, ochreous (10YR6/8, brownish yellow) mottles; diffuse, irregular boundary.
Br	60 - 100+ cm	Very pale brown (10YR8/3) sandy clay; firm; weakly developed medium to coarse block structure; slightly sticky, slightly plastic.
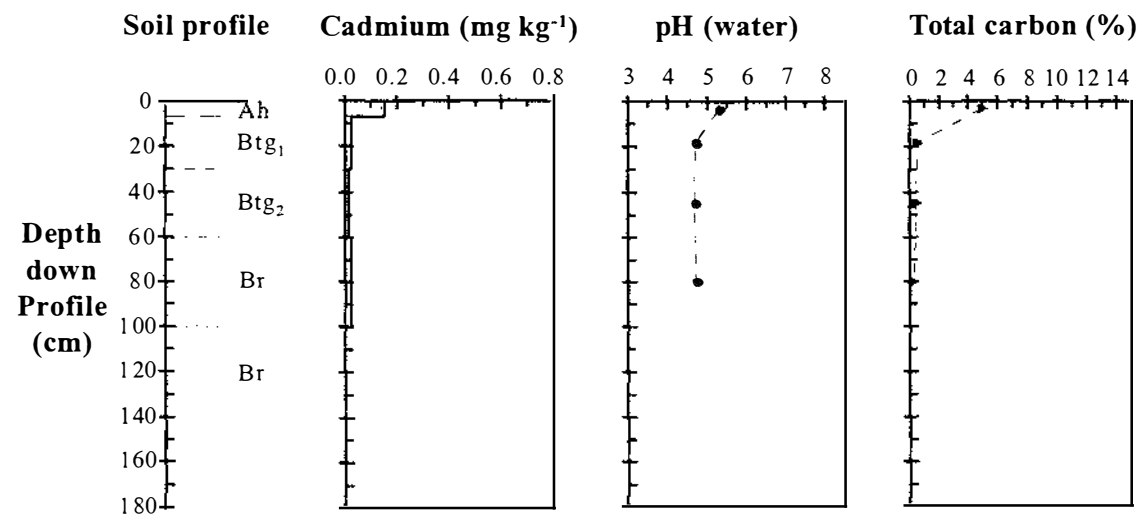
Profile 6: Kotare clay loam (Ktcl)

Location: Limestone Downs
Topography/Relief: Westward sloping, 3 - 5°, hill crest
Vegetation: Rye-clover dominated
Parent material: Hamilton ash
Drainage: Well drained
Soil group: Brown granular loam

Horizon	Depth	Description
Ap	0 - 6 cm	Dark greyish brown (10YR4/2) clay loam; very friable; moderately developed fine crumb to nut structure; non-sticky, slightly plastic; abundant very fine to fine roots; six worms; indistinct, irregular boundary.
AB	6 - 19 cm	Strong brown (7.5YR5/6) clay loam; friable; moderately developed fine to medium nut and block structure; slightly sticky, slightly plastic; many fine to very fine roots; diffuse, irregular boundary.
Bt$_1$	19 - 64 cm	Yellowish brown (10YR5/8) clay loam; firm; moderately developed fine to medium nut and block structure; slightly sticky, slightly plastic; common fine roots; distinct, smooth boundary.
Bt$_2$	64 - 84 + cm	Dark yellowish brown (10YR4/4) clay; very firm; moderately developed medium block and fine prism structure; sticky, plastic; prominent clay skins; no roots.

224
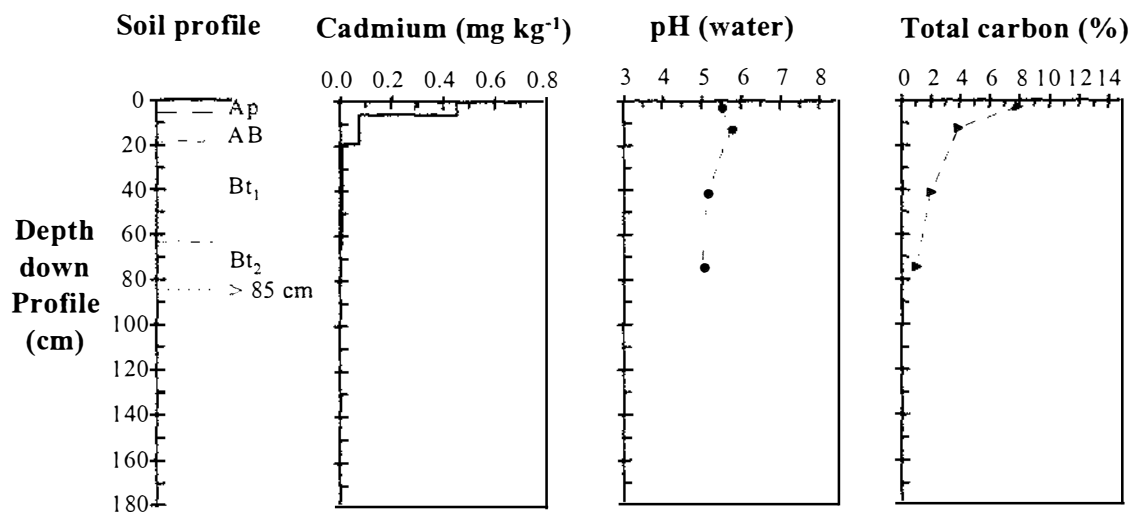
Profile 7:   Ruakiwi Hill soils (RwH)

Location: Limestone Downs
Topography/Relief: East-facing, 22° hill slope
Vegetation: Rye-clover dominated, rushes
Parent material: Calcareous siltstone, with prominent outcrops of bands of
                       calcareous sandstone
Drainage: Imperfectly drained
Soil group: Yellow-brown earth

Horizon	Depth	Description
Ap	0 - 17 cm	Grey (10YR5/1) clay loam; very firm; moderately developed fine to coarse nut and block structure; slightly sticky, plastic; Many fine to medium roots; no worms; sharp, wavy boundary.
Bt	17 - 32 cm	Yellowish brown (10YR5/6) clay; extremely firm; weakly developed medium to coarse block structure; slightly sticky, plastic; few fine roots; distinct, wavy boundary.
Btg	32 - 74 cm	Yellowish brown (10YR5/6) clay; extremely firm; weakly developed medium to coarse block structure; slightly sticky, plastic; common, fine, distinct ochreous (2.5YR4/8, red) mottles with clear boundary; no roots; sharp, wavy boundary.
C	74 - 140+ cm	Weathered , fractured siltstone parent material.

Profile 8:   Dunmore silt loam (Du)

Location: Limestone Downs
Topography/Relief: Flat, 2° west slope
Vegetation: Rye-clover dominated
Parent material: Volcanic ash
Drainage: Well drained
Soil group: Yellow-brown loam

Horizon	Depth	Description
Ap	0 - 13 cm	Very dark brown (10YR2/2) silt loam; very friable; moderately developed coarse to fine granular and crumb structure; non-sticky, slightly plastic; many very fine to fine roots; worms and grass-grub; distinct, wavy boundary.
AB	13 - 29 cm	Dark yellowish brown (10YR4/4) silt loam; very friable; moderately developed fine to medium granular and fine nut structure; non-sticky, slightly plastic; common fine roots; grass-grubs, no worms; indistinct, wavy boundary.
Bt $_1$	29 - 60 cm	Strong brown (7.5YR5/6) clay loam; friable; moderately developed fine to medium nut and block structure; slightly sticky, slightly plastic; few fine roots; distinct, smooth boundary.
Bt $_2$	60 - 100+ cm	Strong brown (7.5YR5/6) clay loam; firm; moderately developed fine to medium block and nut structure; sticky, plastic; no roots.

Soil profile   Cadmium (mg kg^{-1})   pH (water)   Total carbon (%)

226
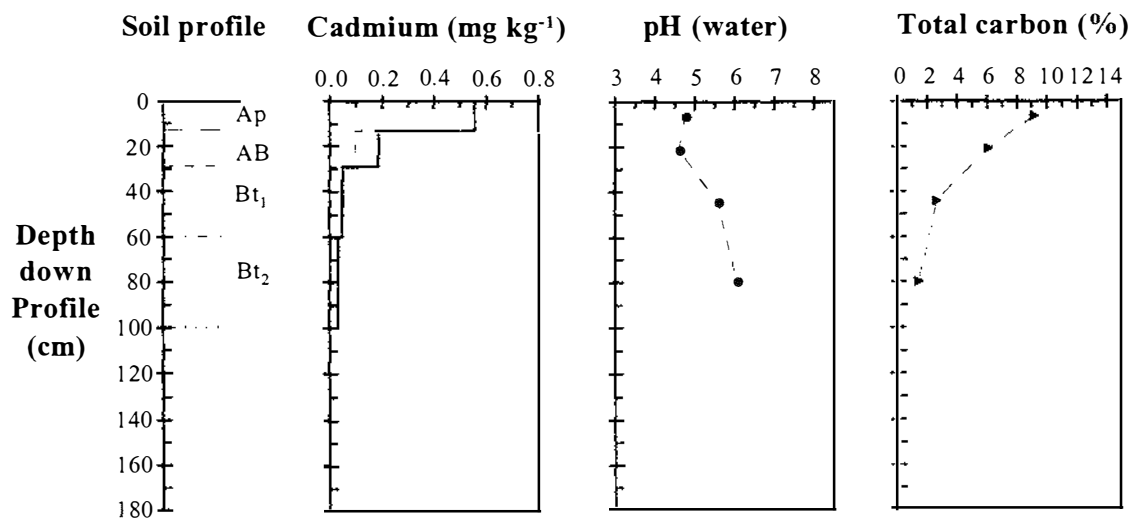
Profile 9:   Kotare fine sandy loam (Kfsl)

Location: Limestone Downs
Topography/Relief: Flat ridge crest between two gullies, 5° slope west
Vegetation: Rye-clover dominated
Parent material: Hamilton ash
Drainage: Well drained
Soil group: Brown granular loam

