The Behaviour of Cadmium in Soil

A thesis submitted in fulfilment of requirements for
the award of the degree of Doctor of Philosophy,
Centre for Plant and Food Science,
College of Health and Science,
University of Western Sydney

Paul James Milham

September 2008
To my family, friends and mentors …
STATEMENT OF AUTHENTICATION AND PUBLICATION

The work presented in this thesis is, to the best of my knowledge and belief, original, except as acknowledged in the text. I hereby declare that I have not submitted this material, either in full or in part, for a degree at this or any other institution.

Paul James Milham
September 2008

The main content of the following Chapters has been published, or submitted for publication, in the following peer-reviewed papers:


The list of manuscripts is provided in Appendix 2.
ACKNOWLEDGEMENTS

I thank: my supervisors, Paul Holford, Anthony Haigh and Jann Conroy for their consistent support; Cedric Hawkins, Ashley Senn and Neel Jinadasa for the soil samples used in this study; Mike Maguire and Ian Vimpany for unpublished data on the clay mineralogy of the soils; Peter Holmes and Gary Kuhn, Incitec-Pivot Pty Ltd, for a sample of Nauru phosphorite; Charles Humphris, Jacques Fabien and Colin Short for trace Cd measurement using ETAAS; Ross Wenzel for \(^{110}\)Cd and \(^{111}\)Cd isotope ratio measurements using ICP–MS; Arthur Day and Graeme Smith for preparation of the grain mounts used in the x-ray microprobe study; Tim Payne, Barry Lai and Zhonghou Cai for contributing to the x-ray micro-probe study at the Advanced Photon Source, Argonne National Laboratory, USA; David Harland and Warwick Dougherty for constructive reading of the papers from this thesis; Jill Kaldor, Paul Nicholls and Damian Collins for experimental design, statistical analysis and modelling; Fredi Celardin, Sébastien Sauvé, Colin Gray and Scott Young for clarifying aspects of their published data; and, Vicki Glover, Cecilia Lawler, Sharman Lugton, Jenni Tarleton and Jane Thompson for library assistance.

My part-time candidature was supported by a post graduate scholarship from the Centre for Plant and Food Science, University of Western Sydney and in kind, by my employer, the New South Wales Department of Primary Industries. Use of the Advanced Photon Source was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program, supported by U.S. Department of Energy, Basic Energy Sciences, Office of Science, under contract No. W-31-109-Eng-38. The research was also partially supported by an FG Swain Award, University of Western Sydney.
# TABLE OF CONTENTS

| LIST OF TABLES | v  |
| LIST OF FIGURES | vi |
| LIST OF MODELS | vii |
| COMMON ABBREVIATIONS | viii |
| ABSTRACT | ix |

## CHAPTERS

### 1. GENERAL INTRODUCTION

1.1 **Summary** 1
1.2 **Background and scope** 1
1.3 **Cadmium—origin, occurrence and properties** 2
1.4 **Soil Cd and the impact of human activity** 3
1.5 **Anthropogenic releases and their impacts on biota** 7
1.6 **Public policy and vegetable cropping** 9
1.7 **Opportunities to minimise the uptake of Cd by vegetables** 10
1.8 **Objectives, hypotheses and hypothesis testing** 12
1.9 **Conclusion** 14

### 2. A CONCEPTUAL FRAMEWORK AND MODEL TO DESCRIBE CADMIUM BEHAVIOUR IN SOILS

2.1 **Summary** 15
4. MODELLING THE EFFECT OF SOIL PROPERTIES ON CADMIUM PARTITIONING

4.1 Summary 50
4.2 Introduction 50
4.3 Multiple linear regression modelling 51
4.4 Results
   4.4.1 The models 53
   4.4.2 Other observations 55
4.5 Discussion
   4.5.1 Modelling statistics 56
   4.5.2 Detailed analysis
      4.5.2.1 The dependent variable 58
      4.5.2.2 The explanatory variables 59
      4.5.2.3 Effects of the background electrolyte 65
      4.5.2.4 Soil type and land-use 66
4.6 Conclusion 67

5. LABILE AND EXTRACTABLE CADMIUM

5.1 Summary 68
5.2 Introduction 68
5.3 Materials and Methods
   5.3.1 The soils 70
   5.3.2 Reagents 71
   5.3.3 Pilot studies 71
   5.3.4 Major study 72
5.4 Results and discussion

5.4.1 Pilot studies 74
5.4.2 Major study 76

5.5 Conclusion 82

6. CAN SYNCHROTRON MICRO-X-RAY FLUORESCENCE SPECTROSCOPY BE USED TO MAP THE CADMIUM DISTRIBUTION IN SOIL PARTICLES?

6.1 Summary 83
6.2 Introduction 83
6.3 Materials and methods 84
6.4 Results and discussion 88
6.5 Conclusion 95

7. GENERAL DISCUSSION

7.1 Towards a general model of Cd partitioning 96
7.2 Does colloidal Cd contribute to measures of Cd in solution? 100
7.3 Cadmium fractionation, binding and distribution 102
7.4 Conclusion 104
7.5 Research leads 105

8. LITERATURE CITED 107

APPENDICES

1. Site and soil properties 136
2. Manuscripts that are either published or in preparation 139
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Number</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Principal global Cd pools</td>
<td>7</td>
</tr>
<tr>
<td>3.1</td>
<td>ETAAS furnace conditions first used for Cd&lt;sub&gt;Ca&lt;/sub&gt;</td>
<td>35</td>
</tr>
<tr>
<td>3.2</td>
<td>ETAAS ashing conditions tested for Cd&lt;sub&gt;Ca&lt;/sub&gt;</td>
<td>35</td>
</tr>
<tr>
<td>3.3</td>
<td>Selected validation data for the measurement of Cd&lt;sub&gt;Ca&lt;/sub&gt;</td>
<td>39</td>
</tr>
<tr>
<td>3.4</td>
<td>Selected properties of the soils used in the modelling of Cd partitioning</td>
<td>41</td>
</tr>
<tr>
<td>3.5</td>
<td>Correlations (r) between pairs of properties used in the partitioning modelling</td>
<td>48</td>
</tr>
<tr>
<td>5.1</td>
<td>The effects of (1) 10 mM CaCl&lt;sub&gt;2&lt;/sub&gt;, (2) 1 M NH&lt;sub&gt;4&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;, and (3) 1 M NH&lt;sub&gt;4&lt;/sub&gt;Cl, and shaking time on the proportion of Cd&lt;sub&gt;t&lt;/sub&gt; exchanged with added &lt;sup&gt;110&lt;/sup&gt;Cd, the mean values of pH (pH&lt;sub&gt;s&lt;/sub&gt;) and Cd&lt;sub&gt;E&lt;/sub&gt; for all three electrolytes, and the values of Cd&lt;sub&gt;NH&lt;sub&gt;4&lt;/sub&gt;Cl&lt;/sub&gt;</td>
<td>76</td>
</tr>
<tr>
<td>6.1</td>
<td>Some properties of the soils examined using the x-ray microprobe</td>
<td>84</td>
</tr>
<tr>
<td>7.1</td>
<td>Concentrations of Cd extracted by 1 M NH&lt;sub&gt;4&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt; (Cd&lt;sub&gt;NH&lt;sub&gt;4&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;) and 1 M NH&lt;sub&gt;4&lt;/sub&gt;Cl (Cd&lt;sub&gt;NH&lt;sub&gt;4&lt;/sub&gt;Cl&lt;/sub&gt;) from the 16 soils of pH ≤6.1 studied in Chapter 5</td>
<td>102</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Number</th>
<th>Caption</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Shaking time effect on Cd&lt;sub&gt;Ca&lt;/sub&gt;</td>
<td>40</td>
</tr>
<tr>
<td>4.1</td>
<td>Measured (Appendix 1) and fitted (Model 4.6) values of log&lt;sub&gt;10&lt;/sub&gt; Cd&lt;sub&gt;Ca&lt;/sub&gt; (mg/L) for farmed (triangles) and unfarmed (circles) soils, with a 1:1 line to assist comparison</td>
<td>57</td>
</tr>
<tr>
<td>5.1</td>
<td>Relation between Cd&lt;sub&gt;t&lt;/sub&gt; and Cd&lt;sub&gt;E&lt;/sub&gt;</td>
<td>78</td>
</tr>
<tr>
<td>5.2</td>
<td>The effect of pH&lt;sub&gt;s&lt;/sub&gt; on Cd&lt;sub&gt;NH4Cl&lt;/sub&gt;/Cd&lt;sub&gt;E&lt;/sub&gt;</td>
<td>80</td>
</tr>
<tr>
<td>5.3</td>
<td>Figure 5.3 The effect of pH on Cd&lt;sub&gt;extracted&lt;/sub&gt;/Cd&lt;sub&gt;E&lt;/sub&gt;. The Cd was extracted in 1 M NH&lt;sub&gt;4&lt;/sub&gt;Cl (this study, open circles) or in 1 M CaCl&lt;sub&gt;2&lt;/sub&gt; (Gray <em>et al.</em> (2003), solid circles).</td>
<td>81</td>
</tr>
<tr>
<td>6.1</td>
<td>Schematic of synchrotron micro-XRFS apparatus</td>
<td>86</td>
</tr>
<tr>
<td>6.2</td>
<td>Cd, Cu, Fe, Zn, Pb and K distributions in a small particle in the mount prepared from #6</td>
<td>89</td>
</tr>
<tr>
<td>6.3</td>
<td>Localisation of Cd, Fe, K and Pb in an assemblage of particles in the grain mount of soil #17A that contained ~100 mg Cd/kg</td>
<td>92</td>
</tr>
<tr>
<td>6.4</td>
<td>Data for the top right corner of Fig.6 3 on an ~4x expanded scale</td>
<td>94</td>
</tr>
<tr>
<td>6.5</td>
<td>Cd and Ca distributions in part of a particle of Nauru rock</td>
<td>95</td>
</tr>
</tbody>
</table>
## LIST OF MODELS

<table>
<thead>
<tr>
<th>Number</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>26</td>
</tr>
<tr>
<td>2.2</td>
<td>27</td>
</tr>
<tr>
<td>3.1</td>
<td>48-49</td>
</tr>
<tr>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td>4.1</td>
<td>53</td>
</tr>
<tr>
<td>4.2</td>
<td>53</td>
</tr>
<tr>
<td>4.4</td>
<td>54</td>
</tr>
<tr>
<td>4.4</td>
<td>54</td>
</tr>
<tr>
<td>4.5</td>
<td>54-55</td>
</tr>
<tr>
<td>4.6</td>
<td>55</td>
</tr>
<tr>
<td>5.1</td>
<td>78</td>
</tr>
<tr>
<td>7.1</td>
<td>98</td>
</tr>
<tr>
<td>7.2</td>
<td>99</td>
</tr>
</tbody>
</table>
# COMMON ABBREVIATIONS

<table>
<thead>
<tr>
<th>Short form</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>Denotes Cd(^{2+}) and/or Cd(^{0}) except where this usage may be confusing</td>
</tr>
<tr>
<td>Cd(_{Ca})</td>
<td>The concentration of Cd in a soil extract in a 10 mM CaCl(_2) solution (mg/kg)</td>
</tr>
<tr>
<td>Cd(_{E})</td>
<td>The concentration of Cd that exchanges rapidly with a (^{110})Cd label, i.e. labile Cd (mg/kg)</td>
</tr>
<tr>
<td>Cd(_{NH_4Cl})</td>
<td>The concentration of Cd in a soil extract in a 1 M NH(_4)Cl solution (mg/kg)</td>
</tr>
<tr>
<td>Cd(_t)</td>
<td>The concentration of Cd extracted from a soil by hot concentrated acid (mg/kg)</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>ECEC</td>
<td>The charge sum of the exchangeable cations Ca, Mg, K, Na and Al, or the surface negative charge (cmol(_c)/kg)</td>
</tr>
<tr>
<td>ETAAS</td>
<td>Electrothermal atomic absorption spectrometry</td>
</tr>
<tr>
<td>FSANZ</td>
<td>Food Standards Australia and New Zealand</td>
</tr>
<tr>
<td>ICP–MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>OM</td>
<td>Soil organic matter (g/kg)</td>
</tr>
<tr>
<td>pH(_{Ca})</td>
<td>The pH of a suspension of soil in 10 mM CaCl(_2)</td>
</tr>
<tr>
<td>(R^2)</td>
<td>Regression coefficient</td>
</tr>
<tr>
<td>rsd</td>
<td>Relative standard deviation</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organisation</td>
</tr>
</tbody>
</table>
ABSTRACT

Long-term low-level ingestion of cadmium (Cd) causes human health problems, and in Australia, vegetables supply ~40% of the Cd in the typical diet. Plants take up Cd from the soil; however, the uptake is poorly predicted by simple soil tests, such as the total concentration of Cd (Cd_t). Therefore, a greater understanding of Cd behaviour in soils is needed to improve the prediction of Cd uptake by plants and open a new path to minimise the risks for human health.

The objectives of the research in this thesis were to: identify key soil properties affecting Cd behaviour, identify/develop selective methods to measure them, and to formulate a conceptual model of Cd partitioning. These objectives were based on the hypothesis that empirical modelling informed by a better understanding of Cd chemistry would accurately describe Cd partitioning in soil.

To test the hypothesis, the key properties were measured on soils from the peri-urban fringe of Greater Sydney (n = 41) and a series of models of increasing complexity were fitted to the data. A model with three explanatory variables—log_{10} Cd_t, pH and log_{10} ECEC (effective cation exchange capacity)—explained 94.6% of variation in log_{10} Cd_{Ca} (the concentration of Cd in solution in a suspension of soil in 10 mM CaCl_2), which strongly supported the hypothesis. The study also indicated that the explanatory variables, Cd_t, pH and ECEC, may describe Cd behaviour in many soils, and that for these general models, partition coefficients, such as log_{10} (Cd_t/Cd_{Ca}), are unsuitable dependent variables.

The preceding model used Cd_t as an explanatory variable, notwithstanding that labile Cd (Cd_E) was mechanistically preferable. However, Cd_E can only be measured using isotopic techniques: a requirement that has constrained the evaluation of Cd_E as an index of Cd behaviour and bioavailability. Therefore, a
simple proxy measure of Cd$_E$ was investigated. The literature indicated that solutions of chloride salts might selectively extract Cd$_E$, and Cd extracted into 1 M NH$_4$Cl (Cd$_{NH_4Cl}$) was compared with Cd$_E$ measured by stable isotope dilution ICP-MS. For 23 soils from the partitioning study, 1 M NH$_4$Cl failed to completely extract Cd$_E$, unless the pH was less than 5. The cause(s) of this effect will be investigated with the aim of developing a universally applicable measure of Cd$_E$ that does not require isotopic measurements.

