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

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

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ABSTRACT

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

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

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

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

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

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

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

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

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

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

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

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

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TABLE OF CONTENTS

	Page
ABSTRACT	i
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF FIGURES	xii
LIST OF TABLES	xv
INTRODUCTION	1

CHAPTER ONE

IMPORTANCE OF Zn AND Cd, ORIGIN OF Zn AND Cd IN SOILS,
AND ADSORPTION OF Zn AND Cd BY SOILS AND SOIL COMPONENTS

1.1 Zinc and Cd in Living Organisms	4
1.1.1 Zinc requirements of organisms	5
1.1.2 Toxic effects of Cd	6
1.1.3 Plant uptake of Cd applied to soils through superphosphate fertiliser	6
1.1.4 Soil-plant-animal relationships	7
1.2 Zinc and Cd in Rocks and Soils	8
1.2.1 Geochemistry, occurrence and content of Zn and Cd in rocks	9
1.2.1.1 Occurrence of Zn and Cd in primary rocks . .	11
1.2.1.2 Content of Zn and Cd in primary rocks . . .	13
1.2.2 Zinc : Cd ratios in rocks	16
1.2.3 Weathering of parent materials	16
1.2.4 Origin of Zn and Cd in soils	17
1.2.5 Total Zn content of soils	17
1.2.6 "Available" Zn content of soils	19
1.2.7 Total Cd content of soils	20

	Page
1.3 Possible Sources of Addition of Potentially Available Zn and Cd in Soils	21
1.3.1 Additions from industrial sources	21
1.3.2 Motor vehicle emissions	22
1.3.3 Municipal wastes	23
1.3.3.1 Plant availability of Zn and Cd added to soils in sludges and composts	26
1.3.4 Superphosphate fertilisers	27
1.3.4.1 Zinc and Cd contents of superphosphate fertilisers	27
1.3.4.2 Plant availability of Zn and Cd in superphosphate fertilisers	29
1.4 Adsorption of Zn and Cd by Hydrous Oxides and Soils	32
1.4.1 The role of hydrous oxides in the chemistry of soil Zn and Cd	32
1.4.2 Properties of the hydrous metal oxide/aqueous interface	34
1.4.2.1 Development of surface charge	34
1.4.2.2 Models proposed to describe charge and potential relationships of charged interfaces	36
1.4.2.2.1 Helmholtz model	36
1.4.2.2.2 Gouy-Chapman model	37
1.4.2.2.3 Stern model	37
1.4.2.2.4 Grahame model	41
1.4.2.3 Charge distribution at oxide surfaces	41
1.4.2.4 Charge variation in the presence of specifically-adsorbed cations	44
1.4.2.5 Iso-electric point of hydrous oxide surfaces	46
1.4.2.6 Points of zero charge in soil components	46
1.4.3 Forms of Zn and Cd ions in solution	47
1.4.3.1 Evidence for existence of complex ions of Zn and Cd in aqueous solution	47

	Page
1.4.4 Adsorption isotherms	52
1.4.4.1 The Freundlich model	55
1.4.4.2 The Langmuir model	56
1.4.5 Proposed models and mechanisms of Zn and Cd adsorption by hydrous oxides	61
1.4.5.1 Proton release in relation to cation adsorption	63
1.4.6 Adsorption of Zn and Cd by clay minerals	68
1.5 Summary	71

CHAPTER TWO

SOIL DESCRIPTIONS, SOIL PROPERTIES AND GENERAL METHODS

2.1 Introduction	73
2.2 Soil Descriptions	73
2.2.1 Soil and site information	74
2.2.2 Preparation of soils	77
2.3 General Methods	77
2.3.1 Adsorption studies	77
2.3.2 Preparation of synthetic hydrous metal oxide gels	78
2.3.3 Analysis for Zn and Cd	79
2.3.4 Soil properties	81
2.4 Results and Discussion	81
2.4.1 Comparison of Zn and Cd adsorption by soils	81
2.4.2 Relationship of Zn and Cd adsorption to soil properties	89