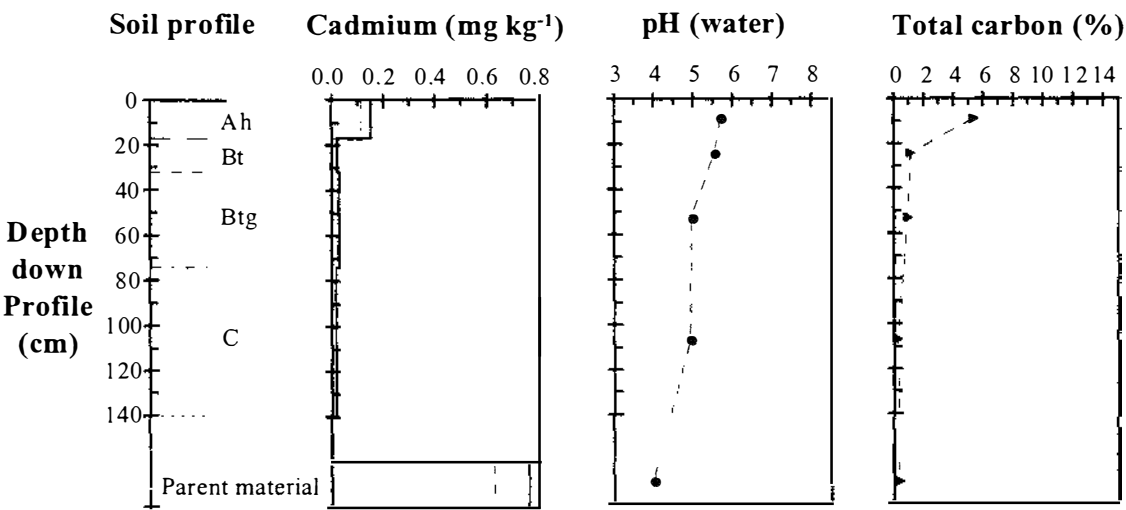| Horizon	Depth	Description
Ap	0 - 22 cm	Very dark brown (10YR2/2) very fine sandy loam; very friable; strongly developed fine to medium granular and fine crumb structure; non-sticky, slightly plastic; about 5% charcoal present; abundant very fine to fine roots; worms; indistinct, irregular boundary.
AB	22 - 39 cm	Dark yellowish brown (10YR4/4) silt loam; very friable; moderately developed medium to fine granular and fine nut structure; very rare charcoal; non-sticky, slightly plastic; many fine to very fine roots; no worms; distinct, wavy boundary.
Bt$_1$	39 - 64 cm	Strong brown (7.5YR5/6) clay loam; friable; moderately developed fine to medium nut and block structure; slightly sticky, slightly plastic; few fine roots; sharp, smooth boundary.
Bt$_2$	64 - 100+ cm	Strong brown (7.5YR5/6) clay loam; firm; moderately developed fine to medium block and nut structure; sticky, plastic; no roots.
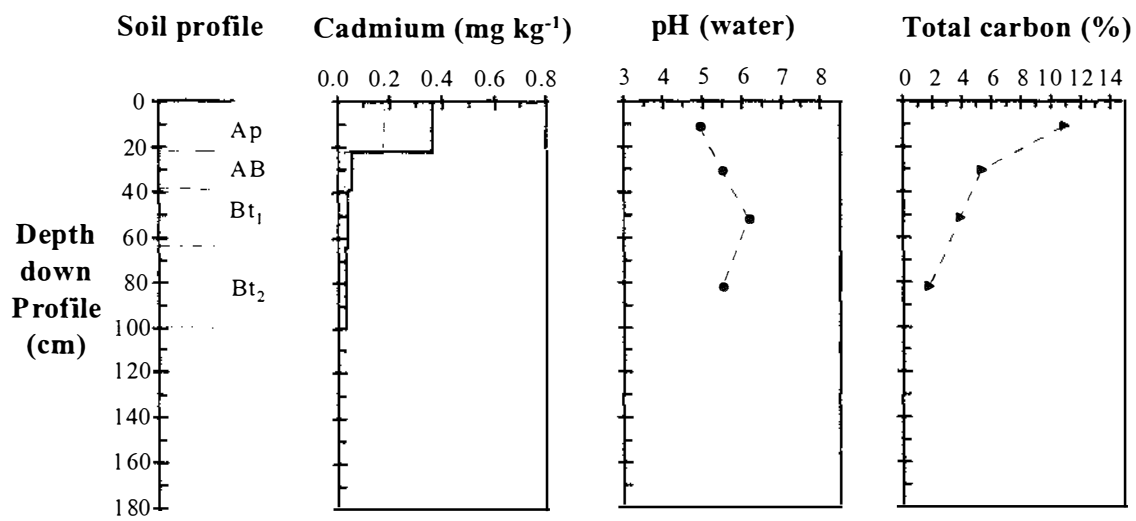
Profile 10: Horea Hill soils (HoH)

Location: Limestone Downs
Topography/Relief: South-west facing hill slope of about 20°
Vegetation: Rye-clover dominated
Parent material: Weathered black sand and admixed volcanic ash
Drainage: Imperfectly drained. Drainage would be worse if not for slope.
Soil group: Intergrades between yellow-brown earths and yellow-brown sands.

Horizon	Depth	Description
Ah	0 - 20 cm	Very dark greyish brown (10YR3/2) fine sandy loam; very friable; moderately developed fine to medium granular, to fine nut structure; non-sticky, slightly plastic; many very fine to fine roots; few worms; indistinct, irregular boundary.
AB	20 - 36 cm	Dark greyish brown (10YR4/2) sandy clay loam; friable; moderately developed fine to medium nut structure; slightly sticky, slightly plastic; lumps or sandy parent material; common very fine roots; rare worms; distinct, wavy boundary.
Bt	36 - 116 cm	Yellowish brown (10YR5/6) sandy clay; firm; weakly developed fine to coarse block structure; sticky, plastic; iron staining around weathered lumps of sand; few very fine roots; indistinct, wavy boundary.
Btg	116 - 150+ cm	Yellowish brown (10YR5/6) sandy clay; firm; very weak blocky structure; sticky, plastic; many, distinct, medium to coarse light grey (10YR6/1) low chroma mottles, with a diffuse boundary; common, distinct, fine ochreous (10R4/6, red) mottles, with clear boundaries; no roots.
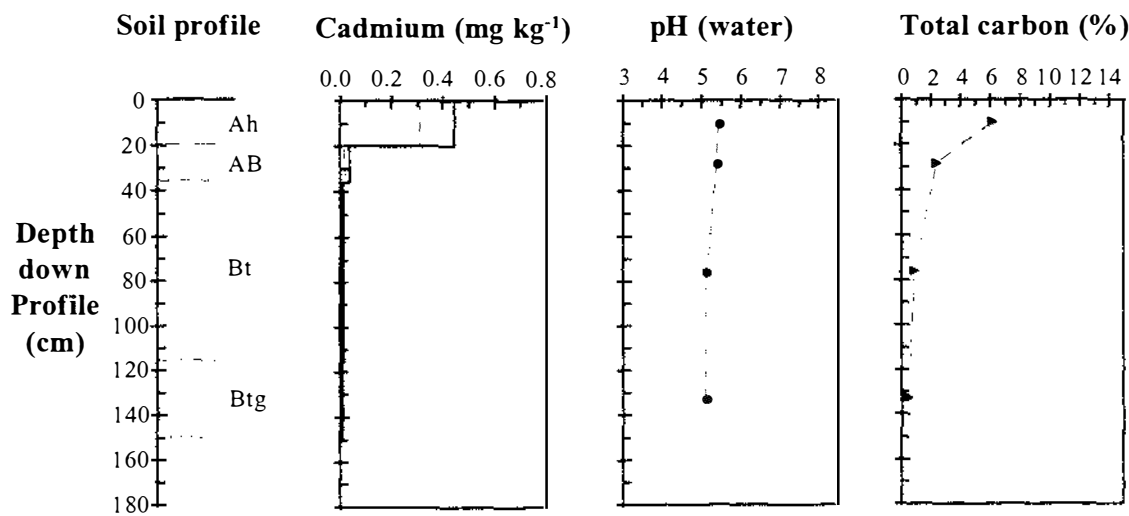
Profile 11:   Horea fine sandy loam (Ho)

Location: Limestone Downs
Topography/Relief: North-facing slope of 7°
Vegetation: Rye-clover dominated, also kikuya and rushes
Parent material: Weathered black sand and admixed volcanic ash
Drainage: Imperfectly drained.
Soil group: Intergrades between yellow-brown earths and yellow-brown
                       sands.

Horizon	Depth	Description
Ah	0 - 40 cm	Very dark brown (10YR2/2) fine sandy loam; friable; moderately developed fine to medium nut structure; slightly sticky, slightly plastic; many very fine to fine roots; few worms; indistinct, wavy boundary.
ABg	40 - 58 cm	Dark greyish brown (10YR4/2) sandy clay loam; firm; weakly developed fine to medium nut structure; sticky, plastic; common, fine, distinct brownish yellow (10YR6/8) ochreous mottles with a diffuse boundary; indistinct, wavy boundary.
Btg	58 - 100+ cm	Yellowish brown (10YR5/4) sandy clay; firm; weakly developed block structure; sticky, plastic; mottles increase from common to many, fine to medium, distinct mottles with clear boundary; low chroma (10YR8/3, very pale brown) mottles are profuse by 100 cm. Water seeps above Btg boundary
Ah-ABg	30 - 50 cm	Shells

Soil profile   Cadmium (mg kg⁻¹)   pH (water)   Total carbon (%)

Shells
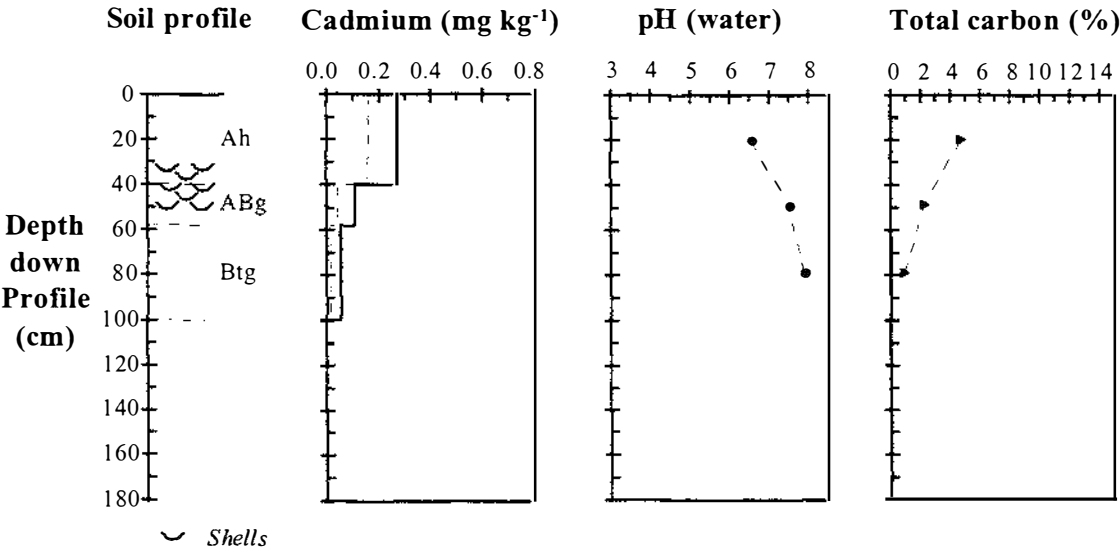
Profile 12:   Tuahu sandy loam (Tu)

Location: Limestone Downs
Topography/Relief: South-facing slope of 15°
Vegetation: Rye-clover dominated
Parent material: Wind-blown sand and minor amounts of volcanic ash
Drainage: Well drained.
Soil group: Yellow-brown sands.