All models of Cd uptake by plants rely on soil properties measured on homogenised samples, although the distribution and bioavailability of Cd vary spatially in the field. Were such variability to increase at the micro-scale, its effects could erode the accuracy with which models could predict Cd behaviour and uptake. Consequently, I tested whether the distribution of Cd could be mapped by using synchrotron micro-x-ray fluorescence spectroscopy (micro-XRFS): the most sensitive method of observation. The soils examined contained 0.3–6.4 mg Cd/kg, i.e. were typical agricultural soils, and one was spiked to ~100 mg Cd/kg. Micro-XRFS mapped the Cd in the spiked soil, and in one particle in the other soils. For typical agricultural soils, the sensitivity realised in this study would have been sufficient to characterise the average Cd binding site, but fell at least 10-fold below that needed to map the Cd distribution in them.

The research satisfied the objectives, advanced knowledge of Cd behaviour in soils, and provided new research leads. These leads include the possibility of developing general models of Cd partitioning in soils, derivatives of which may predict Cd uptake by plants. The accuracy of these models may be strengthened by the use of Cd$_E$ as an explanatory variable, but may be weakened by the effects of in situ variation in the distribution of Cd. The benefits to human health of agricultural practices that decrease dietary Cd justify continuation of research to develop models that accurately predict Cd uptake by plants.
CHAPTER 1—GENERAL INTRODUCTION

1.1 Summary

This Chapter describes:

- The increase in bio-available cadmium (Cd) in the environment, including the human food chain, due to industrialisation.
- The deleterious effects on human health of continued, low-level Cd ingestion in food.
- The rationale for the study, principally being that improved knowledge of Cd behaviour in soils may be used to decrease the availability of Cd to plants and consequently its entry to our food chain.
- The objectives, hypothesis, the supplementary questions that arose during the prosecution of the study, and the research plan.

1.2 Background and scope

Industrialisation and intensive agriculture have increased the concentration of Cd in much of the environment, including the human food chain. The impacts of dietary Cd on health are negative and potentially serious; consequently, it is prudent to consider how to decrease the amount of Cd in the diet.

Plants take up Cd from the soil and, directly or indirectly, are the main dietary source of Cd. The contribution of a plant species to dietary Cd depends on the amount consumed and its Cd concentration: factors that vary regionally. In the Australian context, vegetables supply an appreciable proportion of the Cd and this contribution could be decreased, either by limiting Cd availability in the soil.
(Olsson et al. 2005), or by selecting plants with lower Cd uptake. This study contributes to Cd minimisation in vegetables by advancing knowledge of its behaviour in soils.

1.3 Cadmium—origin, occurrence and properties

Cadmium is formed in supernovae (Hoyle 1947) and is widely distributed in the lithosphere, where its concentration is 0.1–0.5 mg/kg (Nriagu 1980a; Gong et al. 1997). The metal is recovered mainly as a by-product of the extraction and refining of sulfide minerals, especially of zinc (Zn). The Cd content of Zn sulfide minerals is commonly 0.02–1.4% (Nriagu 1980b). Although Cd and Zn are members of the same group in the Periodic Table they are readily separated during refining as Cd has the lower boiling point and its oxide is more easily reduced (Nriagu 1980b).

The stable isotopes of Cd have rounded mass numbers of 106, 108, 110, 111, 112, 113, 114 and 116, with relative abundances (%) of 1.25, 0.89, 12.49, 12.80, 24.13, 12.22, 28.73 and 7.49 (Rosman & Taylor 1997). Isotopic abundance variation is small (Cloquet et al. 2005), so the total Cd concentration can be estimated from, e.g. $^{111}$Cd measured by inductively coupled plasma–mass spectrometry (ICP–MS). Stable- and radio-isotopes are commercially available for isotope dilution studies.

In the environment, Cd occurs predominantly as Cd$^{2+}$ and the properties of this ion, and of many of its salts and complexes, are known (Aylett 1979; Nriagu 1980b). The interactions of Cd$^{2+}$ with other solutes and solid phases, such as those in soils, are characteristic of a ‘soft’ Lewis acid, and contrast with those of ‘harder’ Lewis acids, such as Zn$^{2+}$, so that although Cd$^{2+}$ and Zn$^{2+}$ share a similar
chemistry, Cd\(^{2+}\) bonds more strongly to typical —SH and —NH\(_2\) groups, and more weakly to —COOH groups (Aylett 1979; Sposito 1981; Alloway 1990a; Traina 1999). Coordination numbers are usually 4 and 6. In soils, Cd\(^{2+}\) may undergo hydrolysis, exchange, sorption, complexation and precipitation/occlusion/dissolution (Hayes & Traina 1998), i.e. the number of possible reactions is large. The notional binding of Cd to various soil constituents/fractions has largely been inferred from selective extraction (Calvet et al. 1990; Jeng & Singh 1993) and is justifiably contested (Ma & Uren 1998; Benitez & Dubois 1999; Kinniburgh et al. 1999; Ure & Davidson 2002).

Accurate information about Cd binding sites in soils might be obtained by x-ray absorption fine structure (EXAFS) and nuclear magnetic resonance (NMR), which have revealed the atomic configuration of the average binding sites for Cu\(^{2+}\) and Pb\(^{2+}\) in humic substances (Xia et al. 1997). Again, at high Cd concentrations, the sites of Cd binding have been observed in soil organic matter, using NMR and EXAFS (Hertkorn et al. 2004; Karlsson et al. 2005), and in sewage sludge, using EXAFS (Hettiarachichi et al. 2006). However, the Cd concentrations of interest in agricultural soils are relatively small, so that even a high-flux x-ray microprobe may provide little information about either the average binding site or the Cd distribution.

1.4 Soil Cd and the impact of human activity

Pristine soils have concentrations of Cd that depend on the composition of the parent rock, on the processes of soil formation, including biotic processes, and on aerial deposition. The relative impact of these factors varies spatially, causing wide variation in the concentration of Cd in soils (Alloway 1990a, b; Traina 1999;
Xu & Tao 2004). For example, ‘uncontaminated’ Australian surface soils contain 0.006–2 mg Cd/kg, with a geometric mean of ~0.2 mg Cd/kg (Williams & David 1976; Merry & Tiller 1991; Barzi et al. 1996; Jinadasa et al. 1997).

Human activities typically increase the concentration of Cd in soils, principally by the deposition of particulate emissions to the atmosphere from the smelting of non-ferrous ores, and the burning of municipal wastes and fossil fuels. The particles deposit within 10–30 d, which causes gradients of Cd contamination along radial transects from the sources (Filzec et al. 2004), and greater rates of aerial deposition in the Northern, than in the less industrialised, Southern Hemisphere (Nriagu 1980c; Alloway 1990b; Alloway & Steinnes 1999; Merry & Tiller 1991). For example, Cd deposition in rural areas of industrialised countries in the Northern Hemisphere is ~2 g/ha.y (Alloway & Steinnes 1999), whereas deposition is estimated to be <0.1 g/ha.y across most of Australia (Merry & Tiller 1991).

Soils strongly retain Cd (Pickering 1980; McBride 1991; Sumner & McLaughlin 1996), with typical half-life estimates of hundreds of years (Alloway 1990a). Farm soils receive Cd not only from aerial deposition, but also from fertilisers, organic amendments and gypsum (Williams and David 1976; Alloway 1990a, b; Alloway & Steinnes 1999; Traina 1999; Kpomblekou-A et al. 2002; Sarooshi et al. 2002). The annual amount of Cd removed in crops is typically just a few g/ha (Kikuchi et al. 2007). Therefore, Cd can accumulate from additions as small as 1–5 g/ha.y (Anon. 1996; Christensen & Haung 1999) and is doing so in farmed soils worldwide (Mortvedt 1987; Soon & Abboud 1990; Merry & Tiller 1991;
Holmgren et al. 1993; He & Singh 1993; Cabrera et al. 1994; Jeng & Singh 1993; Zanders et al. 1999). Consequently, the concentration of Cd in agricultural soils usually exceeds that in their unfarmed counterparts (Sánchez-Camazano et al. 1994). However, there are exceptions, e.g. due to enhanced particulate interception by forest canopies (Angehrn-Bettinazzi et al. 1989).

Although the rate of atmospheric Cd deposition on Australian farms is almost negligible (Merry & Tiller 1991), P-fertilisers alone contributed ~9000 t of Cd to these soils during the 20th Century (McLaughlin et al. 1996). Given the large farmed area the risk of excessive land contamination might have been small; however, accessions for vegetable farms were estimated as 40–50 g/ha.y (McLaughlin et al. 1994; Jinadasa et al. 1997). The concentration of Cd in P-fertilisers has declined since those studies (see Section 1.6), indicating that Cd accessions from all sources to vegetable farms may have fallen to perhaps ~20 g/ha.y, although I know of no relevant observations.

Are average Cd accession rates on Australian vegetable farms atypical of those on intensively managed farms generally? Although the rate of atmospheric deposition is less than that in the Northern Hemisphere, this difference is countered by the historically high Cd/P ratio in Australian P-fertilisers (~400 mg Cd/kg P, McLaughlin et al. 1996). Therefore, accessions of Cd to Australian vegetable farms are probably not atypical of those on many intensively managed farms. In any case, one might argue from the foregoing information that total Cd inputs to such soils are an order of magnitude too large to be sustainable.
Cadmium removal from P-fertilisers would not in itself be sufficient to decrease Cd accession rates to sustainable levels on intensively farmed soils because the organic amendments that maintain fertility also contain Cd (Jinadasa et al. 1997). For example, on vegetable farms in Greater Sydney it is usual to apply 5–10 t/ha y of poultry manure (Sarooshi et al. 2002; Chan et al. 2007). (Prospects for decreasing the Cd concentration in organic amendments are discussed in the following paragraph.) Nevertheless, Cd is a contaminant of all the geological phosphates that are the sources of P fertilisers (Van Kauwenbergh 1997). Consequently, Cd removal from P-fertilisers is a first and a necessary step towards sustainability, despite arguments that the manufacturing cost would be prohibitive: an argument that ignores the costs to health and the environment that are discussed in Section 1.5.

If one assumes that the annual applications of organic amendments remain at 5–10 dry t/ha y, and Cd removals are perhaps 2 g/ha y, the concentrations of Cd in these amendments must also decrease, to (say) ~0.2 mg Cd/kg. Poultry manure is the most common organic amendment used in Greater Sydney, and contains 0.2–2 mg Cd/kg (Burgess 1994). This Cd concentration range is similar to that in farmyard manures in the UK (<0.1–0.8 mg/kg) and less than that in many sewage sludges and composts from the same country (Alloway 1990b). Data for the USA are also similar (Kpomblekou-A et al. 2002). The Cd in these organic streams presumably arises from diffuse sources, largely driven by anthropogenic Cd releases (see Section 1.5). Therefore, achieving a typical concentration of ~0.2 mg Cd/kg would require concerted action at a number of levels, i.e. the exercise of political will.
Ensuring that Cd concentrations do not continue to increase in agricultural soils must eventually assume a high priority, given that Cd:

- bioaccumulation generally has undesirable impacts on biota, including humans (see Section 1.5);
- in soil, the bio-availability of past applications declines at a very slow rate, if at all (Jensen & Mosbæk 1990; Hamon et al. 1998);
- decontamination of soils using accumulator plants (Raskin et al. 1997) is not a commercial reality (Chaney et al. 2004; Eapen & D’Souza 2005; Chaney et al. 2007), and cost usually prohibits other forms of remediation, or of soil removal and replacement (Li et al. 2000).

### 1.5 Anthropogenic releases and their impacts on biota

Anthropogenic releases of Cd are highly bioavailable relative to the mineral pools from which they were derived, and much of the released Cd is emitted to the air (Table 1.1). These mineral pools are the major global Cd reservoirs and industrialisation has increased the annual flux of Cd to the air from ~800 t to ~7000 t (Traina 1999), increasing the concentration of Cd in living biota by 10 to 100 times (Nriagu 1980a). Our lungs absorb Cd from the air, but this is a minor source for those not exposed to tobacco smoke or

### Table 1.1 Principal global Cd pools.

<table>
<thead>
<tr>
<th>Description of the pool</th>
<th>Pool size (kg Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>1.5×10⁵</td>
</tr>
<tr>
<td>Hydrosphere</td>
<td></td>
</tr>
<tr>
<td>Oceans</td>
<td>8.5×10¹⁰</td>
</tr>
<tr>
<td>Fresh water</td>
<td>2.0×10⁸</td>
</tr>
<tr>
<td>Glaciers</td>
<td>8.2×10⁷</td>
</tr>
<tr>
<td>Ground- and pore-waters</td>
<td>6.4×10¹⁰</td>
</tr>
<tr>
<td>Biomass</td>
<td></td>
</tr>
<tr>
<td>Marine biota</td>
<td></td>
</tr>
<tr>
<td>Freshwater biota</td>
<td>1.2×10⁷</td>
</tr>
<tr>
<td>Swamps and marshes</td>
<td>7.0×10⁶</td>
</tr>
<tr>
<td>Terrestrial biota</td>
<td>3.6×10⁵</td>
</tr>
<tr>
<td>Terrestrial litter</td>
<td>7.2×10⁸</td>
</tr>
<tr>
<td></td>
<td>1.3×10⁹</td>
</tr>
<tr>
<td>Lithosphere</td>
<td></td>
</tr>
<tr>
<td>Soils to 100 cm</td>
<td>6.6×10¹⁰</td>
</tr>
<tr>
<td>Sedimentary rocks to 45 km</td>
<td>2.8×10¹⁶</td>
</tr>
</tbody>
</table>
industrial fumes (Anon. 1996; Satarug et al. 2004). The main dietary effects on humans are traceable to increased Cd concentrations in agricultural soils and greater uptake of Cd by plants (Sillanpää & Jansson 1992). The kidneys and liver accumulate Cd (Yosumura et al. 1980), and the effects include: kidney damage (Roels et al. 1981; Järup et al. 2000; Moniuszko-Jakoniuk et al. 2005), osteoporosis (Staessen et al. 1999), interference with DNA repair (Hartwig et al. 2002), cancer (Nawrot et al. 2006), pulmonary fibrosis and emphysema (Tátrai et al. 2001), among others (Nriagu 1980d; Friberg et al. 2000). Women are more at risk than men due to differences in Ca metabolism and regulation, body Fe store and kidney sensitivity (Satarug & Moore 2004; Olsson et al. 2002; Nishijo et al. 2004). The adverse effects on humans justify research on the environmental behaviour of Cd; however there are also serious deleterious effects on other biota (Phillips 1980; Sharma 1980; Wong et al. 1980; Tyler et al. 1989; McGrath 1999; McLaughlin et al. 1999; Larison et al. 2000). The only known beneficial effect of Cd on biota is its substitution for Zn, in the carbonic anhydrase of some marine phyto-plankton, when Zn is in short supply (Lee & Morel 1995; Morel & Malcolm 2005).

Deficiencies of Zn, Fe and Ca in the diet increase the toxic effects of Cd in animals and humans (Morgan & Simms 1988; Ewers et al. 1993; Sarasua et al. 1995; Olsson et al. 2002; Reeves & Chaney 2002). Furthermore, recent epidemiological evidence indicates that deleterious health effects may occur at about half the maximum daily intake—1 µg Cd/kg of body weight—recommended by the Codex Alimentarius Commission (Codex) of the World Health Organisation (WHO 1993), even when diets are not known to be deficient
in Zn, Fe or Ca (Satarug et al. 2000; Nordberg & the ChinaCad Group 2003). Thus the recommended maximum Cd intake might be lowered: a consideration with serious potential impacts on international trade (see Section 1.6). In any event, the concentrations of Zn, Fe and Ca in Australian soils—and presumably therefore in diets—are low; consequently, it would be judicious for Australia to independently evaluate the Cd risk to its populace.