CHAPTER THREE

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

3.1	Introduction	94
3.2	Solvent Extraction	95
3.2.1	APDC/MIBK	95
3.2.2	Dithizone	96
3.2.2.1	Dithizone/chloroform	97
3.2.2.2	Dithizone/carbon tetrachloride	97
3.3	A Method for Simultaneous Zn and Cd Determination	98
3.3.1	Procedure	98
3.4	Assessment of the Performance of the Procedure	99
3.4.1	Effect of extraction pH	99
3.4.2	Recovery of Zn and Cd from water	100
3.4.3	Recovery of Zn and Cd from soil extracts	100
3.4.4	Variability of the procedure	101
3.5	Results and Discussion	102

CHAPTER FOUR

ADSORPTION OF Zn AND Cd BY SOILS AND SOIL COMPONENTS

4.1	Introduction	108
4.2	Methods	110
4.2.1	Kinetic studies	110
4.2.2	Time-dependent and equilibrium adsorption isotherms	111
4.2.3	40-hr adsorption isotherms	115
4.2.4	Native-adsorbed Zn and Cd	116

	Page
4.2.5 Experiments with synthetic Fe gel and allophane	116
4.2.5.1 Adsorption experiments	116
4.2.5.2 Effect of pH on Zn and Cd adsorption by Fe gel	117
4.3 Results and Discussion	120
4.3.1 Effect of time of equilibration on Zn and Cd adsorption	120
4.3.2 Evaluation of Zn and Cd adsorption isotherms . . .	125
4.3.2.1 Evaluation of isotherms using the Langmuir equation	125
4.3.2.2 Free energies of adsorption	134
4.3.3 Comparison of 40, 120, 144 and 192 hr adsorption isotherms for Zn and Cd adsorption by Makerua peaty silt loam topsoil and Okaihau gravelly clay subsoil	136
4.3.4 40-hr adsorption isotherms	139
4.3.4.1 k and ΔG values for Zn and Cd adsorption by soils	142
4.3.4.2 b values for Zn and Cd adsorption by soils	145
4.3.5 Zn and Cd adsorption by synthetic hydrous metal oxides	147
4.3.5.1 Description of Zn and Cd adsorption by Fe gel using Langmuir equations	147
4.3.5.2 40-hr adsorption isotherms for Fe gel and allophane	149
4.3.5.3 The effect of pH on Zn and Cd adsorption by Fe gel	157
4.3.6 Summary	160

CHAPTER FIVE

MECHANISMS FOR Zn AND Cd ADSORPTION BY SYNTHETIC Fe GEL

5.1 Introduction	163
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	Page
5.2 Methods	165
5.2.1 Effect of pH on Zn and Cd adsorption by Fe gel . .	165
5.2.1.1 Zn adsorption by Fe gel, with no pH control	165
5.2.1.2 Adsorption of Zn and Cd by Fe gel under controlled pH conditions	166
5.2.2 Proton release	167
5.2.3 Exchangeability of Zn and Cd adsorbed by Fe gel	168
5.2.4 Desorption of Zn adsorbed by Fe gel	171
5.3 Results and Discussion	174
5.3.1 Effect of pH on Zn and Cd adsorption	174
5.3.1.1 Zn adsorption by Fe gel under uncontrolled pH conditions	174
5.3.1.2 Zn and Cd adsorption by Fe gel under controlled pH conditions	177
5.3.2 Proton release	182
5.3.3 Isotopic exchangeability of Zn and Cd adsorbed by Fe gel	187
5.3.4 Desorption of adsorbed Zn from Fe gel by CaCl_2 and CuCl_2 solutions	189
5.4 General Discussion	192
5.4.1 Summary of evidence for the existence of two mechanisms for adsorption of Zn and Cd by Fe gel	192
5.4.2 Mechanisms proposed for Zn and Cd adsorption by Fe gel	195

CHAPTER SIX

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

6.1 Introduction	198
6.2 Materials	199

	Page
6.3 Methods	200
6.4 Results and Discussion	202
6.4.1 Adsorption of Zn and Cd by hydrous ferric oxides	202
6.4.2 Desorption of Zn and Cd from hydrous ferric oxides	209