Horizon	Depth	Description
Ah	0 - 31 cm	Dark brown (10YR3/3) very fine sandy loam; very friable; moderately developed fine to medium granular and fine nut structure; non-sticky, slightly plastic; Abundant very fine to fine roots; few worms; indistinct, irregular boundary.
AB	31 - 59 cm	Dark yellowish brown (10YR4/4) sandy loam; friable; weakly developed medium block to fine nut structure; slightly sticky, slightly plastic; common very fine roots; no worms; sharp, smooth boundary.
Bt	59 - 118 cm	Yellowish brown (10YR5/8) sandy clay loam; friable; weakly developed fine to medium blocky structure; sticky, slightly plastic; no worms and no roots; sharp, smooth boundary.
C	118 - 160+ cm	Very dark greyish brown (2.5Y3/2); structureless.
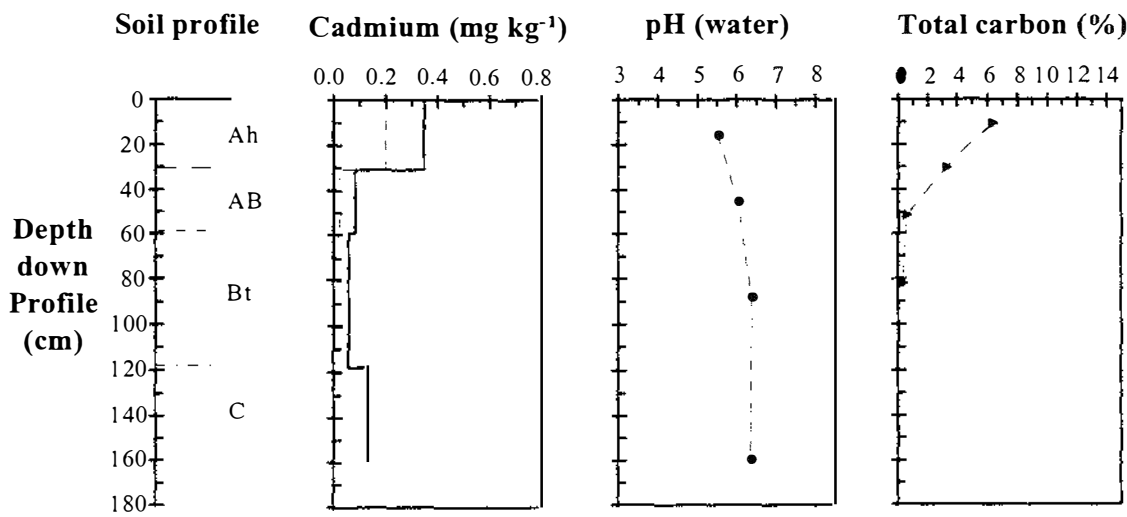
Profile 14: Waingaro steepland soil (WnS)

Location: Limestone Downs
Topography/Relief: South-east-facing slope of 29°
Vegetation: Rye-clover dominated with occasional rushes
Parent material: Argillite and greywacke
Drainage: Imperfectly drained. Drainage would be worse if not for slope.
Soil group: Steepland soils related to yellow-brown earths.

Horizon	Depth	Description
Ah	0 - 8 cm	Dark brown (10YR3/3) clay loam; friable; moderately developed fine to medium granular and fine nut structure; non-sticky, slightly plastic; many fine roots; no worms; distinct, wavy boundary.
AB	8 - 28 cm	Brown (10YR5/3) clay loam (higher clay content than Ah); firm; weakly developed fine to medium block structure; slightly sticky, slightly plastic; common fine roots; distinct, irregular boundary.
Btg	28 - 140 cm	Brownish yellow (10YR6/6) clay; very firm; moderately developed block structure; very sticky, very plastic; few, fine, distinct ochreous (10YR6/8, brownish yellow) mottles with diffuse boundary, decreasing down horizon; distinct, wavy boundary. Decreasing from bottom of horizon upwards: weakly developed medium to coarse block to prism structure; profuse, medium to coarse, prominent low chroma (10YR7/1, light grey) mottles with clear boundaries
C	140+ cm	Weathered fractured greywacke
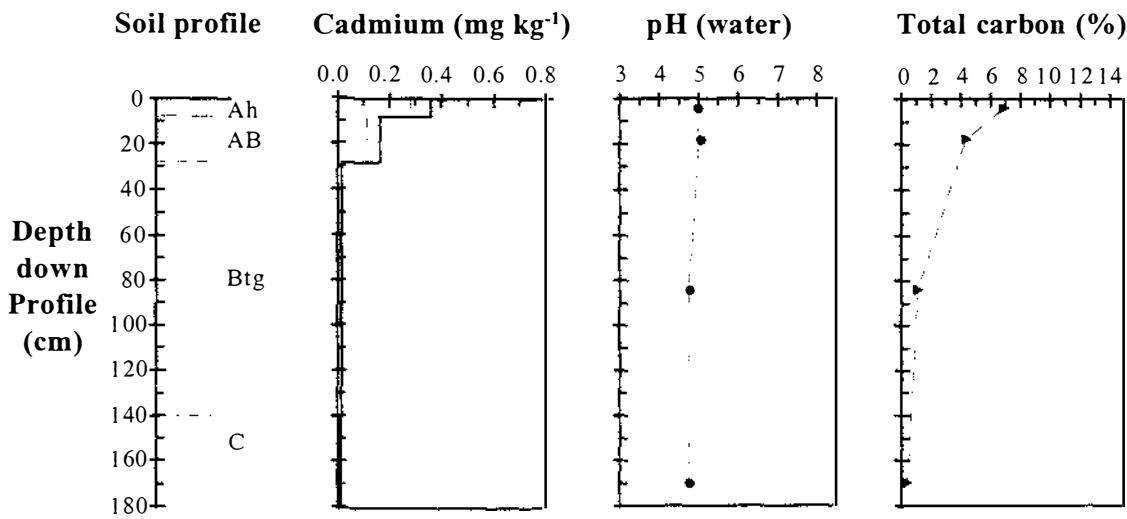
Profile 15:   Kapamahunga steepland soils (KpS)

Location: Limestone Downs
Topography/Relief: South-east-facing slope of 32°
Vegetation: Rye-clover dominated, common rushes
Parent material: Calcareous sandstone
Drainage: Imperfectly drained. Drainage would be worse if not for slope.
Soil group: Steepland soils related to yellow-brown earths.

Horizon	Depth	Description
Ah	0 - 20 cm	Dark brown (10YR3/3) very fine sandy loam; friable; moderately developed fine crumb to nut structure; slightly sticky, slightly plastic; many very fine to fine roots; no worms; indistinct, irregular boundary.
Bt	20 - 66 cm	Brownish yellow (10YR6/6) sandy clay; firm; moderately developed fine nut to medium block structure; sticky, plastic; common, very fine roots; distinct, wavy boundary.
Bts	66 - 110+ cm	Yellowish red (5YR5/8) sandy clay (sandier than Bt); firm; moderately developed medium to coarse block structure; sticky, plastic; no roots.
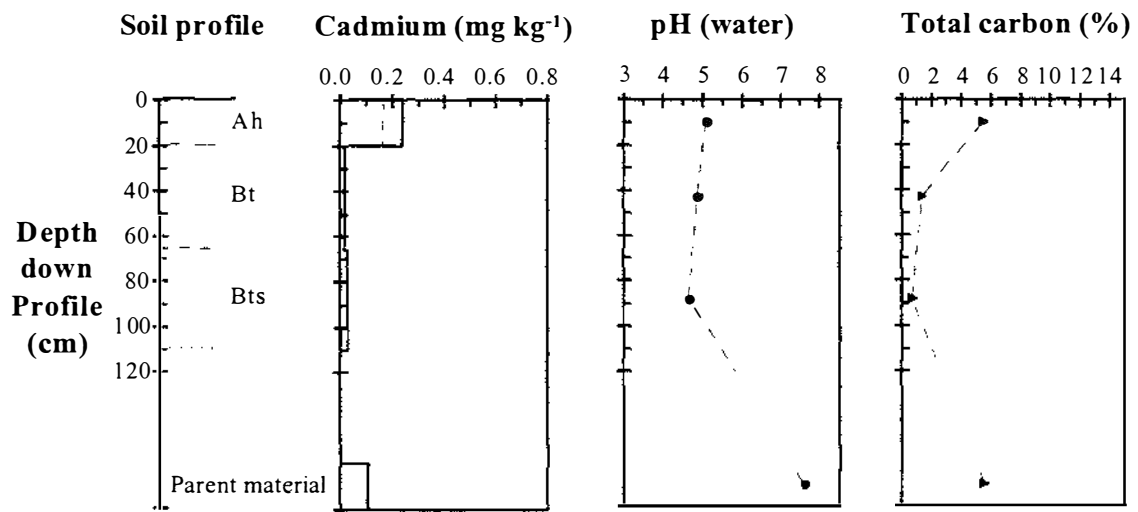
Profile 16:   Kohemarere Hill soils (KeH)

Location: Limestone Downs
Topography/Relief: East-facing slope of 15°
Vegetation: Rye-clover dominated, common rushes
Parent material: Calcareous sandstone, with local bands of siltstone and rare
                      limestone
Drainage: Imperfectly drained.
Soil group: Yellow-brown earths.

Horizon	Depth	Description
Ah	0 - 20 cm	Dark brown (10YR3/3) very fine sandy loam; friable; moderately developed fine crumb and fine nut structure; slightly sticky, slightly plastic; many fine roots; no worms; indistinct, irregular boundary.
Bt	20 - 66 cm	Brownish yellow (10YR6/6) sandy clay; firm; moderately developed fine nut to medium block structure; sticky, plastic; common very fine roots; distinct, wavy boundary.
Btg	66 - 110 cm	Brownish yellow (10YR6/8) fine sandy clay; weakly developed medium to coarse block structure; decreasing down horizon, common, fine to medium, distinct ochreous (2.5YR4/6, red) mottles with diffuse to clear boundaries; starting at 66 cm as few, fine, distinct low chroma (10YR7/1, light grey) mottles with clear boundaries, and becoming many, and coarse at 110 cm; sharp, wavy boundary.
C	110+ cm	Weathered sandstone

234
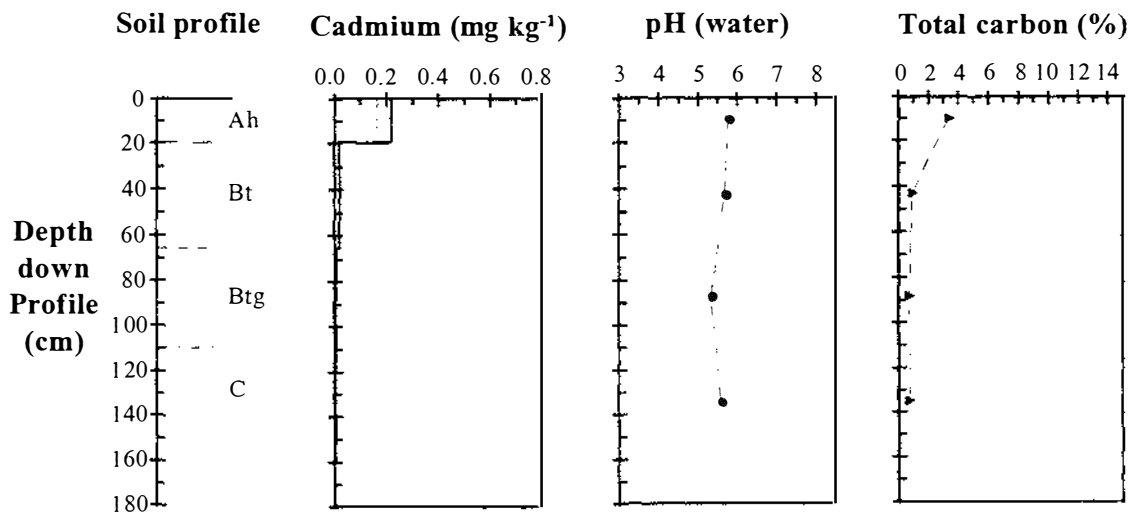
Profile 17:   Tauterei humic fine sandy loam (Tt)

Location: Limestone Downs
Topography/Relief: Site is flat and at the centre of a small depression that once
                     formed a small peat swamp
Vegetation: Rye dominated with rushes and buttercups
Parent material: Peat and inwash alluvium
Drainage: Imperfectly drained. Drainage is not as bad as expected due to
                     sandy nature of soil, and there is sufficient fall in the present
                     drainage system to allow run-off.
Soil group: Gley recent soils.