1.6 Public policy and vegetable cropping

Food Standards Australia and New Zealand (FSANZ) mandates maximum permitted concentrations (MPCs) for contaminants in food that are enforceable in both countries (Anon. 2005). The toxicology of Cd was reviewed by FSANZ during the 1990s, in the context of regional diets and population groups, from which it was inferred that increased Cd exposure posed unacceptable risks to health (Anon. 1996). The study also found that ~40% of the Cd intake of the average Australian was in plant products, mostly vegetables. Notwithstanding, the Cd MPCs set by FSANZ (Anon. 2005) are similar to the Codex values proposed in the same year.

The review of food regulations by FSANZ is part of a co-ordinated strategy by the Australian Government to minimise the impacts of Cd on health and the agricultural industries. (Some Australian agricultural commodities contain concentrations of Cd that concern certain of our trading partners. Consequently, even a small decrease in the WHO-recommended maximum daily Cd intake could impact negatively on access of Australian agricultural products to those markets.) As part of the strategy, all six states of Australia mandated a maximum Cd
concentration for phosphatic fertilisers of 300 mg/kg P. For commercial reasons, the average Cd content of P-fertilisers declined to <100 mg Cd/kg P by 2004 (Stacey et al. 2008). Other governments have acted similarly, e.g. the European Parliament set a maximum concentration of 138 mg Cd/kg P for fertilisers, effective by 2010, decreasing to 46 mg Cd/kg P by 2012 (European Commission 2004). However, not even the lowest of these limits will halt the accumulation of Cd in intensively managed agricultural soils, let alone reverse the trend (see Section 1.4).

The peri-urban fringe of Greater Sydney has a long history of intensive agriculture which has left the farm soils with concentrations of Cd that are at least 10 times those in their unfarmed counterparts (Jinadasa et al. 1997). The concentration of Cd in some leafy vegetables grown there tends to exceed the guideline values (Bower 1994; Jinadasa et al. 1997; Hardy 2002) set by FSANZ (Anon. 1996). This is a concern because the peri-urban fringe of Greater Sydney is the most productive horticultural zone in Australia and supplies much of the perishable vegetables for Sydney’s ~4 million inhabitants (James 2002; Gillespie & Mason 2003).

1.7 Opportunities to decrease the uptake of Cd by vegetables

The rate of ion uptake from solution by plant roots is postulated to be a function of the activity of the free ion (Allen et al. 1996; Parker & Pedler 1997; Nolan et al. 2003a). For well characterised solutions at equilibrium, the free ion activity is reliably estimated using speciation models, such as GEOCHEM (Parker 1995) and there are a number of such models (Loeppert et al. 1995). For Cd in the soil
solution the principal species taken up are probably $[\text{Cd(H}_2\text{O)}_6]^{2+}$ and labile complexes such as those with $\text{Cl}^-$ ligands. However, solutions that have contacted soil contain poorly characterised organic ligands whose reactions with Cd are also poorly characterised, and may not be at equilibrium (Mackey & Zirino 1994). These ligands probably complex Cd because similar molecules do so in aquatic systems (Benedetti et al. 1996; Nimmo & Fones, 1997; Xia 1997; Lores & Pennock 1998; Capodaglio et al. 1998; Kinniburgh et al. 1999; Ellwood 2004). Consequently, speciation models cannot be applied with confidence to such solutions (del Casthilo et al. 1993a; Hesterberg et al. 1993; Xia 1997; Kretzschmar et al. 1999); although this difficulty may be overcome (Tipping 1994; Rachou & Sauvé 2008).

Given the uncertainties of using speciation models for soil solutions/extracts it would be advantageous to be able to measure free Cd$^{2+}$. However, that too is problematic: the speciation measurements seem method-dependent and inconsistent with measurements in aquatic systems (Candelaria et al. 1995; Holm et al. 1995a,b; Andrewes et al. 1996; Benedetti et al. 1996; McBride 1997; Nimmo & Fones 1997; Xia 1997; Capodaglio et al. 1998; Lores & Pennock 1998; Kinniburgh et al. 1999; Ge et al. 2000; Sauvé et al. 2000b). Results obtained by using Donnan membranes appear more promising (Temminghoff et al. 2000; Wu et al. 2000; Nolan et al. 2003b; Cancès et al. 2003; Weng et al. 2005).

The problems confronting a mechanistic description of Cd behaviour in soil/solution (two phase) systems are even greater than those described above for the solution phase (Nakhone 1989; Plette et al. 1999). These difficulties can be
avoided by using regression (empirical) instead of mechanistic modelling. Empirical modelling is a statistical procedure that describes the relationship between one variable (dependent) and several others (explanatory)—soil properties being the relevant variables for Cd partitioning in soils. Empirical modelling needs no prior mechanistic knowledge, and an unfortunate consequence is that mechanistic knowledge has largely been ignored in the choice of properties used as variables, and how those properties should be measured. Finally, empirical models that embody mechanistic principles are usually described as either semi-empirical or mechanistic (Celardin 1999; Sauvé et al. 2000b). Use of this nomenclature should be abandoned because the models clearly remain empirical. Consequently, I coined and have used the clumsy, but more accurate descriptor, mechanistically-informed empirical models.

1.8 Objectives, hypotheses and hypothesis testing

The objectives of my research—were to identify key soil properties affecting Cd behaviour at the soil/solution interface and in solution, to selectively measure those properties, and to formulate a conceptual model of Cd partitioning as the basis for mechanistically-informed empirical modelling.

The hypothesis—was that the effects of soil properties on Cd partitioning may be accurately described by mechanistically-informed empirical modelling.

The hypothesis was tested—by fitting mechanistically-informed empirical models of increasing complexity to the data for a suite of soils with diverse properties.
Two supplementary questions—addressed perceived limitations on the assessment of Cd behaviour, namely can:

1. labile Cd be measured without isotope addition? Ready access to estimates of labile Cd would allow this conceptually important property to be broadly evaluated as an index of Cd behaviour and plant uptake.
2. the distribution of Cd in agricultural soils be mapped? The micro-scale distribution of Cd may affect the accuracy with which the behaviour of Cd in soil and its uptake by plants can be predicted.

Research plan to test the hypothesis:

- Identify the key constituents/properties that control Cd behaviour and use the concepts to formulate a conceptual model and a modelling protocol (see Chapter 2).
- Choose/develop methods of measurement that are selective for the key soil constituents/properties and apply them to a suite of aerobic, acidic mineral soils (see Chapter 3).
- Fit mechanistically-informed empirical models to the data for the measured soil properties and evaluate the results (see Chapter 4).

Research plan to address the two supplementary questions:

- Estimate labile Cd using isotope dilution and compare the amount with that extracted by 1 M NH₄Cl (see Chapter 5).
- Test whether a synchrotron x-ray microprobe can map the distribution of Cd in small soil particles (see Chapter 6).
1.9 Conclusion

Cadmium inputs to intensively cultivated soils are unsustainably large, and the resulting contamination will require management long after inputs are decreased to sustainable levels. This management would be assisted by a better understanding of the effects of soil properties on Cd partitioning, including the development of a new method for the estimation of labile Cd and the testing of micro-x-ray fluorescence spectroscopy to map the spatial distribution of Cd in agricultural soils. The new knowledge developed may indicate the feasibility of developing models of Cd partitioning with wide application. Provided that the concentration of Cd in solution is strongly related to Cd uptake, such models may be the starting point for predicting Cd bioavailability and mobility.
CHAPTER 2—A CONCEPTUAL FRAMEWORK AND MODEL TO DESCRIBE CADMIUM BEHAVIOUR IN SOIL

2.1 Summary

Interactions between Cd and the constituents of acidic, aerobic mineral soils provided the rationale for:

- a hierarchy of key properties that may influence Cd partitioning;
- a conceptual model of those effects on Cd partitioning;
- a suite of methods to measure the properties (applied in Chapter 3);
- multiple regression modelling of the effects of those properties on Cd partitioning (applied in Chapter 4).

2.2 Introduction

The need to predict Cd transport and bioavailability in soils is broadly recognised (van der Zee & van Riemsdijk 1987; Boekhold & van der Zee 1990; Sillpanää & Jansson 1992; Palm 1994; del Castilho & Chardon 1995; Allen & Hansen 1996; Parker & Pedler 1997; Sauvè et al. 2000b; Peijnenburg et al. 2000). However, as argued in Section 1.7:

- a lack of thermodynamic data for reactions at the soil/water interface and in the soil solution has hampered the development of mechanistic models of the behaviour of Cd (Hesterberg et al. 1993; Tipping 1994; Benedetti et al. 1996; Xia 1997; Kinniburgh et al. 1999);
• some reactions between Cd and soils, and soil constituents, are slow and the consequences of assuming equilibrium are untested (Johnson 1990; Barrow 1993; Ainsworth et al. 1994; Mackey & Zirino 1994; Backes et al. 1995; Axe & Anderson 1997; Trivedi & Axe 2000; Hertkorn et al. 2004); therefore, until these difficulties are resolved it is reasonable to use empirical modelling to describe the behaviour of Cd in soils.

An empirical model is represented by an equation in which the dependent variable lies to the left of the equality and the explanatory variables to the right. A traditional model of Cd partitioning in soils might use a partition coefficient, \( \text{Cd}K_d \), as the dependent variable—the ratio of the concentration of Cd in solution to that on the soil, or \textit{vice versa}—and soil/solution properties as explanatory variables. A statistical procedure is used to fit the model to the data. For this study, forward stepwise multiple linear regression was used, which provided useful statistics including:

• a partial regression coefficient for each explanatory variable; and,

• estimates of the reliability of the coefficients (standard errors), the fit of the model (\( R^2 \)), and the proximity of the modelled and the observed values (rsd).

Of these statistics, the partial regression coefficient may need explanation. Briefly, this coefficient is an estimate of the slope of the linear relation between the dependent variable, and that part of the explanatory variable that is uncorrelated with the other explanatory variables.
Before an empirical model is used for predictions it should be validated against data independent of those used in its development. The predictions from validated models may be accurate, though the models are neither mechanistically sound nor complete. Consequently, one should be cautious about their use, e.g. for predictions outside the validated scope or as the basis of mechanistic inference.

Empirical models have been used to describe the behaviour of Cd in soils and I postulated that the modelling would benefit from the inclusion of mechanistic knowledge (see Section 1.8). As the first step in testing this hypothesis I developed a conceptual framework based on the results of studies of Cd (de)sorption by synthetic materials, and by soil separates and whole soils, under acidic, aerobic conditions. The results of chemical extractions and of earlier empirical modelling were also considered. The soils from Greater Sydney to which the modelling would be applied (see Chapter 4) are all acidic; consequently, Cd reactions specific to alkaline soils (O’Connor et al. 1984; Barrow et al. 1989; McLaren et al. 1998; Ramachandran & D’Souza 1999) were outside the scope of the study and have not been considered.

2.3 The conceptual framework

Selective chemical extraction—has been used to operationally define Cd fractions in acidic, aerobic mineral soils, such as:

1. soluble plus exchangeable;
2. specifically sorbed;
3. sorbed to organic matter (OM) or easily reducible Mn and Fe oxides;
4. very strongly sorbed to OM or other oxidisable species; and
Fractions 1–3 are the presumed reservoirs of labile Cd (Cd_E), i.e. participate in rapid exchange with Cd in solution. The rapidity of exchange may explain why the concentration of Cd extracted into dilute solutions of neutral salts, such as CaCl_2, is one of the more reliable predictors of plant uptake (Sauerbeck & Styperek 1985; Whitten & Ritchie 1991; He & Singh 1993; Rayment 1994; Krishnamurti et al. 1995; McLaughlin et al. 1997a). In contrast, fraction 5 is unrelated to Cd bioavailability (Rogers 1996; Sloan et al. 1997); however, chemical fractionation does not otherwise discriminate well between the nominal Cd pools (Nirel & Morel 1990; Jeng & Singh 1993; Ma & Uren 1998; Benitez & Dubois 1999; Hall & Pelchat 1999; Ho & Evans 2000; Ma & Rate 2007). The difficulty of inferring environmental behaviour from soil extractions has been reviewed exhaustively (Lake et al. 1984; Quevauviller et al. 1993; Kennedy et al. 1997; Sauvé 2002; Ure & Davidson 2002). At best, selective chemical extraction appears to be tenuously related to and predictive of Cd behaviour in soils: disappointing when such methods are gaining political traction in the assessment of environmental risk (Quevauviller et al. 1994; Lebourg et al. 1996).

**Mechanistic studies**—are the prime source of information on the reactions of Cd with individual soil components. For example, synthetic goethite (FeOOH) has been the substrate in many studies of Cd sorption, and the results are relevant to soils because goethite is the most abundant hydrous oxide of Fe in aerobic mineral soils (Schwertmann 1964). Hydroxyl ions sorb at the goethite/water interface, causing the surface to have a pH-dependent negative charge. The surface charge is also modified by the sorption of multiply charged anions, e.g. orthophosphate...
(Kuo & McNeal 1984). The negatively charged interface attracts cations (Barrow 1993); consequently, in acidic, aerobic mineral soils, the surface charge is estimated as the sum of the formal charges of the exchangeable cations Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\) and Al\(^{3+}\) (Gillman 1979), i.e. the effective cation exchange capacity (ECEC).

Sorption of the ions of a metal by a hydrous oxide exhibits a sharp increase above a characteristic pH (edge). For Cd on goethite this occurs near pH 5.6 (Johnson 1990; Backes et al. 1995): patchiness in the charge density at the surface, surface defects and internal lattice vacancies provide sites that vary widely in Cd affinity and reaction rate (Barrow & Shaw 1979; Johnson 1990; Rudzinski et al. 1993; Ainsworth et al. 1994; Backes et al. 1995; Axe & Anderson 1997; Trivedi & Axe 2000). The effects of these slower reactions are observed between cycles of sorption and desorption (Barrow 1993) and using NMR (Hertkorn et al. 2004). Cadmium desorption may also slow with time, although other factors may intervene (Jensen & Mosbæk 1990; McLaughlin et al. 1996). Therefore, Cd (de)sorption parameters may prove useful indices of the bioavailability of soil Cd (Boekhold & van der Zee 1990; Palm 1994; del Castilho & Chardon 1995).