CHAPTER SEVEN

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

7.1 Introduction	214
7.2 Methods for Determining Extractable and Total Soil Zn and Cd Contents	215
7.2.1 Extractable Zn and Cd	215
7.2.2 Total soil Zn and Cd contents	216
7.3 Results and Discussion	217
7.3.1 Measured and predicted increases in soil Zn and Cd from superphosphate fertiliser addition	220
SUMMARY	225
BIBLIOGRAPHY	231
APPENDICES	247

LIST OF FIGURES

Figure		Page
1.1	Distribution of ions and potential at a negatively charged interface according to Helholtz	38
1.2	Distribution of ions and potential at a negatively charged interface according to the Gouy-Chapman model. .	39
1.3	Distribution of ions and potential at a negatively charged interface according to the Gouy-Chapman-Stern model	40
1.4	Distribution of ions and potential at a negatively charged interface according to the Grahame model	42
1.5	Distribution of charge and potential at a negatively charged surface showing charge reversal arising from superequivalent adsorption of cations	43
1.6	pH titration curves for goethite in NaCl solutions of different ionic strengths	45
1.7	Soluble Zn species in solution in equilibrium with adsorbed Zn	49
1.8	Zinc speciation in chloride media	50
1.9	Classification of isotherms for solute adsorption . . .	53
1.10	Effect of pH on amount of solute adsorbed by surfaces of hydrous metal oxides	54
2.1	Isotherms (40hr) for the adsorption of Zn by Okaihau (a) and Tokomaru (b) topsoils from 3×10^{-2} M NaCl. . . .	82
2.2	Isotherm (40hr) for the adsorption of Zn by Egmont brown loam topsoil from 3×10^{-2} M NaCl	83
2.3	Isotherms (40hr) for the adsorption of Zn from 3×10^{-2} M NaCl by Okaihau (a), Tokomaru (b), Makerua (c) and Egmont (d) subsoils	84
2.4	Isotherms (40hr) for the adsorption of Cd by Okaihau (a) and Tokomaru (b) topsoils from 3×10^{-2} M NaCl. . . .	85
2.5	Isotherm (40hr) for the adsorption of Cd by Egmont brown loam topsoil from 3×10^{-2} M NaCl	86
2.6	Isotherms (40hr) for the adsorption of Cd from 3×10^{-2} M NaCl by Tokomaru (a), Okaihau (b), Egmont (c) and Makerua (d) subsoils.	87

Figure		Page
4.1	Reciprocal time plot of Zn in solution during adsorption of added Zn by Okaihau gravelly clay subsoil	114
4.2	Effect of final pH on amount of Zn adsorbed by Fe gel from 3×10^{-2} M NaCl after 40hr., at different additions of Zn	119
4.3	Effect of time of equilibration of low initial solution concentrations of Zn and Cd for adsorption of Zn and Cd by Makerua topsoil and Okaihau subsoil . . .	121
4.4	Effect of time of equilibration of high final solution concentrations of Zn and Cd for adsorption of Zn and Cd by Makerua topsoil and Okaihau subsoil . . .	122
4.5	Effect of time of equilibration on solution Zn concentrations for Makerua topsoil and Okaihau subsoil. .	123
4.6	Effect of time of equilibration on solution Cd concentrations for Makerua topsoil and Okaihau subsoil. .	124
4.7	Reciprocal plots of amounts of Zn adsorbed by Makerua peaty silt loam topsoil against equilibrium Zn concentrations	127
4.8	Reciprocal plots of amounts of Zn adsorbed by Okaihau gravelly clay subsoil against equilibrium Zn concentrations	128
4.9	Reciprocal plots of amounts of Cd adsorbed by Makerua peaty silt loam topsoil against equilibrium Cd concentrations	129
4.10	Reciprocal plots of amounts of Cd adsorbed by Okaihau gravelly clay subsoil against equilibrium Cd concentrations	130
4.11	Plots of Zn adsorption (40hr) by Okaihau gravelly clay subsoil showing actual (c), resolved (region I (a) and region II (b)) and recombined (o) isotherms . . .	132
4.12	Plots of Cd adsorption (40hr) by Okaihau gravelly clay subsoil showing actual (c), resolved (region I (a) and region II (b)) and recombined (o) isotherms	133
4.13	Reciprocal plot of adsorption data (40hr) for Zn adsorption by Fe gel showing linear relationship at low final solution concentrations	150
4.14	Reciprocal plot of adsorption data (40hr) for Cd adsorption by Fe gel showing linear relationship at low final solution concentrations	151