Horizon	Depth	Description
Ah	0 - 8 cm	Very dark brown (10YR2/2) very fine sandy loam; very friable; weakly developed fine crumb structure; non-sticky, non-plastic; abundant very fine to fine roots; no worms; distinct, wavy boundary.
Bw	8 - 22 cm	Dark brown (10YR3/3) very fine sandy loam; very friable; weakly developed fine crumb structure; non-sticky, non-plastic; many very fine to fine roots; sharp, smooth boundary.
Peat	22 - 50+ cm	Black (10YR2/1); no visible leaves, twigs, etc.
	50 cm	Water table
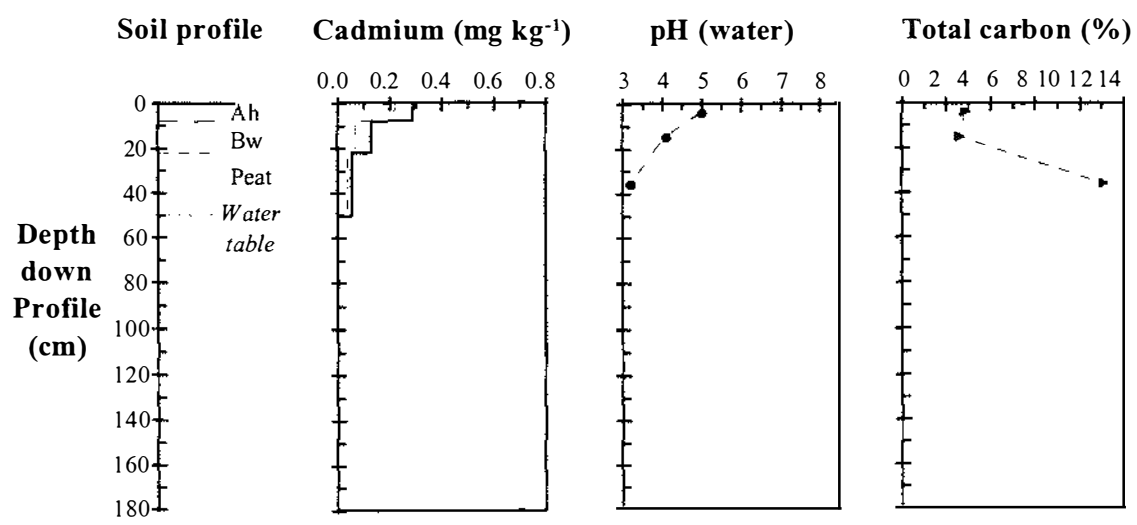
APPENDIX 3

Descriptions of soil profiles used to compare fertilized (pasture) and unfertilized (bush) sites on two soil types: Yellow-brown Loam (YBL) and Yellow-brown Earth (YBE); as recorded by A. S. Palmer (Department of Soil Science, Massey University, Palmerston North). The location of these sites are shown on Map 1 – the Soil Reconnaissance Map of Limestone Downs.

YBL-Fertilized

Vegetation: Pasture
Soil type: Yellow-brown Loam
                   Dunmore silt loam
Location: Limestone Downs
Topography/Relief: On shoulder, slope of 6° to east, and 200 m west of native bush

Horizon	Depth	Description
Ap_1	0 - 11	Dark brown to very dark greyish-brown (10YR3/3 - 3/2); loam; friable; strong fine nutty and fine granular structure; non-sticky, non-plastic; abundance of very fine roots; gradual boundary.
Ap_2	11 - 19	Very dark grey to very dark greyish-brown (10YR3/1 - 3/2); loam; friable; non-sticky, non-plastic; strong fine nutty and fine granular structure; some charcoal < 2%; abundance of very fine roots; gradual boundary.
AB_w	19 - 23	Dark brown (10YR4/3); loam; friable; non-sticky, non-plastic; strong fine nutty and strong fine granular structure; abundance of very fine roots; gradual boundary.
Bw_1	23 - 64	Yellowish brown (10YR5/7 - 5/8); loam; very friable; non-sticky, non-plastic; strong medium crumb and strong fine nutty structure; $^{++}$NaF; many very fine roots; gradual boundary.
Bw_2	64 - 92	Yellowish brown (10YR5/8); clay loam; friable; non-sticky, non-plastic; strong medium nutty structure; $^{++}$NaF; a few dark brown (10YR3/3) coatings on peds; common very fine roots; gradual boundary.
Bw_3	92 - 110+	Yellowish brown to strong brown (10YR5/8 - 7.5YR5/8); clay; firm; slightly sticky, plastic; moderate medium nut and moderate medium blocky structure; $^{++}$NaF; a few dark brown (10YR3/3) and yellowish red (5YR4/6) coatings on peds; no roots.

YBL-Unfertilized 1

Vegetation:	Broadleaf
Soil type:	Yellow-brown Loam
	Dunmore silt loam
Location:	Limestone Downs
Topography/Relief:	On shoulder, slope of 10° to east, 70 m into bush

Horizon	Depth	Description
L/F	2 - 0	Partly decomposed and undecomposed broadleaf litter; loose.
Ah	0 - 15	Dark brown (10YR3/3); loam; friable; non-sticky, non-plastic; strong fine granular and strong medium crumb structure; many very fine to medium roots; gradual boundary.
AB	15 - 23	Dark brown to dark yellowish brown (10YR3/3 - 4/3); loam; very friable; non-sticky, non-plastic; strong medium crumb structure; many very fine to medium roots; gradual boundary.
Bw_1	23 - 42	Yellowish brown (10YR5/7); loam; very friable; non-sticky, non-plastic; strong medium crumb structure; $^{++}$NaF; many very fine to medium roots; gradual boundary.
Bw_2	42 - 90	Yellowish brown (10YR4/6); loam; very friable; non-sticky, non-plastic; strong medium crumb and moderate medium nutty structure; $^{++}$NaF; many very fine to medium roots; gradual boundary.
Bw_3	90 - 110+	Yellowish brown (10YR4/6); clay loam; friable and firm; non-sticky, non-plastic; strong medium crumb and moderate medium nutty structure; $^{++}$NaF; many very fine to medium roots.

YBL-Unfertilized 2

Vegetation:	Podocarp - young and older Rimu trees
Soil type:	Yellow-brown Loam
	Dunmore silt loam
Location:	Limestone Downs
Topography/Relief:	On shoulder, slope of 10° to east, 70 m into bush but 15 m north of Site YBL-Unfertilized 1.

Horizon	Depth	Description
L/F	12 - 10	Mostly rimu litter
H	10 - 0	Dark reddish brown (5YR2.5/2); root mat; very friable; strong fine granular and strong medium crumb structure; spongy root mat and humus; abundance of medium roots; gradual boundary.
Ah	0 - 4	Dark brown (7.5YR3/3); loam; very friable; non-sticky, non-plastic; strong fine granular and strong medium crumb structure; many very fine roots; gradual boundary.
Bw_1	4 - 33	Yellowish brown (10YR5/6); loam; very friable; non-sticky, non-plastic; strong medium crumb structure; many very fine to coarse medium roots; gradual boundary.
Bw_2	33 - 72	Yellowish brown (10YR4/6); loam; very friable; non-sticky, non-plastic; strong medium crumb and moderate medium nutty structure; $^{++}$NaF; many very fine to medium roots; gradual boundary.
Bw_3	72 - 110+	Yellowish brown (10YR4/6); clay loam; friable and firm; non-sticky, non-plastic; strong medium crumb and moderate medium nutty structure; $^{++}$NaF; many very fine to medium roots.

YBE-Fertilized

Vegetation:	Pasture
Soil type:	Yellow-brown Earth
	Kohemarere hill soil
Location:	Limestone Downs
Topography/Relief:	Amongst Glen Massey Blocks, slope of 15° south-west.

Horizon	Depth	Description
Ah	0 - 8	Dark brown (10YR4/3); 5% fine, distinct, strong brown (7.5YR4/6) mottles; clay loam; slightly sticky and slightly plastic; strong medium nutty and fine blocky structure; abundant very fine roots; gradual boundary.
AB_w	8 - 16	80% Yellowish brown (10YR5/4); 10% strong brown (7.5YR5/8); 10% dark brown (10YR4/3) coarse distinct mottles; clay loam; sticky, plastic; moderate medium blocky structure; many very fine roots; gradual boundary.
Bg_1	16 - 38	60% Yellowish brown (10YR5/6); 20% strong brown (7.5YR5/8); 10% pale brown (10YR6/3); 10% yellowish brown (10YR5/4), coarse distinct mottles; clay; firm; very sticky, very plastic; strong medium blocky structure; yellowish brown (10YR5/4) coatings on peds; common very fine roots; gradual boundary.
Bg_2	38 - 75	Yellowish brown (10YR5/6); 10% pale brown (10YR6/3); 5% strong brown (7.5YR5/8) coarse distinct mottles; clay; very firm; very sticky, very plastic; strong medium blocky structure; few very fine roots; gradual boundary.
Bg_3	75 - 110+	40% reddish yellow (7.5YR6/6); 40% brownish yellow (10YR6/6); 10% yellowish brown (5YR5/8); 10% pale brown (10YR6/3), coarse prominent mottles; sandy clay; firm; moderate coarse blocky structure; few reddish coatings on peds; no roots.

YBE-Unfertilized

Vegetation:	Under podocarp with a broadleaf 5 m away
Soil type:	Yellow-brown Earth
	Kohemarere hill soil
Location:	Limestone Downs
Topography/Relief:	Well into bush, on concave foot slope, slope of 12° to south-east

Horizon	Depth	Description
L	5 - 2	Loose podocarp litter
F/H	2 - 0	Dark reddish brown (5YR3/2); humus; friable; abundance of roots; sharp boundary.
Ah	0 - 8	Dark brown (10YR4/3 - 3/3); common black (10YR2/1) mottles; silt loam; friable; slightly sticky, plastic; moderate fine nut and moderate fine block structure; common medium roots; gradual boundary.
AB_w	8 - 21	80% dark brown (10YR4/3); 10% dark brown (10YR3/3); 10% fine distinct, strong brown (7.5YR4/6) mottles; clay loam (sandy); sticky, plastic; moderate medium blocky and nutty structure; common medium roots; gradual boundary.
Bg_1	21 - 32	60% yellowish brown (10YR5/6); 20% strong brown (7.5YR4/6); 10% dark brown (10YR4/3); 10% pale brown (10YR6/3) medium distinct mottles; clay loam (sandy); sticky, very plastic; moderate medium blocky structure; few medium roots; gradual boundary.
Bg_2	32 - 78	80% yellowish brown (10YR5/8); 10% pale brown (10YR6/3); 10% yellowish red (5YR4/6) coarse prominent mottles; clay loam (sandy); very sticky, very plastic; moderate coarse blocky structure; few medium roots; few organic coatings on root channels; gradual boundary.
Bg_3	78 - 110+	80% yellowish brown (10YR5/8); 10% pale brown (10YR6/3); 10% yellowish red (5YR4/6) coarse prominent mottles; clay loam (sandy); very sticky, very plastic; moderate coarse blocky structure; few medium roots; few organic coatings on root channels; a few large stones.