Surface charge affects Cd (de)sorption by soils (Elliott 1983; Naidu et al. 1994), in which the main charged constituents are clays, organic matter (OM) and the hydrous oxides of Fe, Mn and Al for example. This complexity provides many possibilities for Cd binding (Amacher et al. 1986; Boekhold et al. 1993; Mann & Ritchie 1994; Sloan et al. 1997; Hamon et al. 1998; McLaren et al. 1998; Smolders et al. 1999). The surface charge on the hydrous oxides, OM and some
clays is pH-dependent; therefore, more Cd is released from these solid phases into solution as pH decreases (Barrow 1987; Anderson & Christensen 1988; Boekhold et al. 1993; Naidu et al. 1994; Temminghoff et al. 1995). Soil OM may also affect Cd binding by providing a low density of high affinity binding sites, as it does for Cu (Xia 1997). However, this observation was made using extracted, purified soil OM, and typical OM extraction conditions are extreme, raising issues of integrity and hence of relevance to the behaviour of natural OM in situ (Hertkorn et al. 2004; Karlsson et al. 2005). The prospect of observing the average Cd binding site in soils is addressed in Chapter 6.

The hierarchy of soil properties that might therefore be useful explanatory variables of Cd behaviour is: the concentration of sorbed Cd (Cdₖₐ₅), measured operationally as labile Cd (Cdₑ) >pH >OM ≈ surface charge >other variable charge constituents.

In the aqueous phase, the mechanistically appropriate measures for reactions of Cd are the activities of its (chemical) species, which are affected by complexation and ionic strength. Equilibrium speciation models such as GEOCHEM (Parker 1995) can perform such calculations for Cd in simple mixed systems, such as suspensions of goethite in dilute NaCl. In contrast, equilibrium models cannot be used with confidence to speciate Cd in solutions that have been in contact with soils (see Section 1.7), although this situation is in flux (Tipping 1994; Rachou & Sauvé 2008).
Difficulties in speciating Cd in soil extracts and in the soil solution have not deterred interest in the effects of dissolved organic matter (DOM) on the concentration of Cd in solution and on Cd transport through soils (del Castilho et al. 1993a; Hesterberg et al. 1993; Kalbitz & Wennrich 1998; Römkens & Salomons 1998; Elzinga et al. 1999; Sauvé et al. 2000b; Weng et al. 2002; Strobel 2005). Components of the aqueous phase, other than DOM, also affect Cd binding, for example:

- multivalent ions modify surface charge (Pyman et al. 1979; Kuo & McNeal 1984; Undabeytia et al. 1998; Bolan et al. 1999; Hamon et al. 2002a);
- divalent cations compete for sorption sites (Hendrickson & Corey 1981; Christensen 1987; Temminghoff et al. 1995; Wang et al. 1997; Echeverría et al. 1998; Undabeytia et al. 1998; Wilkins et al. 1998); and,

Therefore, the hierarchy of solution properties that may be useful explanatory variables is: pH > DOM ≈ Cl > multivalent ions.

*Effects of soil properties on Cd (de)sorption*—have been noted for single properties in many studies (John 1972; Gerritse & van Driel 1984; Buchter et al. 1989; Jopony & Young 1994; Lee et al. 1996; Gray et al. 1999). However, John (1972) and Levi-Minzi et al. (1976) were among the first to use multiple regression to describe the combined effects of several soil properties on Cd sorption. Unfortunately, the concentrations of Cd used in both studies were orders of magnitude greater than those in most agricultural soils, raising questions about
the general applicability of the results. In contrast, Anderson and Christensen (1988) measured the partitioning of a single, small addition of Cd to 38 soil samples, at three pH values (inexplicably 117 combinations), and a model in which the:

- dependent variable was the log transformation of the ratio of the concentration of Cd in soil to that in solution, i.e. \( \log_{10} \frac{C_{d}}{K_d} \); and
- explanatory variables were pH and the log\(_{10}\) transformations of the concentrations of Mn\(_{ox}\), organic C and Al\(_{dt}\), where the subscripts \( dt \) and \( ox \) denote the fractions extracted by dithionite and oxalate.

The model explained a remarkable 93% of the variation in the dependent variable, perhaps in part because the 38 samples were taken from just 13 soil profiles.

Empirical modelling studies have used a number of soil properties as variables, and these include: Cd\(_s\), Cd\(_E\), total Cd (Cd\(_t\)) and the coefficients of the Langmuir and Freundlich equations (John 1972; Rattan & Sehgal 1989; Basta et al. 1993; McBride et al. 1997; Römkens & Salomons 1998; Springob & Böttcher 1998b; Elzinga et al. 1999; Gray et al. 1999; Schug et al. 1999; Celardin 1999; Sauvé et al. 2000a). If (de)sorption controlled Cd\(_s\), then Cd\(_E\) would be a more mechanistically appropriate explanatory variable than Cd\(_t\). Yet Cd\(_t\) has been used much more frequently than Cd\(_E\), even though Cd\(_E\) is not a fixed proportion of Cd\(_t\) (Gerritse & van Driel 1984; Nakahone & Young 1993; Springob & Böttcher 1998a; Wilkins et al. 1998; Smolders et al. 1999; Young et al. 2000; Degryse et al. 2003). The more frequent use of Cd\(_t\) than Cd\(_E\) may not be perverse, but reflect limited access to the isotope dilution techniques needed to measure Cd\(_E\). In such models, pH is generally an explanatory variable, and the other properties used as
explanatory variables, in decreasing frequency order, are: OM > surface charge > (hydrous) oxides of Fe, Mn and Al.

The parentheses around the prefix *hydrous* above indicate that the methods used to extract the oxides varied widely between studies in selectivity for the sometimes minor hydrous components (Mehra & Jackson 1960; McKeague *et al.* 1971; Parfitt & Childs 1988; Buchter *et al.* 1989; Zachara *et al.* 1993; Holm *et al.* 2003; Agbenin 2003). Such differences in selectivity may have contributed to the conflicted reports of the effects of the oxides (McBride *et al.* 1997; Gray *et al.* 1999; Schug *et al.* 1999; Sauvé *et al.* 2000a). Extraction by oxalate in the dark is selective for the hydrous oxides of Al (Al$_{ox}$) and Fe (Fe$_{ox}$) (Schwertmann 1964) and it is reasonable to assume that co-extracted phosphate (P$_{ox}$) is released largely from the hydrous oxides. The hydrous oxides of Mn may also be selectively attacked by this reagent; however, Mn oxalate is sparingly soluble (CRC Handbook of Chemistry and Physics 2006), and Mn was extracted using hydroquinone in ammonium acetate (Sherman *et al.* 1942).

2.4 Methodological issues

*Selective measures of soil constituents*—the argument in the preceding paragraph raises a generic question, namely: would more-, rather than less-, selective measures of the soil fractions that are presumed to be actively involved in Cd (de)sorption be superior explanatory variables in modelling Cd partitioning? As a chemist, one is inclined to answer “yes”; however, comparisons have not been made, perhaps because the number of potential measures is large. My study has little to add on this topic because the plan was, within practical limits, to use
selective measures for the key properties. The rationale for choosing particular methods of analysis is given below and the protocols themselves are described in detail in Chapter 3.

**Added and native Cd**—there are more studies of the effects of soil properties on the partitioning of *added* than of *native* Cd (Gray *et al.* 1999; Sauvé *et al.* 2000a). (Here the terms *added* and *native* refer to relative residence times of the Cd in the soil, rather than to its origin.) The advantage of Cd additions is that they can be adjusted to simplify the partitioning measurements; however, the disadvantage is that the partitioning of the added and native Cd may differ. One factor that contributes to this uncertainty is the occurrence of slow Cd fixation (Amacher *et al.* 1986; Jensen & Mosbæk 1990; Ainsworth *et al.* 1994; Backes *et al.* 1995; Franchi & Davis 1997; Hamon *et al.* 1998; McLaren *et al.* 1998; Smolders *et al.* 1999). Other systematic differences between the two types of study are that: sorption experiments generally use briefer periods of contact between Cd and the soil, greater Cd loads and more dilute suspensions (Hendrickson & Corey 1981; Sumner 1994; Springob & Böttcher 1998a; Wilkins *et al.* 1998; Chang & Wang 2002). That is, there are reasonable grounds to question how similar the effects of soil properties on the partitioning of added and native Cd may be. As my ultimate goal is to help manage the uptake of predominantly native Cd, I confined this study to the partitioning of native Cd. However, the issue of comparability was too important to avoid—since it bears on whether the totality of the data on Cd behaviour might usefully be combined in a meta-analysis—consequently, the question is addressed inferentially in Chapter 7.
**Soil suspensions**—are more convenient than moist soils in which to observe the partitioning of Cd (Zabowski & Ugolini 1990; Giesler et al. 1996; Holm et al. 1998); consequently, I opted to use suspensions. However, the large dilution during the preparation of suspensions can decrease the ionic strength of the aqueous phase, and cause the pH to increase (Sumner 1994). Since pH has a strong effect on Cd behaviour (see Section 2.3), it is prudent to minimise gross changes in ionic strength if one is concerned about the relevance of Cd behaviour in the suspensions to its behaviour in soils *in situ*. Dilution can be eliminated by preparing a unique electrolyte for each soil to match the major ion composition of its soil solution (Undabeytia et al. 1998). This approach is also onerous and does not accommodate the possibility that minor constituents of the soil solution may influence Cd behaviour—a pragmatic compromise is to suspend soils in a common background electrolyte.

The preferred ions for background electrolytes in studies of the interactions of Cd with a variety of substrates have been Na$^+$, K$^+$, NO$_3^-$ and ClO$_4^-$: ions that have small specific effects on the (de)sorption of Cd either by competition or complexation (Garcia-Miragaya & Page 1976; Hendrickson & Corey 1981; Zachara et al. 1993; Ainsworth et al. 1994; McBride et al. 1997; McLaughlin et al. 1997b). In contrast, Ca$^{2+}$ competes with Cd for sorption and Cl$^-$ forms complexes with Cd (Gerritse & van Driel 1984; Boekhold et al. 1993). However, Ca$^{2+}$ and Cl$^-$ are relatively abundant in soil solutions; consequently, these ions have found increasing favour as constituents of background electrolytes for studies of Cd behaviour in soils (Jopony & Young 1994; Backes et al. 1995; Temminghoff et al. 1995; Houba et al. 1996; Wang et al. 1997; Gray et al. 1999). Finally, the
concentration of Cd extracted in dilute solutions of CaCl$_2$ is related to that in the soil solution (Degryse et al. 2003) and, in some studies, to Cd bioavailability (Sauerbeck & Styperek 1985; Whitten & Ritchie 1991; He & Singh 1993; Rayment 1994). Consequently, I used 10 mM CaCl$_2$ as the background electrolyte.

The use of 10 mM CaCl$_2$ as the background electrolyte—dictated that for mechanistic consistency, the concentration of Cd ($C_{d_{Ca}}$), the pH ($pH_{Ca}$) and the concentration of DOM should be measured in suspensions of soil in this electrolyte. In addition, ECEC is pH dependent in most soils; consequently, ECEC was also measured at a pH near that in 10 mM CaCl$_2$.

Soil OM—was measured by combustion, i.e. total C ($C_t$). In the absence of appreciable amounts of char and macroscopic organic particulates, this measure is selective for soil OM (Baldock & Skjemstad 1999).

2.5 The base model and its application

Literature cited in Section 2.3 shows that pH and the concentration of sorbed Cd, and by inference labile Cd ($C_{d_{E}}$), strongly affect the activity of free Cd$^{2+}$ in solution ($C_{d_{a}}$). Since $C_{d_{a}}$ is likely to be related to the mobility and bioavailability of Cd, my conceptual base model used $\log_{10} C_{d_{a}}$ as the dependent variable and the explanatory variables $pH_{Ca}$ and $\log_{10} C_{d_{E}}$:

$$\log_{10} C_{d_{a}} = \alpha_0 + \alpha_{Cd} \cdot \log_{10} C_{d_{E}} + \alpha_{pH} \cdot pH_{Ca}$$

Model 2.1

where $\alpha_0$ is the intercept, and $\alpha_{Cd}$ and $\alpha_{pH}$ are respectively the partial coefficients for $\log_{10} C_{d_{E}}$ and $pH_{Ca}$. Interestingly, Sauvé (2002) independently arrived at a similar expression commencing from a ‘mass action-driven … surface complexation model’.
Regression models of Cd behaviour in soils more often use log_{10} \text{Cd}_{Kd} than log_{10} \text{Cd}_{a} as the dependent variable (see Section 2.3). The relative merits of these two properties as dependent variables have not been evaluated, perhaps because of the previously noted difficulty of measuring \text{Cd}_{a} (see Section 1.7). (I return to the use of partition coefficients as dependent variables in Chapter 4.) Most partitioning modelling uses \text{Cd}_{t} as the intensity variable, which I did to facilitate direct comparisons with those studies, even though the mechanistically preferable measure would have been \text{Cd}_{E}. Therefore my base model was:

\[
\log_{10} \text{Cd}_{Ca} = \alpha_0 + \alpha_{\text{Cd}t} \log_{10} \text{Cd}_{t} + \alpha_{\text{pH}Ca} \quad \text{Model 2.2}
\]

### 2.6 The modelling protocol

The first step will be to fit the base model to a set of data collected in accordance with the principles described in Sections 2.3–2.5. The second and subsequent steps will add the next highest priority explanatory variable, refit and eliminate non-significant terms, until the list of candidate properties is exhausted. This procedure is described as stepwise forward multiple regression analysis, and its use will facilitate comparisons with other modelling in which the range of explanatory variables was less complete and will demonstrate the effects of particular explanatory variables.

The rationale for the order of addition of the explanatory variables to the base model (Model 2.2) was presented in Sections 2.3–2.5 and is summarised below:

**Priority 1: OM**—much of \text{Cd}_{E} in soils may be bound to OM, and OM has a strong effect on Cd behaviour.
**Priority 2: ECEC**—is a proxy for surface charge, which has a strong mechanistic foundation for affecting Cd behaviour, although it has not frequently been tested as an explanatory variable.

The properties OM and ECEC are usually positively related, and the relation is affected by pH. All three of these properties are listed among my high priority explanatory variables. Relations among explanatory variables can cause statistical problems during regression modelling; however, any adverse effects can be detected as described Chapter 4.

**Priority 3: hydrous oxides of Fe, Al and Mn**—strongly sorb Cd, nonetheless on the few occasions that measures of these oxides have been tested as explanatory variables their effects have conflicted (Anderson & Christensen 1988; del Castilho *et al*. 1993a; Bolton & Evans 1996; Gray *et al*. 1999; Schug *et al*. 1999). There are several reasons for this conflict. For example, some of the studies extracted more/less reactive oxide fractions (see Section 2.3), and there was no consideration of the effects of the Cd ‘sorption edges’.

A ‘sorption edge’ is the pH threshold for a particular cation/substrate combination above which sorption of the cation increases rapidly with increase in pH, e.g. the sorption edges for Cd on goethite (Fe), alumina (Al) and hausmannite (Mn) fall in the pH ranges 5–6, 7–8 and 3–4 (Backes *et al*. 1995; Spark *et al*. 1995). The effect of sorption edges is tested during the modelling (see Chapter 4). So far as I can determine, this is the first
proposal to test the use of sorption edges in an empirical model of Cd partitioning in soil.

**Priority 4: DOC, Cl and Ca**—the priority of these properties was downgraded in the expectation that their effects would be suppressed by the use of 10 mM CaCl₂ as the background electrolyte (del Castilho et al. 1993a, b; McLaughlin et al. 1997b; Elzinga et al. 1999; Römkens & Dolfing 1998; Römkens & Salomons 1998; Holm et al. 1995a,b; Xia 1997; Impellitteri et al. 2002).