Figure		Page
4.15	Isotherms for the adsorption of Cd by Fe gel (a) and allophane (b) from $3 \times 10^{-2}\text{M}$ NaCl after 40hr at pH 6.40 over the final concentration range of 0-60 $\mu\text{mol Zn l}^{-1}$	155
4.16	Isotherms for the adsorption of Cd by Fe gel (a) and allophane (b) from $3 \times 10^{-2}\text{M}$ NaCl after 40hr at pH 6.40 over the final concentration range of 0-30 $\mu\text{mol Cd l}^{-1}$	156
4.17	Zinc adsorption isotherms (40hr) determined at different pHs for the adsorption of Zn by Fe gel from $3 \times 10^{-2}\text{M}$ NaCl over the final solution concentration range of 0-46 $\mu\text{mol Zn l}^{-1}$	158
4.18	Cadmium adsorption isotherms (40hr) determined at different pHs for the adsorption of Cd by Fe gel from $3 \times 10^{-2}\text{M}$ NaCl over the final solution concentration range of 0-30 $\mu\text{mol Cd l}^{-1}$	159
5.1	Flow diagram showing the method of sequential desorption of Zn by $1 \times 10^{-2}\text{M}$ CaCl_2 and $1 \times 10^{-2}\text{M}$ CuCl_2 solutions	173
5.2	Adsorption (40hr) of Zn by Fe gel from $3 \times 10^{-2}\text{M}$ NaCl at three different pHs.	176
5.3	Effect of pH (controlled), on the adsorption of Zn and Cd by Fe gel in $3 \times 10^{-2}\text{M}$ NaCl	178
5.4	Effect of pH on percent of initial Zn or Cd added, adsorbed by Fe gel in $3 \times 10^{-2}\text{M}$ NaCl	179
5.5	Base consumed in maintaining a constant pH (pH 6.40) during Zn (a) and Cd (b) adsorption by Fe gel from $3 \times 10^{-2}\text{M}$ NaCl, as a function of the amount of Zn or Cd adsorbed	183
5.6	Desorption of adsorbed Zn from Fe gel by $1 \times 10^{-2}\text{M}$ CaCl_2 (a), $1 \times 10^{-2}\text{M}$ CuCl_2 after desorption by CaCl_2 (b) and total amount of Zn desorbed by $\text{CaCl}_2 + \text{CuCl}_2$ (c)	190
6.1	X-ray diffraction peaks for a natural goethite sample from Biwabik, Minnesota	201
6.2	Time-dependent adsorption of Zn by Fe gel (a), natural goethite (b) and synthetic goethite (c).	203
6.3	Time-dependent adsorption of Cd by Fe gel (a), natural goethite (b) and synthetic goethite (c).	204
6.4	Desorption of Zn from hydrous ferric oxides.	212
6.5	Desorption of Cd from hydrous ferric oxides.	213

LIST OF TABLES

Table		Page
1.1	Naturally occurring Zn-containing minerals	10
1.2	Zinc contents of primary rocks	14
1.3	Cadmium contents of primary rocks	15
1.4	Range of total Zn contents of soils from various countries	18
1.5	'Available' Zn content of a range of soils	19
1.6	Total Zn and Cd content of sewage sludges	25
1.7	Zinc and Cd contents of rock phosphates	28
1.8	Zinc and Cd contents of some superphosphate fertilisers	30
2.1	Site data for soils used in the study	75
2.2	Instrument parameters for Zn and Cd analysis by atomic absorption spectrophotometry	80
2.3	Amounts of Zn and Cd adsorbed by soils, and the ratio of Zn to Cd adsorbed from $3 \times 10^{-2} \text{M}$ NaCl after 40hr. at two final solution concentrations	88
2.4	Soil properties of possible importance in Zn and Cd adsorption	90
3.1	Effect of extraction pH on recovery of $0.038 \mu\text{mol}$ Zn and $0.022 \mu\text{mol}$ Cd from de-ionised water	103
3.2	Effect of level of addition of Zn and Cd on recovery from de-ionised water	104
3.3	Recovery of Zn and Cd added to calcium chloride extracts of soils	106
3.4	Within- and between-day variability in amounts of Zn and Cd extracted from soils by calcium chloride	107
4.1	Initial additions of Zn and Cd used to study adsorption kinetics	112
4.2	Effect of time of equilibration on the adsorption parameters for Zn adsorption by Makerua and Okaihau soils	137