APPENDIX 4

Plots of: **(a)** *the Cd concentration in the leachate; and* **(b)** *the final Cd concentration profile in the soil column; for replicated columns of Manawatu soil leached with 2.5 mM CaCl$_2$.*

The data were obtained during Experiment 1 (section 6.5.2) and Experiment 4 (6.5.5) of the laboratory-based leaching experiments discussed in Chapter 6.

Figure 1 presents the results from Cd-amended columns and Figure 2 presents the results from control columns. These figures illustrate the close agreement between results obtained from four replicated columns.
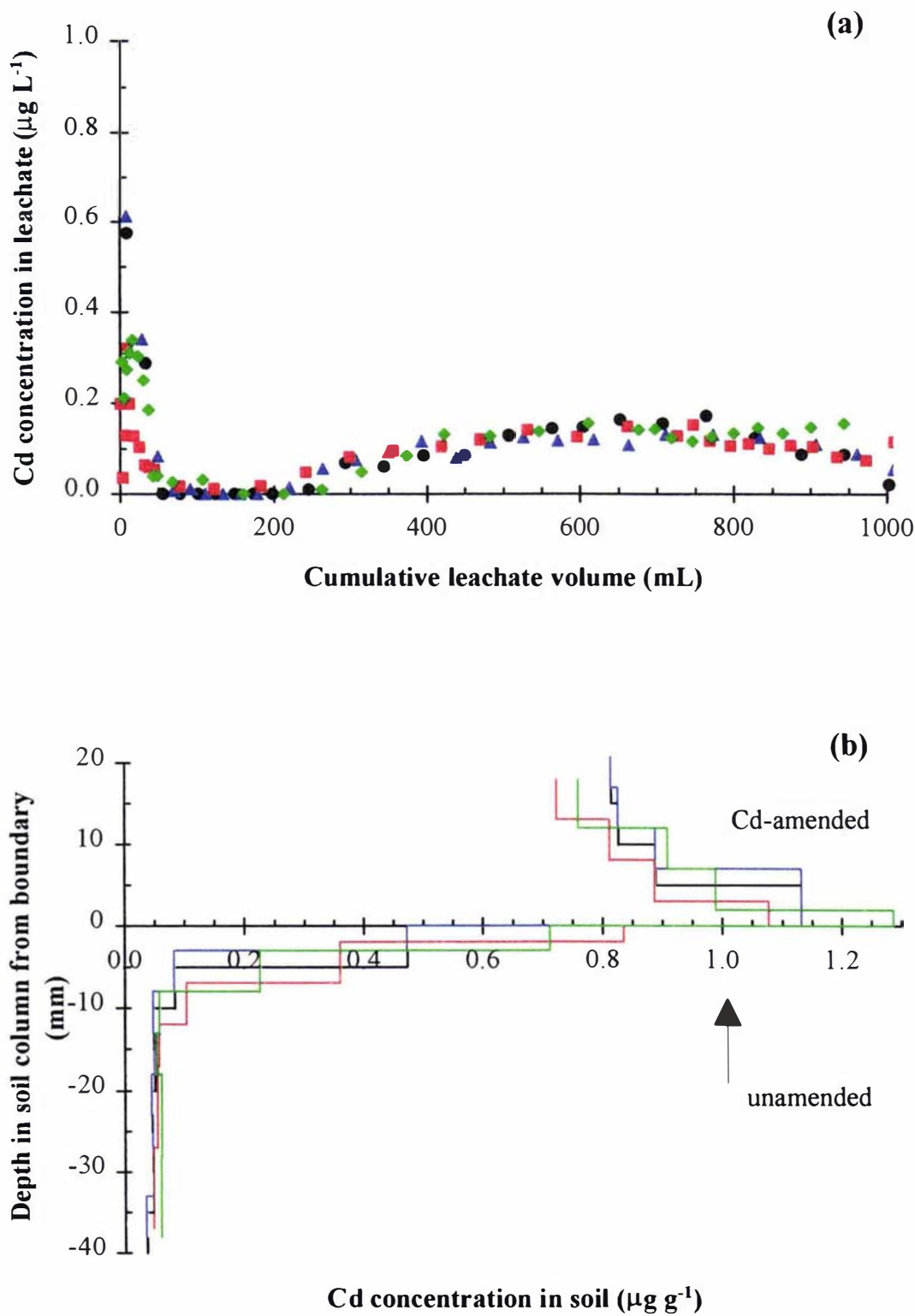
Figure 1 Plots of: *(a)* the Cd concentration in the leachate; and *(b)* the final Cd concentration profile in the soil column; for replicated Cd-amended columns of Manawatu soil leached with 2.5 mM $CaCl_2$. Arrow indicates initial Cd concentration in the Cd-amended soil of the top layer.
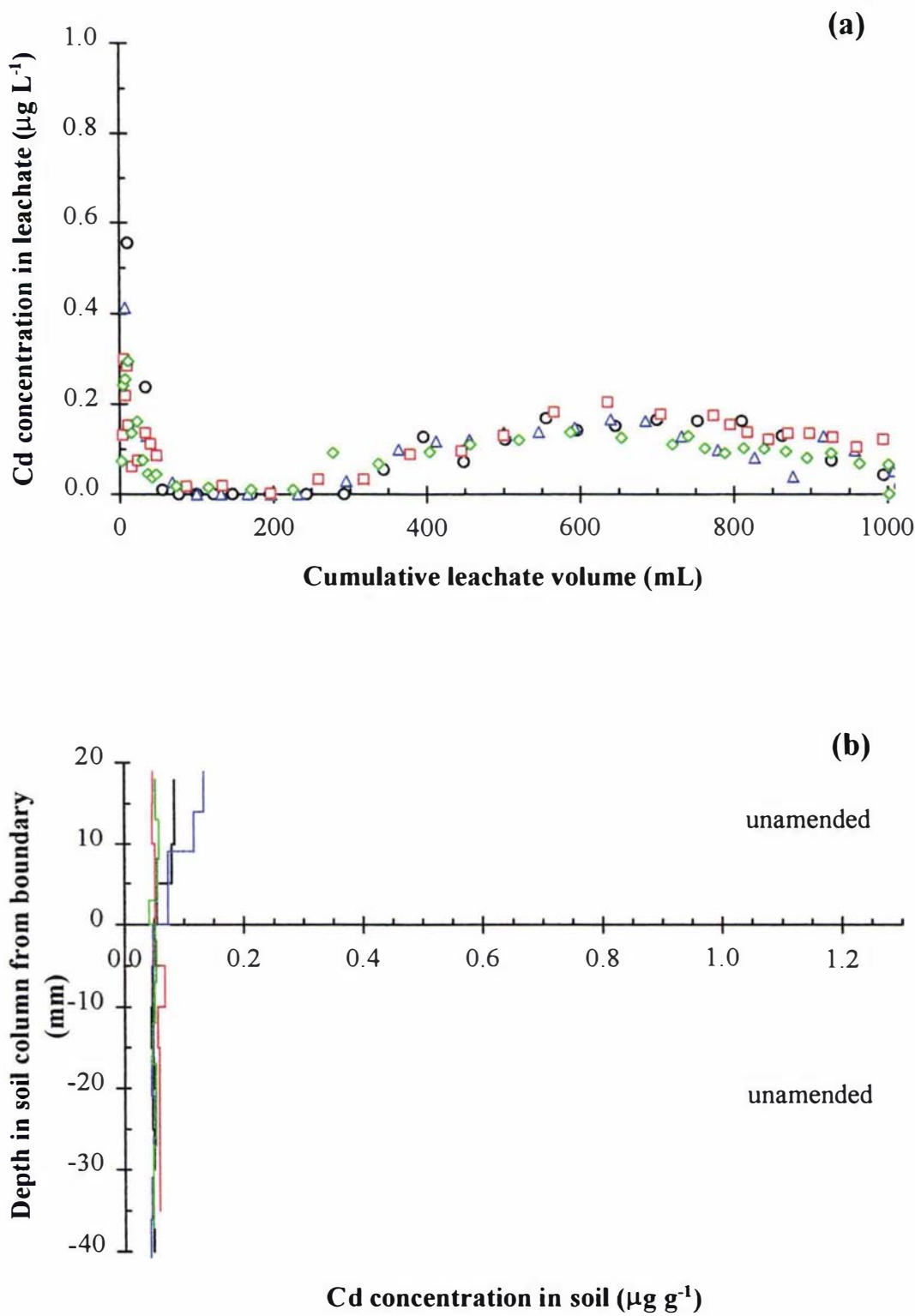
Figure 2 Plots of: *(a)* the Cd concentration in the leachate; and *(b)* the final Cd concentration profile in the soil column; for replicated control columns of Manawatu soil leached with 2.5 mM $CaCl_2$.

APPENDIX 5

*This appendix provides an explanation of, and the code for, the computer programme
used in Chapter 7 to model Cd movement through columns of repacked soil.*

Based on convection-dispersion theory and the linear isotherm, the programme uses a
conceptual soil column of length L divided into a series of discrete sections or
compartments of depth dz, Figure 1. Each section has the same volumetric water content
θ, bulk density ρ_b, and experiences identical water flow.
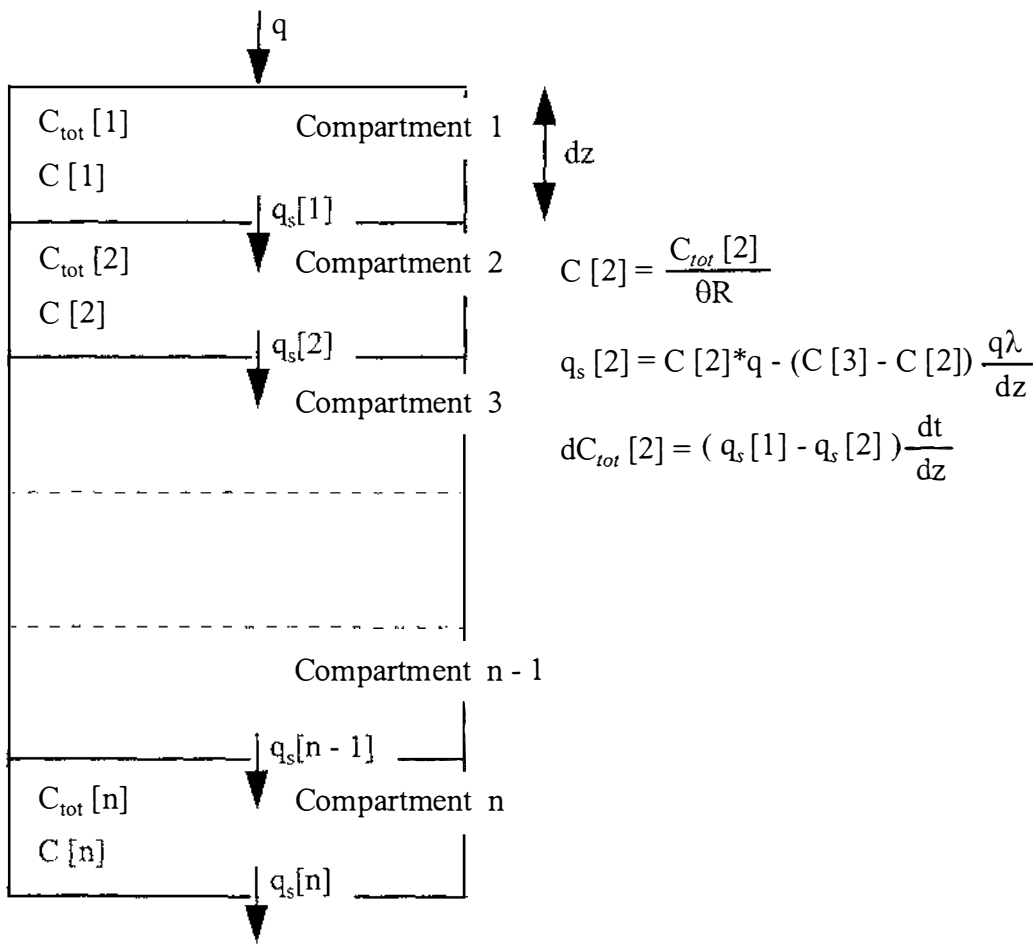
Figure 1. Schematic diagram of computational model showing discreet
compartments and example calculations for solute flux densities and
solution solute concentrations.