### 2.7 Conclusion

There was sufficient mechanistic and other information to: identify the key soil constituents/properties that influence Cd behaviour, allow the principles to be applied to their measurement to be described, and to design a conceptual model of the effects of soil properties on Cd partitioning. Stepwise forward regression modelling will test the hypothesis that mechanistically-informed empirical modelling may accurately describe the partitioning of Cd in aerobic, acidic mineral soils. The modelling will also facilitate comparisons with earlier studies, and may provide new insights into the effects of particular explanatory variables.
3.1 Summary

- Selective methods of analysis for the properties identified in Chapter 2 are described and applied to 41 soils from Greater Sydney, of which 29 were from vegetable farms and 12 from unfarmed reference sites.
- The results show that the soils have diverse properties, some of which are affected by land-use.

3.2 Introduction

The key soil properties affecting Cd partitioning, and principles for their measurement were laid out in Chapter 2. In this Chapter I describe the laboratory procedures that gave effect to those principles and the data acquired when the procedures were applied to a suite of 41 soils from Greater Sydney.

For the mechanistic reasons given in Section 2.3, 10 mM CaCl$_2$ was used as the background electrolyte for soil suspensions. The complementary operational reasons for this choice were that:

- 10 mM CaCl$_2$ is unbuffered and is the preferred electrolyte for soil pH measurement in Australia ($\text{pH}_{\text{Ca}}$);
- the $\text{pH}_{\text{Ca}}$ protocol is validated and robust;
- the concentration of Cd in 10 mM CaCl$_2$ ($\text{Cd}_{\text{Ca}}$) is measurable using electrothermal atomic absorption spectrometry (ETAAS) without pre-concentration: ETAAS was accessible for this part of the study; and,
if pH were measured in 10 mM CaCl$_2$, 10 mM BaCl$_2$ could be used to displace the exchangeable cations—their sum (ECEC) is an estimate of surface charge—because the pH of the soil suspensions in both electrolytes would be similar and surface charge is pH dependent (see Section 2.3). A similar strategy was used by Khanna et al. (1986).

The immediate challenge was to validate a method to extract Cd into 10 mM CaCl$_2$ (Cd$_{Ca}$), and to accurately measure it. Suspensions of soil in 10 mM CaCl$_2$ flocculate readily. However, even centrifugation may not remove any co-extracted colloids, and these may be associated with Cd (del Castilho et al. 1993b; Jopony & Young 1994; Kretzschmar et al. 1999; Impellitteri et al. 2002; Simpson 2002; Lombi et al. 2003). The presence of Cd associated with micro-particulates could inflate the values of Cd$_{Ca}$, because ETAAS does not discriminate well between Cd in solution and Cd associated with particulates (Lieser et al. 1982). In addition, micro-particulate Cd might vary between soils. As a precaution against serious inflation of Cd$_{Ca}$ by Cd associated with micro-particulates, I analysed extracts before and after ultra-filtration.

3.3 Materials and methods

3.3.1 Sites

The sites were sampled during 1994 to survey Cd accumulation in the soils on which vegetables are grown commercially in Greater Sydney (Jinadasa et al. 1997). There were 29 farmed and 12 unfarmed sites across five soil types. The soil on each of the unfarmed (reference) sites was paired taxonomically with that on at least one farmed site. Unfarmed sites were identified as near as possible to
the corresponding farmed sites, e.g. in fence lines, and areas of remnant native vegetation. Farming practices included: the use of lime, gypsum, inorganic fertilisers and poultry manure; intensive tillage; irrigation and multiple cropping. Typical of the industry, the farms were small family enterprises (Gillespie & Mason 2003). The land-use history of a site relied on the knowledge of the current land holders; consequently, it is unlikely that all the ‘unfarmed’ sites were pristine or that the farming histories were complete.

3.3.2 Sampling
Within a site, soil cores were taken from an apparently uniform area of 150–500 m² at 3–6 locations, the greater the area the more locations. At each location, debris was cleared from the surface and a stainless steel tube was driven into the soil to a depth of ~300 mm. (The tube diameter was ~75 mm, which minimised compaction of the core.) The tube and intact core were extracted, the core was extruded using a wooden rod and the surface 150 mm retained. Within a sampling area, the 0–150 mm sections of the individual cores were combined to give a composite sample.

3.3.3 Sample preparation, storage and use
Samples were air-dried at ~40°C and crushed using a stainless steel mortar and pestle. Stones and plant debris were discarded, and the fraction passing a 2 mm plastic sieve was put into a 500 mL polycarbonate screw-capped jar. A representative sub-sample of 50 g of this coarse material was ground in a tungsten carbide geological ring mill (model 100, Tema, United Kingdom). The mill was run for 10 s, within which the soil was reduced to a powder, all of which passed a
0.2 mm sieve. This fine material was placed into a 50 mL polycarbonate screw-capped jar. During crushing, grinding and sieving, cross-contamination was minimised by processing clean sand between samples. The polycarbonate storage containers had been cleaned before use as described for laboratory plastic-ware in Section 3.3.4. Air-dry samples were stored in the dark at room temperature (~22°C) and remixed prior to removing aliquots for analysis. Aliquots of masses >1.0 g and ≤1.0 g were drawn respectively from the coarser (<2 mm) and the more finely (<0.2 mm) ground materials. These procedures maintained sample integrity and allowed representative sub-sampling.

### 3.3.4 Laboratory reagents, operations and quality assurance

The water and all the chemicals were of at least reagent quality, e.g. reagent grade HNO₃ was purified by sub-boiling distillation from a quartz vessel in a laminar-flow cabinet. Where practicable, extracts and solutions were prepared and diluted by mass, or the volumetric dilutions were confirmed gravimetrically. Unless noted otherwise, the protocols used had been validated prior to this study and were subjected to proficiency audits as part of a national accreditation program.

All the chemical analyses presented in Appendix 1 and summarised in this Chapter, are means of at least two independent measurements. Duplicate analyses that varied by more than ±10% from the mean were repeated by re-analysing in duplicate and obtaining a consensus mean. Other steps taken to assure data quality included the analysis of reference materials, reagent blanks and ‘spike’ recoveries.

Special precautions were taken to minimise Cd contamination and loss. Soil extracts and standard solutions contacted only clean plastic-ware, and extracts were
analysed within 48 h of preparation (Sekaly et al. 1999). New plastic-ware was washed in detergent and rinsed. Rinsed items were soaked for at least 16 h in the first of 2 baths of ~5% v/v HNO₃ (the ‘dirty’ bath). Items were transferred from the ‘dirty’ to the ‘clean’ bath and soaked for at least a further 16 h. Plastic-ware was removed from the ‘clean’ bath immediately before use and rinsed: it was dried only if necessary. When the concentration of Cd in the ‘clean’ bath reached ~10 μg/L, the bath was down-graded to ‘dirty’, whereupon the acid in the previous ‘dirty’ bath was replaced and its status upgraded to ‘clean’. Used plastic-ware was rinsed and cycled through the HNO₃ baths to ensure that Cd contamination was small and uniform.

3.3.5 Development of a validated CdₙCa protocol

Validating the method of Cd measurement—was a prerequisite to investigating the extraction of Cd into 10 mM CaCl₂. The ETAAS instrument (model 5000, Perkin Elmer USA) was fitted with a pyrolytic graphite furnace and L’vov platform. The instrument was operated with Zeeman background correction and an auto-sampler that dispensed both the sample (20 μL) and a matrix modifier (20 μL)—consisting of Mg(NO₃)₂ and NH₄H₂PO₄—into the depression in the centre of the platform. The furnace was sheathed from the air by a stream of argon gas. The Cd solutions used to calibrate the instrument were prepared in a 1% HNO₃ matrix from a solution certified to contain 1000 mg Cd/L (Alpha Resources, USA). Absorbance was measured at 228.8 nm in the peak area mode, which provides more reliable concentration data than peak height (Dubois 1991; Imai et al. 2004).
Initial settings of the ETAAS furnace (Table 3.1) were taken from a validated Cd method for acid digests of soils and plants (Colin Short, unpublished data). As explained in detail in Section 3.4.1, these conditions for the ETAAS furnace proved unsatisfactory for soil extracts in 10 mM CaCl₂ and I tested other conditions (Table 3.2).

Validation of the measurement of Cd₇ included the analysis of replicate extracts (prepared to also examine the effect of extraction time and micro-particulates), the recovery of standard additions, and a comparison with an independent laboratory using a different measurement technique, i.e. ICP mass-spectrometry (ICP–MS).

The Cd₇ and Cd₆ data presented in Appendix 1, and summarised in this Chapter, were obtained using ETAAS furnace conditions modified from those described in Table 3.1, by changing the ashing temperature to 550°C and the dwell time to 50 s. The limit of detection was ~1 µg Cd/L. When the Cd concentration in an extract was 1–5 µg/L, at least four additional replicate extracts were analysed, and the mean reported. At Cd concentrations >0.2 mg/L, ETAAS results were confirmed using inductively coupled plasma–optical emission spectroscopy (ICP–OES).

### Table 3.1 ETAAS furnace settings first used for Cd₇.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Description/conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Inject</td>
<td>solution and matrix modifier at RT</td>
</tr>
<tr>
<td>2. Evaporate</td>
<td>Ramp RT–120°C and dwell for 60 s</td>
</tr>
<tr>
<td>3. Ash</td>
<td>Ramp 120–900°C and dwell for 30 s</td>
</tr>
<tr>
<td>4. Measure</td>
<td>Jump 900–1300°C and dwell for 6 s</td>
</tr>
<tr>
<td>5. Purge</td>
<td>Jump 1300–2600°C and dwell for 10 s</td>
</tr>
</tbody>
</table>

### Table 3.2 ETAAS ashing* conditions tested for Cd₇.

<table>
<thead>
<tr>
<th>Treatment number</th>
<th>ETAAS furnace conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature</td>
</tr>
<tr>
<td>1</td>
<td>900</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
</tr>
</tbody>
</table>

*Ashing is operation 3 in Table 3.1.
To simplify the models presented in Chapter 4, concentrations of Cd and Cd_{Ca} are reported in the same units (mg/kg soil), despite their typically large concentrations differences, e.g. the respective medians were 0.85 and 0.042 mg/kg (Table 3.4).

**The extraction of Cd by 10 mM CaCl₂ solutions**—was investigated using a subset of four samples (# 11, # 27, # 28 and # 17A) that had widely different compositions (Appendix 1). Extracts were prepared by shaking 10 g of soil with 50 mL of 10 mM CaCl₂ solution, end-over-end at ~30 rpm and ~25°C. Four replicate suspensions were prepared for each sample, i.e. a total of 16 suspensions. Replicate suspensions were randomised and blocked, and aliquots were withdrawn at 0.5, 1, 2 and 6 h. Aliquots were centrifuged and part of the supernatant was passed through a 10 kDa polyether sulfone cut-off filter (Millipore, USA)*. Both the filtered and unfiltered extracts were analysed for Cd using the optimised ETAAS conditions already described. The effects of shaking time were evaluated using analysis of variance, and of ultra-filtration, using a paired t-test.

The protocol used to acquire the Cd_{Ca} data was to weigh 10 g of soil and shake it with 50 mL of 10 mM CaCl₂ solution, end-over-end at ~30 rpm and ~25°C for 2 h. About 20 mL of the soil suspension was decanted into a 25 mL polypropylene tube, which was then capped and centrifuged. An aliquot was acidified (1% HNO₃) and analysed for Cd_{Ca} using the validated ETAAS procedure above.

---

* A separate 10 kDa polyether sulfone cut-off membrane was used to filter each extract. The membrane was located at the base of an ~250 µL cylinder. The open end had a flange that prevented the cylinder passing inside the top of a tapered, polypropylene centrifuge tube, and the assembly was loosely capped. Ultra-filtration relied on centrifugal force. These filter devices were chosen because the materials used in their construction withstood soaking in dilute HNO₃, i.e. the risk of Cd contamination appeared minimal, and they had a cut-off diameter of ~3 nm, which is very small relative to clays, which are defined as having diameters <2 µm. To my knowledge these devices had not previously been used in trace metal studies.
3.3.6 Other methods of analysis

**pH**<sub>Ca</sub> and dissolved organic carbon (DOC)—were measured on the suspensions in 10 mM CaCl<sub>2</sub> (see above). DOC was determined on part of the supernatant removed for Cd<sub>Ca</sub> determination, using a DOC analyser (Shimadzu model TOC 5000, Japan), and pH<sub>Ca</sub> on the remaining suspension. (Separation of the aliquot for the measurements of Cd<sub>Ca</sub> and DOC, before immersion of the combination pH/reference electrode, avoided any possible effects on Cd<sub>Ca</sub> and on DOC of the potassium chloride that leaks from the salt bridge of the reference electrode.) The pH meter (Radiometer model PHM 250, Denmark) was calibrated using buffers certified at approximate pH values of 7 (phosphate) and 4 (potassium hydrogen phthalate). Suspensions were allowed to settle and the bulb of the glass electrode was immersed in the layer of settled soil, with the liquid junction of the reference electrode in the supernatant (Milham & Vimpany 1987). The liquid junction of the reference electrode was fast-leaking and the potential was checked daily (NATA 1995). Suspension pH was measured to 0.01 units and rounded to 0.1 units.

‘Total’ elements—were extracted from soil (0.2-1.0 g) using reverse *aqua regia* (5 mL) assisted by microwave heating (“Ethos” model, Milestone USA) in sealed poly-fluorocarbon vessels (Long & Martin 1989). Sample weight and extract dilution were adjusted to optimise the Cd concentration for measurement by ETAAS. Diluted digests were centrifuged to remove coarse suspended particles. Element concentrations, e.g. Zn (Zn<sub>t</sub>), were measured using ICP-OES Appendix I).

**Total carbon** (C<sub>t</sub>)—was determined using a Leco C analyser (model CN 2000, USA), which converts organic C to CO<sub>2</sub> and measures the CO<sub>2</sub> using infrared gas analysis. In acidic soils that contain little char or macroscopic organic particulates
this measure is selective for the C in soil OM (Baldock & Skjemstad 1999).

*The net surface charge*—of a soil is negative and balanced by the charge on the exchangeable cations (ECEC). In aerobic, acidic mineral soils the main exchangeable cations are Ca$^{2+}$, Mg$^{2+}$, K$^{+}$, Na$^{+}$ and Al$^{3+}$ (Gillman 1979; Khanna et al. 1986). I leached these cations from 4 g of soil using 200 mL of 10 mM BaCl$_2$ (Milham & Vimpany 1987) and measured their concentrations using ICP–OES.

*Hydrous oxides*—of Fe ($\text{Fe}_{\text{ox}}$) and Al ($\text{Al}_{\text{ox}}$) were extracted in the dark using an acidic solution of ammonium oxalate (Schwertmann 1964). $\text{Fe}_{\text{ox}}$ and $\text{Al}_{\text{ox}}$, and co-extracted P ($\text{P}_{\text{ox}}$), were measured using ICP-OES. Oxalate is not suitable for the extraction of the hydrous oxides of Mn, because Mn oxalate is sparingly soluble (CRC Handbook of Chemistry and Physics 2006). Therefore, the easily reducible, presumably hydrous, oxides of Mn, were extracted using hydroquinone in 1 M ammonium acetate (Sherman et al. 1942) and measured by flame AAS (Mn$_{\text{hq}}$).