Table		Page
4.3	Effect of time of equilibration on the adsorption parameters for Cd adsorption by Makerua and Okaihau soils	138
4.4	Comparison of slopes and intercepts fitted by regression analysis and "by inspection" for Zn and Cd adsorption by Okaihau topsoil	140
4.5	Langmuir parameters (b,k) and free energies of adsorption (ΔG) for Zn adsorption by Okaihau, Tokomaru, Egmont and Makerua topsoils and subsoils . . .	143
4.6	Langmuir parameters (b,k) and free energies of adsorption (ΔG) for Cd adsorption by Okaihau, Tokomaru, Egmont and Makerua topsoils and subsoils . . .	144
4.7	Ranges of adsorption maxima (b) and adsorption energy contents (k values) for Zn and Cd adsorption by soils, as reported in the literature	146
4.8	Comparison of % organic carbon and short-range order Fe with b values for adsorption of Zn and Cd by soils	148
4.9	Adsorption parameters for Zn and Cd adsorption by Fe gel and allophane gel from $3 \times 10^{-2}M$ NaCl (pH 6.40, 40hr)	153
4.10	Comparison of Langmuir parameters and free energies of adsorption for Zn and Cd adsorption by Fe gel and soils	154
4.11	Parameters describing Zn and Cd adsorption (40hr) by Fe gel from $3 \times 10^{-2}M$ NaCl at two pH values	161
5.1	Effect of time of equilibration on the isotopic exchangeability of Zn and Cd adsorbed by Fe gel	170
5.2	pH ₅₀ values for Zn and Cd adsorption by Fe gel	180
5.3	A summary of published data relating to the effects of pH on percentage adsorption of Zn and Cd by iron oxides	181
5.4	Mole ratios of base consumed to Zn and Cd adsorbed, as a function of Zn and Cd concentration and pH, for Fe gel in $3 \times 10^{-2}M$ NaCl	185
5.5	Isotopic exchangeability of Zn and Cd adsorbed on Fe gel as affected by pH and level of addition . . .	188

Table	Page
5.6 Distribution of Zn adsorbed by Fe gel and desorption against $1 \times 10^{-2}\text{M}$ CaCl_2 and $1 \times 10^{-2}\text{M}$ CuCl_2	191
5.7 Proportion of more-tightly held Zn and Cd, expressed as a percentage of total adsorption as given by desorption, isotopic exchange and Langmuir adsorption data	194
6.1 Solution Zn concentrations and Index of Completion of adsorption at various times following Zn addition to Fe gel, natural goethite and synthetic goethite	206
6.2 Solution Cd concentrations and Index of Completion of adsorption, at various times following Cd additions to Fe gel, natural goethite and synthetic goethite.	207
6.3 Amounts and percentages of Zn desorbed by $1 \times 10^{-2}\text{M}$ CaCl_2 and 1×10^{-2} CuCl_2 from hydrous ferric oxides	210
6.4 Amounts and percentages of Cd desorbed by $1 \times 10^{-2}\text{M}$ CaCl_2 and $1 \times 10^{-2}\text{M}$ CuCl_2 from hydrous ferric oxides	211
7.1 H_2O -extractable, CaCl_2 -extractable, CuCl_2 -extractable and total Zn contents of soils treated with long-term superphosphate additions	218
7.2 H_2O -extractable, CaCl_2 -extractable, CuCl_2 -extractable and total Cd contents of soils treated with long-term superphosphate additions	219
7.3 Comparison of measured and predicted increases in total Zn and Cd contents of soils due to long-term superphosphate fertiliser additions	221