The Cd concentration in solution (C) in each compartment is determined from the total
Cd (C_{tot}, mg Cd m^{-3}) in that compartment using equations 7.10 and 7.11. Cadmium flux

between compartments, the rate of solute movement across unit area of boundary, is determined from equation 7.3. However, for practical purposes D_s is substituted for by D (equation 7.5) . In equation 7.3, the term dC/dz defines the concentration gradient across the lower boundary of a compartment, and is therefore the driving force for molecular diffusion of the solute. The diffusion distance, dz, is equal to the compartment depth, also dz. The value of dC is calculated by taking the solute concentration difference between compartment n and compartment $n+1$. The convection component of equation 7.3 is evaluated by assuming that solution leaving compartment n enters compartment $n+1$.

Once the solute flux density, q_s, has been determined, the change in solute mass present in each compartment over a time step dt can be calculated by: 'what came in minus what went out' (equation 7.6). The new total Cd concentration (C_{tot}) in a particular compartment is therefore the sum of what was present before, and the change in solute mass during dt.

Because the columns in this study had soil with added-Cd making up a part of the column at the start of leaching, the computer model splits the column into two sections. The top layer, making up one-third of the column, has compartments with high Cd concentrations; the bottom layer has compartments with low Cd concentrations.

As most adsorption isotherms had positive intercepts on the vertical axis (section 7.3), a mass of Cd (per unit volume) was defined as being unavailable for desorption into solution (*Non-desorb*). This value is subtracted from the total Cd in a compartment (C_{tot}) to remove it from the calculation which determines Cd concentrations in solution (equation 7.11).

One difficulty when using a multi-compartment model to simulate a real system is numerical dispersion – the overestimation of dispersion effects when infinitely small increments dz are approximated with finite and practicable increments Δz. Solute entering through the top boundary of a compartment is immediately spread over the whole of that compartment and thereby increases the apparent dispersion (Frissel and

Reiniger, 1974). This is corrected by replacing the concept of dispersivity with an estimated *effective dispersivity* (Campbell, 1985).

A further modification to the numerical model is required for column end-effects. The bottom-most compartment has no following compartment with which to calculate a diffusion concentration gradient (equation 7.3), and therefore has its solute flux density determined only from convection. To remove this complication from the simulation, several extra compartments were added to the base of the "column". Cadmium concentrations in the simulated leachate were then calculated from the average solution concentration in the (true) final compartment and the compartment following.

Definition of variables used in program CDEmodel

Variable	Description	Units
area	Cross-sectional area of the column.	m^2
bulkd	Bulk density of soil packed into column.	$kg\ m^{-3}$
Cdfluxden[n]	Mass of Cd moving across the lower boundary of compartment n per unit time.	$mg\ m^{-2}\ h^{-1}$
Cdlayer	Number of compartments which begin with high-Cd 'soil'.	
col_length	Height of column (excluding the extra compartments from 'nolayer' to 'endlayer').	m
disp	Dispersivity, a measure of how much the solute front spreads out.	m
dt	Specified time steps at which Cd concentrations and flux densities in the column are recalculated.	h
dtotalcn	Change in Cd mass in compartment over time interval dt.	$mg\ m^{-3}$
dz	The depth of each compartment.	m
effdisp	Effective dispersivity, a measure of dispersivity incorporating correction for numerical dispersion.	m
endlayer	Total number of compartments in theoretical column after adding extra layers to avoid end-effects because dispersion cannot be calculated.	
I	Amount of solution which has passed through column.	m
Imax	Maximum amount of leaching solution which is to pass through column.	m
initial_Cd	Mass of Cd in column at beginning as determined by summing the mass of Cd in all compartments.	mg
Kd	Distribution constant obtained from the linear sorption isotherm.	$m^3\ kg^{-1}$
leachcn	Cd concentration of the leachate leaving the column at compartment 'nolayer'.	$mg\ m^{-3}$
Madd	Concentration of Cd (mass per unit volume) in layers containing high-Cd soil.	$mg\ m^{-3}$
Mresident	Concentration of Cd (mass per unit volume) in layers containing low-Cd soil.	$mg\ m^{-3}$
nolayer	Number of compartments of interest in theoretical column.	
q	Darcy flux density, the flow rate of solution entering and leaving the column and each compartment.	$m\ h^{-1}$
R	Retardation coefficient calculated using Kd.	
solncn[n]	Cd concentration in soil solution of compartment n	$mg\ m^{-3}$
t	Time or duration of leaching.	h
theta	Volumetric water content of column during leaching.	$m^3\ m^{-3}$
totalcn[n]	Total Cd concentration in compartment n, a defined volume of soil.	$mg\ m^{-3}$

```pascal
 program CDEmodel;
{$E+} {$N+}
uses
   Crt;
const
soiltype='Manawatu, linear isotherm';
```

{Soil column parameters}
```pascal
nolayer=30;              Cdlayer=nolayer/3;        endlayer=nolayer+5;
col_length=60*10^-3;     dz=col_length/nolayer;    area=1.59*10^-3;
mw=65.1*10^-3;           ms=102*10^-3;             bulkd=1070;
theta=(mw/ms)*bulkd/1000;
```

{Leaching solution parameters}
```pascal
q=1.32*10^-3;    Imax=630*10^-3;        dt=0.1;        dI=dt*q;
```

{Cd concentrations and retardation coefficient}
```pascal
Madd=1.014*bulkd;    Mresident=0.050*bulkd;  Nondesorb=0.070*bulkd;
influentCd=0.60;     Kd=0.0539;              R=1+(Kd*bulkd)/theta;
disp=3*10^-3;        effdisp=disp-(dz-q*dt/theta)/2;

res_prin=200;   width=25;   width2=10;

var
   data: text;   {text is short for 'file of char'}
   extfile: string[20];
   counter: integer;
   leachcn, dtotalcn, t, I: double;
   Cd_leach, Cd_col, initial_Cd: double;
   solncn, totalcn: array[1..endlayer] of double;
   Cdfluxden: array[0..endlayer] of double;
end;
```

procedure initialize; *{Sets programme variables at their starting values}*
```pascal
begin
   t := 0;              I := 0;          initial_Cd := 0;
   Cd_col := 0;     Cd_leach := 0;   Cdfluxden[0] := influentCd*q;
   counter := res_prin;
end;
```

procedure col_setup; *{Assigns Cd concentrations to the solid and solution phase in each compartment of the column prior to leaching}*
```pascal
var
   n: integer;
begin
   For n := 1 to endlayer do
   begin
   if n <= Cdlayer then
      totalcn[n] := Madd
   else totalcn[n] := Mresident;
```

```
        if totalcn[n] < Nondesorb then
        solncn[n] := 0
        else
        solncn[n] := (totalcn[n]-Nondesorb) / theta / R;        {Equation 7.11}
    end;
    For n :=1 to nolayer do
        initial_Cd := initial_Cd + totalcn[n] * area * dz;
end;                            {Calculates total mass of Cd in column before leaching}
```

procedure soluteflux; *{Calculates the Cd flux density across each compartment-boundary of the column}*

```
var
  n: integer;
begin
    Cdfluxden[endlayer] := solncn[endlayer] * q;        {Equation 7.2}
    For n :=1 to (endlayer-1) do
        Cdfluxden[n] := solncn[n]*q - effdisp*q*(solncn[n+1]-solncn[n])/dz
end;                                                    {Equation 7.3}
```

procedure newconcs; *{Calculates the Cd concentrations in each compartment of the column after an increment of time, dt}*

```
var
  n: integer;
begin
    For n := 1 to endlayer do
    begin
        dtotalcn := (Cdfluxden[n-1] - Cdfluxden[n])*dt/dz;  {Equation 7.6}
        totalcn[n] := totalcn[n] + dtotalcn;
        if totalcn[n] < Nondesorb then
        solncn[n] := 0
        else
        solncn[n] := (totalcn[n]-Nondesorb) / theta / R        {Equation 7.11}
    end
end;
```

procedure printleach; *{Prints the Cd concentrations in the leachate for each increment of time, dt}*

```
begin
    writeln(data,t:width2:2, I*1000:width2:4, I*area*1000000:width:4, leachcn:width:3);
    counter :=0;
end;
```

procedure printcol; *{Prints the Cd concentrations in each compartment of the column at the completion of leaching}*

```
var
  n: integer;
begin
                        writeln(data, 'mean depth, mm':width, 'soil [Cd], mg/kg':width,
                            'solution [Cd], g/L':width);
```

```pascal
        For n := 1 to nolayer do
        begin
    write(data,(dz*n-dz/2)*1000:width:2);
    write(data,totalcn[n]/bulkd:width:3);
    writeln(data,solncn[n]:width:3);
    Cd_col:=Cd_col+(totalcn[n]*area*dz);
  end;
  writeln(data,'Cd mass balance:');
  writeln(data,'Initial Cd in column, µg: ',initial_Cd*1000:6:3);
  writeln(data,'Cd gained from Leaching solution, µg: ',influentCd*1000*I*area:5:3);
  writeln(data);
  writeln(data,'Cd lost to leachate, µg: ',Cd_leach*1000:6:3);
  writeln(data,'Cd remaining in soil column, µg: ',Cd_col*1000:6:3);
end;


begin    {Main programme}
ClrScr;
if (effdisp > 0) then
begin
  writeln('Enter name of data file: ');
  readln(extfile);
  assign(data,extfile);
  rewrite(data);
  writeln(data, 'CDE calculations for ', soiltype);
  writeln(data, 'time, h':width2, 'I, mm':width2, 'leachate volume, ml':width,
          'leachate [Cd], mg/m3':width);
  initialize;
  col_setup;
  while (I <= (Imax+0.001)) do
    begin
    t := t + dt;
    I := q * t;
    soluteflux;
    leachcn := (solncn[nolayer] + solncn[nolayer + 1])/2;
    Cd_leach := Cd_leach + leachcn*dI*area;
    if (counter >= res_prin) then printleach
    else counter := counter + 1;
    newconcs;
    end;
    writeln(data);    writeln(data);
    printcol;
    close(data);
  end
  else  writeln('effective dispersion was < 0: ',effdisp*1000:8:4)
end.
```

APPENDIX 6

Contained in this Appendix are the fertilizer histories for each site of the Wharekohe Development Sequence studied in Chapter 8. Included are the estimated additions of Cd and P for each fertilizer application. The soils were sampled in the spring of 1990 and the estimated total additions of Cd and P up to this date are shown at the base of each Table. These estimated additions are presented in the main thesis in Table 8.4.