*Electrical conductivity and soluble chloride*—were determined on the supernatant of a suspension of soil (10 g) in water (50 mL) that were shaken end-over-end at ~30 rpm and ~25°C for 1 h. Electrical conductivity (EC) was measured in the supernatant (Milham & Vimpany 1987) using a conductivity bridge (Radiometer model CDM 230, Denmark). An aliquot of the supernatant was analysed for Cl$^-$ by titration with Ag$^+$ (Corning model 926, USA).

*Soil type*—descriptions were based on parent material, age (as reflected in the profiles), and landscape position (Walker & Hawkins 1957; Hawkins & Walker 1960; Hawkins & Haddad 2005).
Soil texture and approximate clay content—were estimated after Northcote (1979).

3.4 Results

3.4.1 Validation of the Cd\textsubscript{Ca} protocol

*ETAAS conditions*—the method for Cd measurement in acid digests of plants and soils had been validated prior to this study (see Section 3.3.5) and at 5–50 \( \mu \text{g Cd/L} \) the results had a coefficient of variation of \( \sim 5\% \). I obtained similar precision for Cd in 10 mM CaCl\(_2\). In contrast, the coefficient of variation for soil extracts in 10 mM CaCl\(_2\) averaged \( \sim 60\% \) (Table 3.3) and the recovery of added Cd was low and variable.

Independent analysis of the same extracts using ICP–MS confirmed that the recovery/ reproducibility problem resided in the ETAAS measurements (Table 3.3).

The four combinations of temperature and dwell time tested for the ETAAS furnace (Table 3.2) produced a range of apparent Cd concentrations in replicate extracts of the same four soils. As the ashing temperature was decreased from 900\(^\circ\)C to 600\(^\circ\)C the mean values for each soil increased and the variation between replicates declined. The decrease in temperature from 600\(^\circ\)C to 500\(^\circ\)C had no further effect.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>( \text{Cd}_{\text{Ca}} ) values measured under different conditions (mg/kg)</th>
<th>ETAAS(^2)</th>
<th>ICP–MS(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Validated</td>
<td>Initial</td>
</tr>
<tr>
<td>11</td>
<td>0.01</td>
<td>0.021</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>(±60)</td>
<td>(±6)</td>
<td>(±5)</td>
</tr>
<tr>
<td>27</td>
<td>0.02</td>
<td>0.054</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>(±60)</td>
<td>(±4)</td>
<td>(±5)</td>
</tr>
<tr>
<td>28</td>
<td>0.002</td>
<td>0.0040</td>
<td>0.0042</td>
</tr>
<tr>
<td></td>
<td>(±80)</td>
<td>(±15)</td>
<td>(±6)</td>
</tr>
<tr>
<td>17A</td>
<td>0.03</td>
<td>0.060</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>(±50)</td>
<td>(±3)</td>
<td>(±4)</td>
</tr>
</tbody>
</table>

\(^1\)Full sample descriptions are in Appendix 1.

\(^2\)ETAAS furnace conditions: initial as in Table 3.1 and validated: ashing temperature 550\(^\circ\)C and a dwell time of 50 s.

\(^3\)Results from an independent laboratory.
Repetition of the ETAAS analyses using an ashing temperature of 550°C and a dwell time of 50 s, gave a mean for each of the four soils that did not differ from the ICP–MS values \((P < 0.01\), Table 3.3). The standard deviations of the means for both ETAAS and ICP–MS were also similar, except for soil # 28. Ashing at 550°C with a dwell time of 50 s proved equally effective for measuring Cd; consequently, these were the conditions used for all the Cd measurements (Table 3.4 and Appendix 1).

**Preparation of 10 mM CaCl\(_2\) extracts**—for soils # 11, 27, 28 and 17A there was a tendency for the concentration of Cd to increase with shaking time from 30 min to 1 h; longer shaking times (<6 h) had no further effect \((P < 0.01\). The trends were similar for all 4 soils, so typical data are presented (Fig. 3.1). Ultra-filtration of the supernatants before analysis also had no effect on the values of Cd\(_{Ca}\) \((P < 0.01\).

![Figure 3.1 Shaking time effect on Cd\(_{Ca}\).](image)

The value of Cd\(_{Ca}\) at a given time is expressed as a percentage of that at 6 h. Each data point is for a single replicate.
### 3.4.2 Soil properties

The soils displayed a wide range of properties within and between the five types, e.g. the textures represent approximate clay contents of 5–40% (Appendix 1). For soil properties such as Cd\textsubscript{t}, Cd\textsubscript{Ca}, and P\textsubscript{t}, a few relatively large values caused the means to considerably exceed the medians (Table 3.4). In addition, land-use changed the values of some properties, e.g. it typically increased Cd\textsubscript{t}, Cd\textsubscript{Ca}, Zn\textsubscript{t}, ECEC, pH\textsubscript{Ca} and all measures of P, and decreased C\textsubscript{t} (Table 3.4 and Appendix 1).

### Table 3.4 Selected properties of the soils used in the modelling. The complete data set is in Appendix 1.

<table>
<thead>
<tr>
<th>Property with the units in parentheses</th>
<th>For the 29 farmed soils</th>
<th>For the 12 unfarmed soils</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range median mean</td>
<td>Range median mean</td>
</tr>
<tr>
<td>Cd\textsubscript{Ca} (mg/kg)</td>
<td>0.001–0.30 0.042 0.066</td>
<td>0.002–0.30 0.008 0.037</td>
</tr>
<tr>
<td>Cd\textsubscript{t} (mg/kg)</td>
<td>0.11–6.4 0.85 1.43</td>
<td>0.02–1.93 0.04 0.36</td>
</tr>
<tr>
<td>pH\textsubscript{Ca}</td>
<td>4.1–6.8 5.2 5.3</td>
<td>4.3–5.7 4.5 4.6</td>
</tr>
<tr>
<td>C\textsubscript{t} (%)</td>
<td>0.71–3.1 1.65 1.61</td>
<td>1.3–3.9 2.33 2.39</td>
</tr>
<tr>
<td>ECEC (cmol\textsub{c}/kg)</td>
<td>2.0–39 11 13</td>
<td>1.0–18 8.71 9.45</td>
</tr>
<tr>
<td>Fe\textsub{ox} (mg/kg)</td>
<td>410–7300 2900 3300</td>
<td>460–5900 2800 3000</td>
</tr>
<tr>
<td>P\textsub{t} (mg/kg)</td>
<td>320–7500 1150 1500</td>
<td>17–800 200 300</td>
</tr>
</tbody>
</table>

1 The methods of analysis are described in Sections 3.3.5 and 3.3.6.

### 3.5 Discussion

#### 3.5.1 Cd measurements

*Cadmium partitioning was the focus of the study*—so a considerable effort was made to ensure that the Cd measures were accurate. The protocol for Cd\textsubscript{t} had been validated prior to this study, whereas that for Cd\textsubscript{Ca} had not. The initial Cd recoveries from soil extracts in 10 mM CaCl\textsubscript{2} were low and variable, which prompted a study of the operating conditions for the ETAAS furnace (Table 3.3). Once the ETAAS measurement was functioning I investigated the time taken for
the Cd concentration to ‘stabilise’ in the extracts (Fig. 3.1) and the effect of ultra-filtration of the extracts before analysis. These results are discussed in the following paragraphs.

**Cd loss from 10 mM CaCl$_2$ extracts in the ETAAS furnace**—the ashing stage removes volatiles that may otherwise interfere during the Cd measurement. (This is less of a concern when using ETAAS instruments fitted with Zeeman background correction, such as the instrument used in this study.) Consequently, the temperature reached during ashing is the hottest of the pre-measurement stages (Table 3.1). Since Cd and some of its compounds are volatile, the low variable Cd recoveries (Table 3.3) pointed towards volatilisation losses during ashing.

The Cd losses that occurred from the soil extracts did not occur when Cd was added to 10 mM CaCl$_2$, i.e. the loss from the extracts was not due to the volatilisation of CdCl$_2$, even though the ashing temperature of 900°C exceeded its melting point (568°C, Aylett 1979). However, the soil extracts contained DOC (Appendix 1), and pyrolysis of DOC during ashing might reduce Cd$^{2+}$ to the metal (Cd$^0$), which has a boiling point of only 767°C (Aylett 1979), and much of any Cd$^0$ formed could volatilise at the temperature used for ashing (900°C, Table 3.1).

Cadmium is entrained in tobacco smoke (Saratug & Moore 2004), which is consistent with the postulated reduction of Cd$^{2+}$ to Cd$^0$ during ashing in the ETAAS. Nevertheless, the losses should be limited at ashing temperatures well below its boiling point, and the use of such temperatures is not uncommon (Bermejo-Barrera *et al.* 1998; Imai *et al.* 2004). Consistent with this reasoning, ashing at 550°C (for 50 s) restored recoveries of Cd and minimised variation
between repeated/replicated measurements, i.e. the data validated the use of these conditions for the quantitative measurement of $C_d_{Ca}$. Only one discrepancy remained between the ETAAS and ICP–MS results, i.e. for soil #28, the CV of the ETAAS mean exceeded that for the ICP–MS mean (Table 3.3). This difference occurred because, for this sample alone, the Cd concentration was approaching the limit of detection for ETAAS, but not of ICP–MS.

**Shaking time**—the lack of effect of shaking times greater than 1 h on $C_d_{Ca}$ (Fig. 3.1) is consistent with the results of other short-term batch ‘equilibration’ studies on acidic soils (Amacher *et al.* 1986; Franchi & Davis 1997; Wang *et al.* 1997; Harper *et al.* 1998; Gray *et al.* 1999). The exchange of isotopically labelled Cd in soils is also rapid (Nakahone & Young 1993; Hamon *et al.* 1998; Smolders *et al.* 1999; Gérard *et al.* 2000; Gray *et al.* 2004), as is the exchange of Na and Cd ions on zeolite (Biškup & Subotić 2004), and of water molecules coordinated to Cd in solution (Inada *et al.* 2005). Therefore, the requirement to shake suspensions of soils for 30 min to 1 h for the concentration of Cd to apparently stabilise presumably reflects the time taken for pseudo-equilibrium to be established between the solution and the internal surfaces of soil particles that may have had diameters as large as 2 mm (Jain & Ali 2000).

The 6 h maximum shaking time (Fig. 3.1) was too brief to reveal the effects of the slow fixation/release reactions that occur between Cd and the soil (Johnson 1990; Ainsworth *et al.* 1994; Backes *et al.* 1995; Axe & Anderson 1997; Trivedi & Axe 2000; Barrow 1993; Mackey & Zirino 1994; Hertkorn *et al.* 2004). However, soils in the field are dynamic systems, and rapid Cd (de)sorption reactions may dominate Cd bio-availability, which is why I focussed on the rapid reactions.
Ultra-filtration—of the supernatants after centrifugation did not decrease the concentration of Cd measured by either ETAAS or ICP-MS. In evaluating these data one needs also to know that ETAAS does not completely recover metals from micro-particulates (Lieser et al. 1982), whereas ICP-MS does. Consequently, little of the Cd in the extracts seems to have been associated with micro-particulates. However, the ultra-filtered extracts contained DOC (Appendix 1), i.e. colloidal organic material (Jensen & Christensen 1999; Kretzschmar et al. 1999; Peña-Mendez et al. 2005), and such colloids can be associated with Cd and other metals (Lieser et al. 1990; del Castilho et al. 1993b; Jopony & Young 1994; Kretzschmar et al. 1999; Impellitteri et al. 2002; Simpson 2002; Lombi et al. 2003). In addition, anodic stripping voltammetry indicates that part of the Cd in soil extracts in 50 mM CaCl₂ may be organically complexed (Andrewes et al. 1996). That is, the lack of effect of ultra-filtration is insufficient to prove that Cd associated with micro-particulates did not inflate the values of Cd₇₆. This topic merits further comment and is addressed inferentially during in Sections 4.5 and 7.2.

Sporadic Cd contamination dogged the ultra-filtration experiment. The caps of the centrifuge tubes in which the 1 kDa filters were mounted were colour coded green, and the green pigment contained Cd…

3.5.2 Soil properties

Soil type and land-use affected the ranges of many of the properties (Table 3.4 and Appendix 1). These effects are apposite to the use of these properties as variables in the modelling (see Chapters 2 and 4).

Cadmium—the Cd values for some soils on the Triassic shale, and the most recent
river terrace, were 1–6 mg/kg, which is considerably greater than previously reported for the cultivated layer of Australian agricultural soils (Rayment 1994; McLaughlin et al. 1997a) and New Zealand (Gray et al. 1999). However, Cd concentrations <20 mg/kg occur in other shale soils, e.g. in California and Derbyshire (Alloway 1990b). In addition, the full range of Cd concentrations (0.02–6 mg/kg, Appendix 1) is not unusual compared to that for agricultural soils worldwide (Sillanpää & Jansson 1992; Sánchez-Camazano et al. 1994).

The increase in Cd during farming (Table 3.4), is similar to that on intensively managed soils that also have low rates of aerial Cd deposition (Merry & Tiller 1991; Barzi et al. 1996; McLaughlin et al. 1996; McLaughlin & Singh 1999). However, Cd accessions to the farmed soils may have been larger than inferred from the measured increases of Cd in the surface layer, because not all the applied Cd may have remained there (Rothbaum et al. 1986; McGrath & Lane, 1989).

Studies of Cd partitioning have used many background electrolytes, so there are limited data pertaining to any one, and, such data are even rarer for Australian soils. However, Michael McLaughlin (CSIRO, Adelaide) had unpublished CdCa data on soils from ~140 vegetable farms from across Australia and kindly provided them: the range of CdCa values was <0.001–0.32 mg/kg, which is comfortably similar to my range of 0.001–0.30 mg/kg (Table 3.4).

\(pH_{Ca}\) values were acidic and the range was increased by farming (Table 3.4) because amendments of lime and dolomite were common. The lowest pHCa value (4.1) is extremely acidic and the upper value (6.8) is almost neutral, i.e. the range is consistent with my focus on Cd behaviour in acidic soils.
OC—is selectively estimated as C_t in acidic soils such as those from Greater Sydney, provided that no appreciable amounts of char and macroscopic organic particulates are present (Baldock & Skjemstad 1999). I removed as much of the organic particulates as possible during sample preparation; nevertheless, some would have remained. The soils would also have contained char, as the area has a long fire history (Russell-Smith et al. 2007). The extent of the contributions of organic particles and char to C_t is unknown and may have varied between samples. The C_t content of the samples varied across a considerable range of values.

ECEC—values had a wide range (1.0–39 cmol_c/kg, Table 3.4) as a consequence of the sampling strategy. The farmed soils had greater ECEC values than their unfarmed counterparts, a difference largely attributable to the concomitant increase in pH_{Ca} noted above, and its effect on ECEC (see Model 3.1).