Part of the College 4 site was developed later than the rest. This development began in the Autumn of 1962 and therefore this section received fertilizer applications for 1 year that were different to older areas of the site. The full fertilizer history for both parts of this site are given in the appropriate tables. The value for the total Cd applied to the College 4 site was taken as an average of these two fertilizer histories.

A footnote to all Tables presented here:

† At each site a fertilizer application of Trace element mix was made in spring 1989. This trace element mix consisted of 1 tonne made up of:

943.3 kg 15% K Longlife + 50 kg borate + 5 kg selenium prills + 1.5 kg CoSO4

Site: Pa 1
Development Age: 8 years

Date		Fertilizer	Description and application rate	Estimated Added Cd	Estimated Added P
		kg ha^{-1}	Fertilizer type	g ha^{-1}	kg ha^{-1}
Spring	1981	800	800 kg SSP + 190 kg KCl + 10 kg Cu (ha^{-1})	28.45	72.80
Spring	1982	600	15% K-SSP + Co	18.14	46.41
Spring	1983	600	20% KCl serpentine SSP	12.80	32.76
Summer	1985	407	15% K-SSP	12.30	31.48
Autumn	1986	485	15% K-SSP	17.02	37.00
Spring	1986	600	15% K-Longlife + Cu	20.86	52.55
Summer	1987	400	15% K-Longlife + Cu	13.90	35.03
Autumn	1989	350	15% K-Longlife	12.17	30.65
Spring	1989	200	Trace Element mix†	6.56	16.52
Autumn	1990	400	15% K-Longlife	13.90	35.03
At sampling			**Total element added over 8 years**	**156 g Cd ha^{-1}**	**390 kg P ha^{-1}**

Site: M Farm
Development Age: 23 years

Date		kg ha^{-1}	Fertilizer type	Estimated Added Cd g ha^{-1}	Estimated Added P kg ha^{-1}
Autumn	1965	750	SSP	47.35	68.25
Autumn	1967	1000	15% K-SSP	53.66	77.35
Spring	1967	430	30% K-SSP	19.00	27.39
Autumn	1968	630	15% K-SSP	33.81	48.73
Spring	1968	390	30% K-SSP	17.23	24.84
Autumn	1969	390	30% K-SSP	17.23	24.84
Spring	1969	390	30% K-SSP	17.23	24.84
Autumn	1970	390	30% K-SSP	17.23	24.84
Spring	1970	500	50% K-SSP	15.78	22.75
Spring	1971	500	50% K-SSP	10.34	22.75
Spring	1972	375	30% K-SSP + Cu + S	8.69	19.11
Autumn	1973	375	50% K-SSP	7.76	17.06
Autumn	1974	250	15% K-SSP	8.79	19.34
Spring	1974	275	50% K-SSP (1% Cu, 2% S)	5.69	12.51
Autumn	1975	250	50% K-SSP + S	4.14	9.10
Spring	1975	300	30% K-SSP	8.69	19.11
Autumn	1976	250	50% K-SSP + S	4.14	9.10
Spring	1976	400	50% K-SSP	8.27	18.20
Autumn	1977	250	50% K-SSP + S	4.14	9.10
Spring	1977	540	30% K-SSP	15.63	34.40
Spring	1978	500	30% K-SSP	14.48	31.85
Spring	1979	275	SSP	9.78	25.03
Spring	1980	455	50% K sulphurised serpentine super	4.85	12.42
Spring	1981	600	15% K-SSP	18.14	46.41
Spring	1982	600	30% K-SSP + S + Mo	11.95	30.58
Summer	1984	400	20% K-SSP+ S	9.11	23.30
Summer	1985	407	15% K-SSP	12.30	31.48
Autumn	1986	485	15% K-SSP	17.02	37.00
Spring	1986	400	15% K-Longlife + Cu	13.90	35.03
Summer	1988	315	15% K-Longlife + Cu	10.95	27.59
Autumn	1989	350	15% K-Longlife	12.17	30.65
Spring	1989	200	Trace Element mix[†]	6.56	16.52
Autumn	1990	400	15% K-Longlife	13.90	35.03
At sampling			**Total element added over 23 years**	**480 g Cd ha^{-1}**	**917 kg P ha^{-1}**

Site:　　　　　　L Block
Development Age:　25 years

Date		kg ha^{-1}	Fertilizer type	Estimated Added Cd g ha^{-1}	Estimated Added P kg ha^{-1}
Autumn	1965	950	SSP	59.97	86.45
Spring	1965	260	SSP	16.41	23.66
1966		650	SSP	41.04	59.15
1967		650	SSP	41.04	59.15
1968		650	SSP	41.04	59.15
1969		376	30% K-SSP	16.63	23.97
1970		376	30% K-SSP	16.63	23.97
1971		376	30% K-SSP	10.89	23.97
Spring	1972	502	50% K-SSP + Cu	10.38	22.83
1973		376	30% K-SSP	10.89	23.97
1974		376	30% K-SSP	10.89	23.97
1975		376	30% K-SSP	10.89	23.97
1976		376	30% K-SSP	10.89	23.97
1977		750	15% K-SSP	26.37	58.01
Spring	1979	388	20% K-SSP	11.04	28.25
Spring	1980	500	50% K sulphurised serpentine super	5.34	13.65
Autumn	1982	645	30% K-SSP	16.06	41.09
Spring	1982	600	30% K-SSP + S + Mo	11.95	30.58
Summer	1984	400	20% K-SSP+ S	9.11	23.30
Summer	1985	407	15% K-SSP	12.30	31.48
Autumn	1986	485	15% K-SSP	17.02	37.00
Spring	1986	400	15% K-Longlife + Cu	13.90	35.03
Summer	1988	315	15% K-Longlife + Cu	10.95	27.59
Autumn	1989	350	15% K-Longlife	12.17	30.65
Spring	1989	200	Trace Element mix[†]	6.56	16.52
Autumn	1990	400	15% K-Longlife	13.90	35.03
At sampling			**Total element added over 25 years**	**464 g Cd ha^{-1}**	**886 kg P ha^{-1}**

Site: College 4, part 1
Development Age: 30 years

Date		Fertilizer Description and application rate		Estimated Added Cd	Estimated Added P
		kg ha^{-1}	Fertilizer type	g ha^{-1}	kg ha^{-1}
Autumn	1960	753	SSP	47.51	68.49
Spring	1960	376	SSP	23.76	34.24
Autumn	1961	376	SSP	23.76	34.24
Spring	1961	376	SSP	23.76	34.24
Autumn	1962	251	SSP	15.84	22.83
Spring	1962	251	SSP	15.84	22.83
Autumn	1963	376	SSP	23.76	34.24
Spring	1963	376	SSP	23.76	34.24
Autumn	1964	376	SSP	23.76	34.24
Spring	1964	376	SSP	23.76	34.24
Autumn	1965	255	SSP	16.12	23.24
Autumn	1966	255	SSP	16.12	23.24
Autumn	1967	255	SSP	16.12	23.24
1968		376	30% K-SSP	16.63	23.97
1969		376	30% K-SSP	16.63	23.97
1970		376	30% K-SSP	16.63	23.97
1971		376	30% K-SSP	10.89	23.97
Spring	1972	502	50% K-SSP + Cu	10.38	22.83
1973		376	30% K-SSP	10.89	23.97
1974		376	30% K-SSP	10.89	23.97
1975		376	30% K-SSP	10.89	23.97
1976		376	30% K-SSP	10.89	23.97
1977		376	30% K-SSP	10.89	23.97
Summer	1978	500	30% K-SSP + Cu	14.48	31.85
Spring	1979	313	20% K-SSP+S+Cu	7.12	18.23
Spring	1980	500	50% K sulphurised serpentine super	5.34	13.65
Spring	1982	600	30% K-SSP+S+Mo	11.95	30.58
Summer	1984	400	20% K-SSP+S	9.11	23.30
Summer	1985	407	15% K-SSP	12.30	31.48
Autumn	1986	380	15% K-SSP	13.33	28.99
Summer	1988	315	15% K Longlife+Cu	10.95	27.59
Autumn	1989	350	15% K Longlife	12.17	30.65
Spring	1989	200	Trace Element mix[†]	6.56	16.52
Autumn	1990	400	15% K Longlife	13.90	35.03
At sampling			**Total element added over 30 years**	**537 g Cd ha^{-1}**	**950 kg P ha^{-1}**

Site: College 4, part 2
Development Age: 30 years

Date		Fertilizer	Description and application rate	Estimated Added Cd	Estimated Added P
		kg ha^{-1}	Fertilizer type	g ha^{-1}	kg ha^{-1}
Autumn	1962	753	SSP	47.51	68.49
Spring	1962	376	SSP	23.76	34.24
Autumn	1963	376	SSP	23.76	34.24
Spring	1963	376	SSP	23.76	34.24
Autumn	1964	376	SSP	23.76	34.24
Spring	1964	376	SSP	23.76	34.24
Autumn	1965	376	SSP	23.76	34.24
Spring	1965	376	SSP	23.76	34.24
Autumn	1966	376	SSP	23.76	34.24
Spring	1966	376	SSP	23.76	34.24
Autumn	1967	376	SSP	23.76	34.24
1968		376	30% K-SSP	16.63	23.97
1969		376	30% K-SSP	16.63	23.97
1970		376	30% K-SSP	16.63	23.97
1971		376	30% K-SSP	10.89	23.97
Spring	1972	502	50% K-SSP + Cu	10.38	22.83
1973		376	30% K-SSP	10.89	23.97
1974		376	30% K-SSP	10.89	23.97
1975		376	30% K-SSP	10.89	23.97
1976		376	30% K-SSP	10.89	23.97
1977		376	30% K-SSP	10.89	23.97
Summer	1978	500	30% K-SSP + Cu	14.48	31.85
Spring	1979	313	20% K-SSP+S+Cu	7.12	18.23
Spring	1980	500	50% K sulphurised serpentine super	5.34	13.65
Spring	1982	600	30% K-SSP+S+Mo	11.95	30.58
Summer	1984	400	20% K-SSP+S	9.11	23.30
Summer	1985	407	15% K-SSP	12.30	31.48
Autumn	1986	380	15% K-SSP	13.33	28.99
Summer	1988	315	15% K Longlife+Cu	10.95	27.59
Autumn	1989	350	15% K Longlife	12.17	30.65
Spring	1989	200	Trace Element mix[†]	6.56	16.52
Autumn	1990	400	15% K Longlife	13.90	35.03
At sampling			**Total element added over 30 years**	**537 g Cd ha^{-1}**	**950 kg P ha^{-1}**

258

Site: Pylon 2
Development Age: 32 years

Date		kg ha⁻¹	Fertilizer type	Estimated Added Cd g ha⁻¹	Estimated Added P kg ha⁻¹
Autumn	1958	878	SSP	55.43	79.90
Spring	1958	376	SSP	23.76	34.24
Autumn	1959	376	SSP	23.76	34.24
Autumn	1960	314	SSP	19.80	28.54
Autumn	1961	627	SSP	39.59	57.07
Autumn	1962	251	SSP	15.84	22.83
Autumn	1963	251	SSP	15.84	22.83
Autumn	1964	251	SSP	15.84	22.83
Autumn	1965	251	SSP	15.84	22.83
Spring	1965	251	SSP	15.84	22.83
Autumn	1966	251	SSP	15.84	22.83
Spring	1966	251	SSP	15.84	22.83
1967		376	30% K-SSP	16.63	23.97
1968		376	30% K-SSP	16.63	23.97
1969		376	30% K-SSP	16.63	23.97
1970		376	30% K-SSP	16.63	23.97
1971		376	30% K-SSP	10.89	23.97
Spring	1972	502	50% K-SSP	10.38	22.83
1973		376	30% K-SSP	10.89	23.97
1974		376	30% K-SSP	10.89	23.97
1975		376	30% K-SSP	10.89	23.97
1976		376	30% K-SSP	10.89	23.97
1977		376	30% K-SSP	10.89	23.97
Summer	1978	500	30% KCl Cu-SSP	14.48	31.85
Spring	1979	313	20% K-SSP+S+Cu	7.12	18.23
Spring	1980	500	50% K sulphurised serpentine super	5.34	13.65
Spring	1982	600	30% K-SSP+S+Mo	11.95	30.58
Summer	1984	400	20% K-SSP+S	9.11	23.30
Summer	1985	333	15% K-SSP	10.07	25.76
Spring	1985	500	15% K-SSP	15.12	38.68
Spring	1986	400	15% K Longlife	13.90	35.03
Summer	1988	315	15% K Longlife+Cu	10.95	27.59
Autumn	1989	350	15% K Longlife	12.17	30.65
Spring	1989	200	Trace Element mix†	6.56	16.52
Autumn	1990	400	15% K Longlife	13.90	35.03
At sampling			**Total element added over 32 years**	**546 g Cd ha⁻¹**	**983 kg P ha⁻¹**

APPENDIX 7

Summary calculations for Cd removal from the soil system via animal products and plant uptake.

Development age	8 years	23 years	25 years	30 years	32 years
Herbage Cd in 1991 (mg Cd kg DM^{-1})	0.070	0.109	0.172	0.222	0.390
Soil Cd in 1990 for 0-3 cm (mg Cd kg soil^{-1})	0.364	0.433	0.499	0.377	0.589
Total Cd taken up in herbage (g Cd ha^{-1})	5.56	21.91	25.35	36.45	44.25
Plant Cd ingested by stock (g Cd ha^{-1}): 86% pasture utilization	4.78	18.84	21.80	31.35	38.01
Soil Cd ingested by stock (g Cd ha^{-1}): 15.6 sheep ha^{-1}; 75 kg soil sheep^{-1} yr^{-1}	3.41	11.01	12.18	14.39	15.77
Total Cd ingested by stock over development time (g Cd ha^{-1})	8.19	29.85	33.98	45.74	60.02

Total mass of Cd removed from soil system during pasture development period (g Cd ha^{-1}):

	8 years	23 years	25 years	30 years	32 years
Cd lost as animal product: 1% of that ingested by stock	0.08	0.30	0.34	0.46	0.60
Cd in standing pasture at time of soil sampling	0.07	0.11	0.17	0.22	0.39

The use of a soil ingestion rate of 75 kg soil animal^{-1} year^{-1} has led to a much higher estimate for Cd intake from soil than is normally found. Reported values for Cd intake from soil ingestion include 2 to 4% (Longhurst *et al.*, 1994) and 2 to 5% during most seasons, but 10% during winter (Loganathan *et al.*, 1995). Nevertheless, this overestimation of Cd intake does not influence the conclusions of this study.
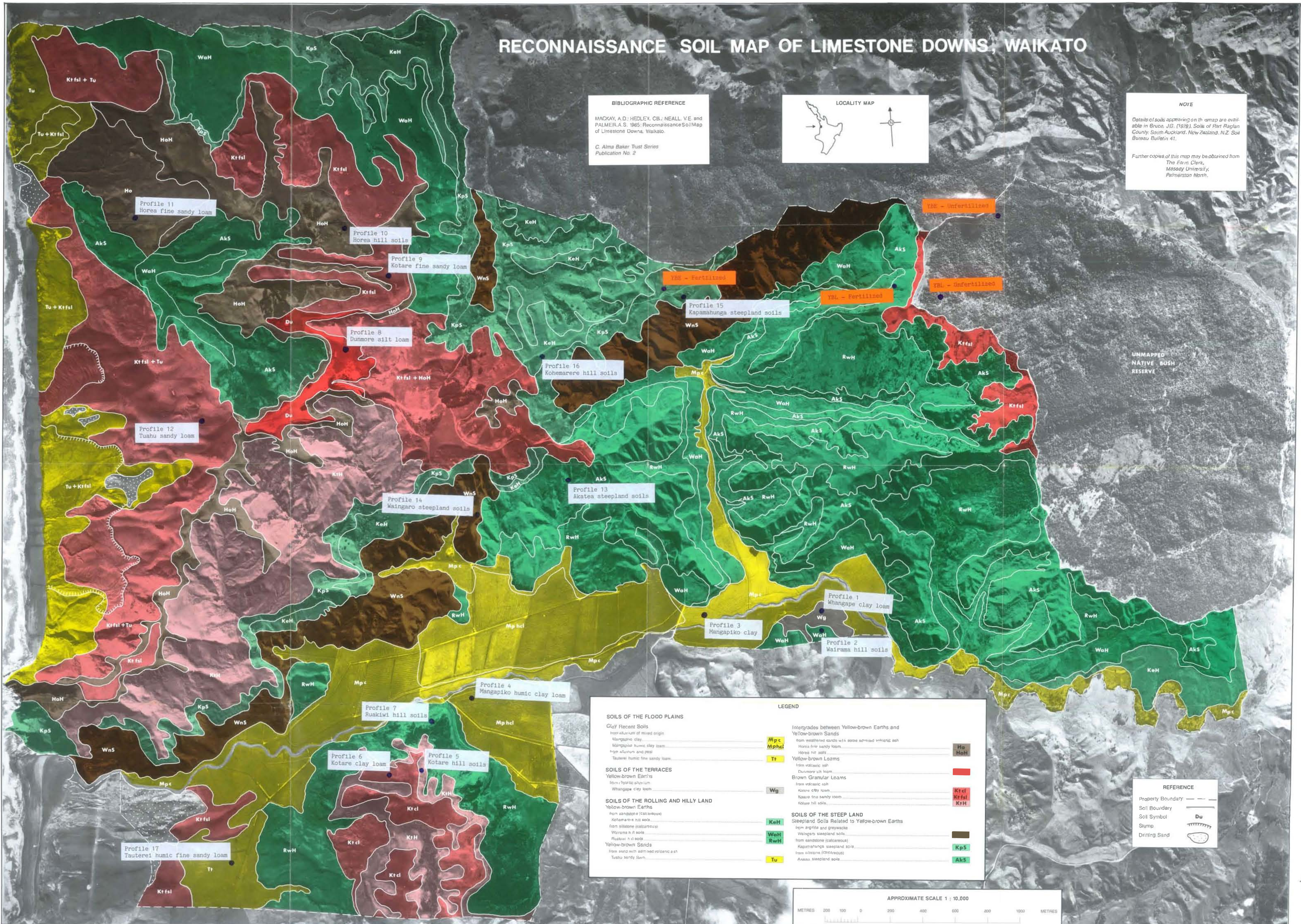
RECONNAISSANCE SOIL MAP OF LIMESTONE DOWNS, WAIKATO

LOCALITY MAP

NOTE

Details of soils appearing on the map are available in Bruce, J.G. (1978). Soils of Port Raglan County, South Auckland, New Zealand. N.Z. Soil Bureau Bulletin 41.

Further copies of this map may be obtained from
The Farm Clerk,
Massey University,
Palmerston North.

TBE – Unfertilized
TBE – Fertilized
YBL – Fertilized
YBL – Unfertilized

UNMAPPED
NATIVE BUSH
RESERVE

Profile 11
Horea fine sandy loam

Profile 10
Horea hill soils

Profile 9
Kotare fine sandy loam

Profile 15
Kapamahunga steepland soils

Profile 8
Dunmore silt loam

Profile 16
Kohemarere hill soils

Profile 12
Tuahu sandy loam

Profile 14
Waingaro steepland soils

Profile 13
Akatea steepland soils

Profile 1
Whangape clay loam

Profile 3
Mangapiko clay

Profile 2
Wairama hill soils

Profile 4
Mangapiko humic clay loam

Profile 7
Ruakiwi hill soils

Profile 6
Kotare clay loam

Profile 5
Kotare hill soils

Profile 17
Tauterei humic fine sandy loam

LEGEND

SOILS OF THE FLOOD PLAINS

Gley Recent Soils
from alluvium of mixed origin
Mangapiko clay .... Mpc
Mangapiko humic clay loam .... Mphcl
Horea alluvium and peat
Tauterei humic fine sandy loam .... Tt

SOILS OF THE TERRACES

Yellow-brown Earths
from rhyolitic alluvium
Whangape clay loam .... Wg

SOILS OF THE ROLLING AND HILLY LAND

Yellow-brown Earths
from sandstone (calcareous)
Kohemarere hill soils .... KeH
from siltstone (calcareous)
Wairama hill soils .... WaH
Ruakiwi hill soils .... RwH

Yellow-brown Sands
from sand with admixed volcanic ash
Tuahu sandy loam .... Tu

Intergrades between Yellow-brown Earths and
Yellow-brown Sands
from weathered sands with some admixed volcanic ash
Horea fine sandy loam
Horea hill soils .... Ho, HoH

Yellow-brown Loams
from volcanic ash
Dunmore silt loam ....

Brown Granular Loams
from volcanic ash
Kotare clay loam .... Ktcl
Kotare fine sandy loam .... Ktfsl
Kotare hill soils .... KtH

SOILS OF THE STEEP LAND

Steepland Soils Related to Yellow-brown Earths
from argillite and greywacke
Waingaro steepland soils
from sandstone (calcareous)
Kapamahunga steepland soils .... KpS
from siltstone (calcareous)
Akatea steepland soils .... AkS

REFERENCE

Property Boundary .... — — —
Soil Boundary .... —
Soil Symbol .... Du
Slump ....
Drifting Sand ....

APPROXIMATE SCALE 1 : 10,000

METRES   200 100   0   200   400   600   800   1000   METRES