The hydrous oxides—too exhibited a considerable range of concentrations (e.g. 410–7300 mg Fe_{ox}/kg, Table 3.4), and the values are not atypical of other Australian soils (Vimpany et al. 1997).

The concentrations of DOC—were similar to those reported for other soils (John et al. 1988; Romkens & Dolfing 1998), but less than occur in municipal wastes and pig slurry (del Castilho et al. 1993b; Kaschl et al. 2002). However, the concentrations of DOC may have been greater had the soils been suspended in pure water instead of a background electrolyte that contained 10 mM Ca^{2+} (Romkens & Dolfing 1998). Since Cd in solution may be associated with DOC (see Section 3.5.2) it is not unreasonable to surmise that the 10 mM Ca^{2+} may also
have influenced $\text{Cd}_{\text{Ca}}$. However, this presumed negative effect is opposed by competition between $\text{Cd}^{2+}$ and $\text{Ca}^{2+}$ for sorption, and by the formation of chloro complexes of Cd (Gerritse & van Driel 1984; Boekhold et al. 1993). Consequently, the net result of these effects is unclear.

**EC, Cl and soil texture**—merit no special comment.

**Other interesting effects of farming**—of less importance to this study than those discussed above include an increase in the median $\text{P}_t$ from ~200 to ~1150 mg/kg (Table 3.4). Low $\text{P}_t$ levels are typical of the soils in the Region (Hawkins & Haddad 2005). Although $\text{P}_t$ is not generally a useful agronomic index of P status, the values for the unfarmed soils were so low that, they explain why poor agricultural productivity on these soils threatened the survival of early European settlement (Haworth 2003). Interestingly too, despite repeated large applications of organic amendments, vegetable farming was associated with a decline in $\text{C}_t$ (Table 3.4). There is other evidence that vegetable farming in Greater Sydney exploits soil organic matter (Sarooshi et al. 2002, Chan et al. 2007). Therefore, even with improved soil management practices, access to organic amendments that are low in Cd (say ~0.2 mg Cd/kg), will remain important to sustainable intensive production on these soils (see Section 1.4).

### 3.5.3 Relations among soil properties

Some pairs of soil properties were related (Table 3.5), and a highly relevant, if predictable, relationship was that of $\text{pH}_{\text{Ca}}$ and $\log_{10}\text{Cd}_{\text{Ca}}$ (see Section 2.3). This relation was affected by land-use and is but one example of the many effects of land-use on relations between the measured properties (Table 3.5).
There was also a strong relation between $P_t$ and $Fe_{ox}$ for the unfarmed soils ($r = 0.91$, Table 3.5). This relation is consistent with that for virgin Australian soils (Norrish & Rosser 1983), supporting the relatively unfarmed status of the reference sites. The relation was weaker for the farmed soils ($r = 0.61$), presumably because of the effect of additions of P fertiliser on $P_t$ (Tables 3.4 and 3.5).

Table 3.5 Correlations ($r$) between pairs of properties used in the partitioning modelling. The $r$ values in bold are significant at $P < 0.05$. Data are for the 29 farmed soils, and in parentheses, for the 12 unfarmed soils. The properties are as described in Table 3.4 and raw data are in Appendix 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>$\log_{10} Cd_t$</th>
<th>$\log_{10} Cd_{Ca}$</th>
<th>$\log_{10} ECEC$</th>
<th>$pH_{Ca}$</th>
<th>$\log_{10} Fe_{ox}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log_{10} Cd_{Ca}$</td>
<td>$0.59(0.76)$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\log_{10} ECEC$</td>
<td>$0.61(0.39)$</td>
<td>-0.18(-0.18)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$pH_{Ca}$</td>
<td>0.19(0.45)</td>
<td>-0.59(-0.17)</td>
<td><em>0.57(0.60)</em></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\log_{10} Fe_{ox}$</td>
<td>$0.50(0.33)$</td>
<td>-0.09(-0.16)</td>
<td><em>0.88(0.93)</em></td>
<td>0.26(0.47)</td>
<td>-</td>
</tr>
<tr>
<td>$\log_{10} C_t$</td>
<td>0.27(0.14)</td>
<td>-0.27(-0.10)</td>
<td><em>0.73(0.67)</em></td>
<td>0.31(0.09)</td>
<td><em>0.66(0.60)</em></td>
</tr>
<tr>
<td>$\log_{10} P_t$</td>
<td>0.39(0.40)</td>
<td>-0.35(-0.11)</td>
<td><em>0.76(0.97)</em></td>
<td><em>0.66(0.55)</em></td>
<td><em>0.61(0.91)</em></td>
</tr>
</tbody>
</table>

There were also more complex relations among groups of properties, e.g. $\log_{10} ECEC$ was affected by $pH_{Ca}$, and by ($\log_{10}$ transformed values of) clay content, $C_t$ and $Fe_{ox}$. Kaolinite was probably the dominant clay mineral (Michael Maguire & Ian Vimpany, unpublished data). The surface charge of this clay, and that of soil OM and of the hydrous oxides of Fe, are pH dependent; therefore, it is not surprising that these properties together explained >90% of the variation in $\log_{10} ECEC$ (Model 3.1). The effect of $Fe_{ox}$ interacted with farming ($p < 0.01$). For brevity I simply present the relation for the more numerous group of farmed soils:

$\log_{10} ECEC = -0.13 \pm 0.272 + 0.292 \pm 0.126 \log_{10} C_t$  
$+ 0.116 \pm 0.030 \cdot pH_{Ca} + 0.009 \pm 0.003 \cdot {\text{clay}}$  
$+ 0.331 \pm 0.097 \log_{10} Fe_{ox}$
Model 3.1

$R^2 = 0.945, n = 29$

where the standard errors of the coefficients are in parentheses.

### 3.6 Conclusion

The methods used to measure the soil properties satisfy the main conceptual requirements laid down in Chapter 2. The properties of the 41 soils, and the relations among those properties, are not atypical of Australian soils. Most of the properties have a large range of values and, with some exceptions, the ranges for the farmed and unfarmed soils overlap considerably. Consequently, the data appear suitable to challenge the hypothesis that mechanistically-informed empirical modelling may accurately describe the partitioning of Cd in aerobic, acidic, mineral soils.
CHAPTER 4—MODELLING THE EFFECT OF SOIL PROPERTIES ON CADMIUM PARTITIONING

4.1 Summary

• The base model of Cd partitioning (Model 2.2) was fitted to the data for 41 soils presented in Chapter 3 ($R^2 = 0.885$). Soil type and land use had strong effects ($P < 0.01$).

• Other explanatory variables were then added stepwise, in the order: log$_{10}$ $C_t$, log$_{10}$ ECEC and log$_{10}$ $Fe_{ox}$, as prioritised in Chapter 2.

• Log$_{10}$ ECEC displaced log$_{10}$ $C_t$ and the effects of soil type from the model, and improved the fit ($R^2 = 0.946$).

• Log$_{10}$ $Fe_{ox}$ also had an effect above pH 5.6 ($P < 0.01$) and improved the $R^2$ to 0.974; nonetheless, the effect of land-use persisted ($P < 0.01$). None of the other properties had an effect.

• The strength of the modelling supported the hypothesis that mechanistically-informed empirical modelling may describe the effects of soil properties on Cd partitioning (see Section 1.8).

4.2 Introduction

In Chapter 2, soil constituents that react with Cd were identified and this information was used to formulate a conceptual model of Cd solubility. The base model (Model 2.2) is repeated here for convenience as Model 4.0:

$$\text{Log}_{10} \Cd_{Ca} = \alpha_0 + \alpha_{Cd}\text{log}_{10} \Cd_t + \alpha_{pH}\text{pH}_{Ca}$$

Model 4.0
where ‘α’ represents a coefficient and the subscript to the right of the ‘α’ indicates the associated variable, $\text{Cd}_i$ is the total Cd concentration in the soil, and $\text{Cd}_{Ca}$ and $\text{pH}_{Ca}$ are respectively, the concentration of Cd and the pH of the aqueous phase of a soil suspension in 10 mM CaCl$_2$. It was argued that Model 4.0 should be used to describe Cd partitioning and that the effects of additional constituents should be added and tested serially in the order: OM, ECEC, the hydrous oxides of Fe, Al and Mn, DOC, exchangeable Ca and soluble Cl (see Section 2.5), i.e. by stepwise forward multiple linear regression.

Chapter 3 described the methods of analysis used to selectively measure the preceding soil properties, presented the results for 41 soils from Greater Sydney, and concluded that the data appeared suitable to test the hypothesis that mechanistically-informed empirical modelling may accurately describe the effects of soil properties on the partitioning of Cd (see Section 1.8).

In this Chapter the modelling method and the data described above are used to test the preceding hypothesis. The results are presented and discussed in the context of previous modelling studies.

### 4.3 Multiple linear regression modelling

*This statistical procedure*—adjusts the coefficient of an explanatory variable for the effects of correlations with other explanatory variables, to produce a partial regression coefficient. The partial coefficient estimates the slope of the linear relation between the dependent variable and the uncorrelated part of the explanatory variable. Consequently, for the same two variables, the value of the
partial coefficient may differ from that of the coefficient in the simple linear regression relation. Also when explanatory variables are strongly correlated, the estimates of their partial regression coefficients may become unreliable. To detect such effects, added variable plots (Cook & Weisberg 1982), and the variance inflation factors of the partial coefficients (Montgomery & Peck 1982), were examined to assess the partial regressions, as were the patterns of residuals for each soil property.

I followed the protocol described in Sections 2.5 and 2.6, i.e. the base model represented by Model 4.0 was fitted to the data for soils from 29 farmed and 12 unfarmed sites, from 5 soil types, on the peri-urban fringe of Greater Sydney (Appendix 1). The values of all soil properties, other than pH$_{Ca}$, were log$_{10}$ transformed, and Cd$_{t}$ and Cd$_{Ca}$ were both expressed in mg Cd/kg.

The order of addition of other soil properties was: OM, ECEC, Fe$_{ox}$, Al$_{ox}$, Mn$_{pq}$, P$_{ox}$, DOC, Cl, and Ca$_{ex}$. On the addition of each property a pair of multiple linear regression models was fitted. The first model consisted of the linear effects only. The second was an extended model, which included the quadratic effects of the soil properties, the effects of land-use and soil type, and the interactions of land-use and soil type with the linear effects. Each model was reduced by removing all terms that were non-significant ($P > 0.05$); although model hierarchy was preserved for the extended models, i.e. if a quadratic term was significant, the corresponding linear term was retained, significant or not (see Model 4.4). The statistical package used for the modelling was ASReml (Gilmour et al. 2002). Models are presented with coefficients of determination ($R^2$) and residual standard
deviation (rsd) values. The partial regression coefficients of explanatory variables are followed by standard errors in parentheses.

4.4 Results

4.4.1 The models

The base model:

\[ \text{Log}_{10} \text{Cd}_{\text{Ca}} = 1.39 (\pm 0.30) + 0.98 (\pm 0.06) \text{log}_{10} \text{Cd}_t - 0.66 (\pm 0.06) \text{pH}_{\text{Ca}} \]

\[ (n = 41, R^2 = 0.885, \text{rsd} = 0.245) \]  

Model 4.1

As explained in Section 3.3, land-use and soil type are factors in the data, and when added to Model 4.1 both had strong effects on \( \text{log}_{10} \text{Cd}_{\text{Ca}} \) \( (P < 0.001) \). However, there were no interactions with either \( \text{log}_{10} \text{Cd}_t \) or \( \text{pH}_{\text{Ca}} \) \( (P > 0.1) \).

In Model 4.1, inclusion of the effects of land-use and soil type improved the values of \( R^2 \) (0.951) and \( \text{rsd} \) (0.171). However, the strength of the soil type and land-use effects may have been due, at least in part, to the absence from the model of some highly influential explanatory variables. Therefore, presentation of models that include the effects of land-use and soil type is deferred until most of the other highly influential explanatory variables were in the models, i.e. Model 4.4.

The addition of \( \text{log}_{10} \text{C}_t \) to Model 4.1 gave:

\[ \text{Log}_{10} \text{Cd}_{\text{Ca}} = 2.02 (\pm 0.32) + 0.94 (\pm 0.05) \text{log}_{10} \text{Cd}_t - 0.64 (\pm 0.05) \text{pH}_{\text{Ca}} - 0.61 (\pm 0.17) \text{log}_{10} \text{C}_t \]

\[ (n = 41, R^2 = 0.914, \text{rsd} = 0.214) \]  

Model 4.2

When added to Model 4.2, land-use and soil type factors behaved as in Model 4.1, and their inclusion improved the values of \( R^2 \) (0.963) and \( \text{rsd} \) (0.151).
The addition of log$_{10}$ ECEC to Model 4.2—gave an extended model in which the partial regression coefficient for log$_{10}$ ECEC ($-0.69 \pm 0.15$) was significant ($P < 0.001$), while that for log$_{10}$ $C_t$ ($0.10 \pm 0.21$) was not ($P > 0.5$). Therefore, log$_{10}$ ECEC replaced log$_{10}$ $C_t$:

$$\log_{10} Cd_{Ca} = 1.36 (\pm 0.21) + 1.10 (\pm 0.05) \log_{10} Cd_t - 0.53 (\pm 0.04) pH_{Ca} - 0.64 (\pm 0.10) \log_{10} ECEC$$

(n = 41, $R^2 = 0.946$, rsd = 0.170)  
Model 4.3

In Model 4.3, land-use interacted with log$_{10}$ Cd$_t$ ($P < 0.01$) and appeared to interact with log$_{10}$ ECEC ($P < 0.05$), while soil type had no effect ($P > 0.1$). In addition, the land-use interaction with log$_{10}$ ECEC was not as strong as the quadratic effect of log$_{10}$ ECEC ($P < 0.01$); therefore, the model representing the quadratic effect is shown:

$$\log_{10} Cd_{Ca} = 0.77 (\pm 0.20) + [1.34 (\pm 0.05) \log_{10} f^f Cd_t] \text{ or } [1.01 (\pm 0.04) \log_{10} u^f Cd_t]$$

$$- 0.43 (\pm 0.04) pH_{Ca} - 0.05 (\pm 0.21) \log_{10} ECEC$$

$$- 0.47 (\pm 0.13) [\log_{10} ECEC]^2$$

(n = 41, $R^2 = 0.974$, rsd = 0.122)  
Model 4.4

where $f^f Cd_t$ and $u^f Cd_t$ are values of Cd$_t$ for farmed and unfarmed soils.

When log$_{10}$ Fe$_{ox}$ was added to Model 4.3—this new term was significant ($P < 0.05$), but only for pH$_{Ca}$ values $>5.6$ ($\text{pH} > 5.6 \text{Fe}_{ox}$). Of the 41 soils, only 12 of the farmed soils and one unfarmed soil had pH$_{Ca}$ values $>5.6$ (Appendix 1). Therefore, to enable a direct comparison of the coefficients in Model 4.5 with those in the earlier models, all 41 soils were retained in the model, requiring a slope coefficient for log$_{10}$ pH$^{>5.6} \text{Fe}_{ox}$, a corresponding constant term, and a separate constant term for the 28 soils with pH$\leq 5.6$:

$$\log_{10} Cd_{Ca} = [1.33 (\pm 0.20) \text{ for pH}_{Ca} \leq 5.6] \text{ or } [2.48 (\pm 0.56) \text{ for pH}_{Ca} > 5.6]$$
+ 1.09 (± 0.04) log$_{10}$ Cd$_t$ - 0.54 (± 0.04) pH$_{Ca}$ - 0.56 (± 0.10) log$_{10}$ ECEC

− 0.33 (± 0.15) log$_{10}$ pH$>$5.6 Fe$_{ox}$

(R$^2 = 0.952$, rsd = 0.163) Model 4.5

The effect of log$_{10}$ pH$>$5.6 Fe$_{ox}$ was also significant when added to Model 4.4 ($P < 0.01$), and either the land-use interaction with log$_{10}$ ECEC, or alternatively the quadratic effect of log$_{10}$ ECEC, was not significant ($P > 0.05$), thus:

Log$_{10}$ Cd$_{Ca}$ = [1.18 (± 0.15) for pH$_{Ca}$$\leq$5.6] or [2.69 (± 0.42) for pH$_{Ca}$$>$5.6]

+ [1.33 (± 0.05) log$_{10}$ [Cd$_t$] or [1.01 (± 0.04) log$_{10}$ ufCd$_t$]

− 0.49 (± 0.03) pH$_{Ca}$ - 0.69 (± 0.08) log$_{10}$ ECEC

− 0.43 (± 0.12) log$_{10}$ pH$>$5.6 Fe$_{ox}$

(n = 41, R$^2 = 0.974$, rsd = 0.121) Model 4.6

In Model 4.6, little variation remained to test the effects of Mn$_{hq}$ Al$_{ox}$, P$_{ox}$, P$_t$, Zn$_t$, DOM, Ca$_{ox}$, EC and Cl, and of differences in the effect of log$_{10}$ Fe$_{ox}$ as pH$_{Ca}$ increased above 5.6. Of these factors, only Mn$_{hq}$ had an effect that bordered on significance ($P < 0.10$). Finally, adjustment of Cd$_t$ for the small amount of Cd desorbed into 10 mM CaCl$_2$ did not appreciably change the land-use effect on the coefficient of log$_{10}$ Cd$_t$.

### 4.4.2 Other observations

**Correlations among explanatory variables**—can adversely influence the quality of estimates of the partial regression coefficients; therefore, although it was a judicious precaution to check for such effects, none was detected.

**The relative merits of linear and non-linear models**—could not be tested for two reasons. First, there was little overlap between the values of Cd$_{Ca}$ from the farmed and unfarmed sites, yet there was substantial overlap for the values of ECEC.
(Appendix 1). Second, only a small proportion of variation remained once log$_{10}$ Cd, pH$_{Ca}$ and log$_{10}$ ECEC were included as explanatory variables.

4.5 Discussion

4.5.1 Modelling statistics

The partial coefficients—for log$_{10}$ Cd, changed little between Models 4.1 and 4.6 as explanatory variables were added; however, the effects on the values of other coefficients were larger. For example, the coefficient for pH$_{Ca}$ took values of –0.66 (± 0.06) and –0.53 (± 0.04) in Models 4.1 and 4.3 respectively, i.e. no mechanistic significance should be attached to these values.

The effects of individual soil properties in the modelling, and of the methods used to measure them, are discussed in Section 4.5.2.

Measured and fitted values of log$_{10}$ Cd$_{Ca}$—The following 10 studies also used multiple regression models to describe Cd behaviour, and R$^2$ values were reported for most (Anderson & Christensen 1988; McBride et al. 1997; Römkens & Salomons 1998; Springob & Böttcher 1998; Celardin 1999; Elzinga et al. 1999; Gray et al. 1999; Schug et al. 1999; Sauvé et al. 2000; Degryse et al. 2003). The R$^2$ values in these studies typically fell in the range 0.7–0.9. That is, Model 4.6 with an R$^2$ value of 0.974, satisfies the hypothesis that mechanistically-informed empirical modelling may accurately describe the effects of soil properties on Cd partitioning in aerobic, acidic mineral soils (see Section 1.8). In using models for predictive purposes, it is the rsd that conveys information about the agreement between the fitted and measured values (Montgomery & Peck 1982). The rsd for
Model 4.6 was 0.12 log_{10} units, which is a small value, and shows that the agreement between the fitted and measured values of log_{10} Cd_{Ca} is close (Fig 4.1): nevertheless, it would be unwise to use Model 4.6 to make predictions without first having validated it against an independent set of data.

Fig. 4.1 Measured (Appendix 1) and fitted (Model 4.6) values of log_{10} Cd_{Ca} for farmed (triangles) and unfarmed (circles) soils, with a 1:1 line to assist comparison.
The rsd is a useful statistic, so it is surprising that rsd values were given for just two of the 10 studies cited in the previous paragraph. In the first, Jopony & Young (1994) described the effects of soil properties on the concentration of desorbed Cd for 30 contaminated samples and the model had an rsd of 0.30 log\(_{10}\) units. In the second, the model described data compiled from ~70 sources and the rsd was 0.62 log\(_{10}\) units (Sauvé et al. 2000a). These rsd values are considerably larger than that for Model 4.6 (0.12 log\(_{10}\) units); nonetheless, an rsd of 0.12 log\(_{10}\) units is clearly towards the upper limit for quantitative modelling: the measured values of Cd\(_{\text{Ca}}\) all fell within ±58% of the back-transformed estimates of log\(_{10}\)Cd\(_{\text{Ca}}\), and the median deviation was ±17%.

4.5.2 Detailed analysis

4.5.2.1 The dependent variable—used was log\(_{10}\) Cd\(_{\text{Ca}}\), because my ultimate interest is in predicting Cd bioavailability, which I assume is a function of the Cd concentration in the soil solution. To detect possible bias in the Cd\(_{\text{Ca}}\) values due to Cd associated with micro-particulates, I passed the extracts through a 10 kDa filter, which did not decrease the Cd concentration measured by ETAAS or ICP-MS (see Section 3.4.1). Note that DOC also had no effect in the modelling. Therefore, the weight of the evidence points towards Cd attached to micro-particulates having had little effect on the estimation of Cd\(_{\text{Ca}}\). However, if such an effect occurred and were pH dependent (Lombi et al. 2003), it could explain why land-use affected Cd partitioning in the models.

The effects of changing the dependent variable are explored further in Chapter 7.
4.5.2.2 The explanatory variables

$Cd_t$—$\log_{10} Cd_t$ is a variable in most models that describe the effects of soil properties on Cd partitioning (Celardin 1999; Elzinga et al. 1999; Sauvé et al. 2000a; Degryse et al. 2003) and in all my models $\log_{10} Cd_t$ had a strong positive effect on $\log_{10} Cd_{Ca}$. It is mechanistically reasonable to suggest that $Cd_t$ should be adjusted for desorbed Cd; however, adjustment did not improve the modelling, perhaps because $Cd_{Ca}$ was a small proportion of $Cd_t$ (Appendix 1). The other mechanistic adjustment that might be made would be to substitute $Cd_E$ for $Cd_t$, on the assumption that $Cd_{Ca}$ is drawn from the labile pool, and because $Cd_E$ constitutes a variable proportion of $Cd_t$ (Gerritse & van Driel 1984; Nakahone & Young 1993; Springob & Böttcher 1998a; Wilkins et al. 1998; Smolders et al. 1999; Young et al. 2000; Degryse et al. 2003; Gray et al. 2003). In the one comparative study I found, $Cd_E$ was a superior explanatory variable to $Cd_t$ (Degryse et al. 2003). However, one should remember that the property $Cd_E$ is operationally defined (Hamon et al. 2002b; Gray et al. 2004).

$pH_{Ca}$—the correlation between $\log_{10} Cd_{Ca}$ and $pH_{Ca}$ was weak ($-0.31$, Table 3.5) relative to the strong correlations often reported (Whitten & Ritchie 1991; El-Falaky et al. 1991; Rayment 1994); however, in these studies the soils typically had narrower ranges of other properties than my 41 soils. Therefore, it is not surprising that, after adjusting for the effects of $\log_{10} Cd_t$, $\log_{10} ECEC$ and $\log_{10} pH^{\geq 5.6} Fe_{ox}$ in Model 4.6, the partial correlation for $pH_{Ca}$ was also strong ($-0.93$).

Soil pH is an explanatory variable in most multiple regression models of the effect of soil properties on Cd partitioning. As with any coefficient, the value of the pH
coefficient may be affected by the other properties used as explanatory variables (see Models 4.1–4.6), and its sign by the dependent variable chosen, e.g. Cd_{Ca} or Cd_{t}; therefore, it is the absolute values that are compared between models. Quantitative comparisons between the partial pH coefficients are also often limited by the lack of standard errors for the coefficients. Even so, the estimates of the pH coefficient seem to be converging towards an absolute value of ~0.50 (Elzinga et al. 1999; Sauvé et al. 2000a; Degryse et al. 2003). This topic is discussed further in Chapter 7.

$C_t$ and $ECEC$—the effect of $\log_{10} C_t$ in Model 4.2 was significant ($P < 0.01$), and the sign of the partial regression coefficient was negative. Both these characteristics are consistent with: other regression models (Gerritse & van Driel 1984; Anderson & Christensen 1988; Basta et al. 1993; McBride et al. 1997; Gray et al. 1999; Sauvé et al. 2000a; Degryse et al. 2003); the proposition that much of the Cd in soils may be bound to OM (Calvet et al. 1990; Jeng & Singh 1993); and with spectroscopic data that –COOH and –SH groups on OM bind Cu and Zn (Xia 1997) and, presumably, Cd. Nevertheless, the value of the coefficient of $\log_{10} C_t$ varies between studies that use the same properties as explanatory variables, e.g. –0.61 (± 0.17) and –0.81 (± 0.05) for Model 4.2 and the model of Sauvé et al. (2000a) that described the data from ~70 published studies. Contrast the size of this difference with that below, where the explanatory variable is $\log_{10} ECEC$ instead of $\log_{10} C_t$.

A measure of negative surface charge, rather than OM, has been an explanatory variable in some mechanistic and empirical models of Cd (de)sorption (Kuo &
McNeal 1984; Barrow 1993; Römkens & Salomons 1998; Celardin 1999; Elzinga et al. 1999; Gray et al. 1999; Springob & Böttcher 1998b; Degryse et al. 2003). There are two commonly used measures of surface charge, namely ECEC and CEC: of these I chose ECEC because it is estimated at a pH similar to that which pertains during Cd desorption in 10 mM CaCl$_2$, rather than CEC, which is estimated at a fixed pH (Rayment & Higginson 1992).

When log$_{10}$ ECEC was added to Model 4.2 it displaced log$_{10}$ C$_t$ (Model 4.3). In Model 4.3 and in Models 4.4–4.6, the effect of log$_{10}$ ECEC on log$_{10}$ Cd$_{ca}$ was highly significant ($P < 0.01$), and the sign of the partial regression coefficient was negative. In addition there was remarkable agreement between the value of the coefficient of log$_{10}$ ECEC in Model 4.3 and that in a similar model applied by Elzinga et al. (1999) to describe 1125 published observations of Cd sorption, i.e. 0.64 ($\pm$ 0.10) and 0.63 ($\pm$ 0.03) respectively. The closeness of these values contrasts with the large discrepancy for the coefficients of log$_{10}$ C$_t$ noted above.

Holm et al. (2003), as I did, found that log$_{10}$ ECEC displaced log$_{10}$ C$_t$ from a model describing Cd behaviour in 49 soils from Denmark at pH 5.3; however, at pH 6.7 the result was reversed. Inconsistent effects of ECEC and C$_t$ also occur between studies (Anderson & Christensen 1988; Basta et al. 1993; Römkens & Salomons 1998; Gray et al. 1999; Degryse et al. 2003). Understanding what may be causing such differences is complicated because OM and surface charge are often related, as occurred in our data (Table 3.5 and Model 3.1). I speculate that surface charge may sometimes displace C$_t$ from the models because although the acidic functional groups on OM that contribute to surface charge may complex a
considerable proportion of Cd, (Calvet et al. 1990; Jeng & Singh 1993; Xia et al. 1997), the ‘density’ of these groups does not directly influence estimates of OM. In addition, for my soils the C₄ values included an unknown proportion of char, which could have weakened the explanatory power of this measure. However, avoiding char effects on conventional measures of OM is difficult.

That is, the relative efficacy of OM and ECEC as explanatory variables deserves further comparison. In making this comparison measures of OM that include char should be avoided, or the soils should be chosen so that char is not a concern.

**Fe, Mn and Al**—oxides such as goethite (Fe), hausmannite (Mn) and alumina (Al), have large ratios of surface area to mass, and avidly sorb Cd when the pH exceeds their sorption edges, i.e. pH 5–6, 3–4 and 7–8 respectively (Backes et al. 1995; Spark et al. 1995). The (hydrous)oxides of these metals that occur naturally in soils appear to behave similarly (Zachara et al. 1992; Murphy & Zachara 1995; Tessier et al. 1996); furthermore, sequential chemical extraction of soils indicates that a considerable portion of Cd may be associated with the (hydrous)oxides of Fe and Mn in some soils (Jeng & Singh 1993; Benitez & Dubois 1999). Therefore, increased concentrations of the (hydrous)oxides of Fe, Mn and Al in soils should, if anything, be associated with increased sorption.

The apparent lack of effect of the (hydrous)oxides of Fe, Mn and Al on Cd partitioning in some modelling studies might be attributed to their concentrations being either too small or too similar between samples, or to the use of extraction procedures that are non-selective for the relatively less abundant hydrous fractions.
(McKeague et al. 1971; Parfitt & Childs 1988; Buchter et al. 1989; Zachara et al. 1993; Holm et al. 2003; Agbenin 2003). In contrast, I selectively extracted the hydrous fractions of the oxides of Fe, Mn and Al (Sherman et al. 1942; Schwertmann 1964), the soils contained a considerable range of concentrations of these hydrous oxides (Appendix 1), and I applied the concept of sorption edges.

A sorption edge is the unique pH for a sorbent/sorbate combination, above which sorption increases rapidly. For Cd and synthetic goethite (hydrous ferric oxide) the sorption edge is ~5.6 (Johnson 1990; Ainsworth et al. 1994; Axe & Anderson 1997). Goethite is also a major component of the hydrous iron oxides in aerobic mineral soils (Schwertmann 1964) and log$_{10}$ Fe$_{ox}$ had an effect in Model 4.6 that was consistent with this information, i.e. the effect occurred when pH$_{Ca}$ exceeded ~5.6 ($P <0.05$). Unfortunately I had too few soils with pH$_{Ca}$ values >5.6 (n = 13) to permit a more detailed modelling of the pH dependence. This is the first application of the phenomenon of sorption edges in empirical modelling of the effects of soil properties on Cd partitioning.

In an extension of Model 4.6, log$_{10}$ Mn$_{bq}$ had a mechanistically consistent, weak effect ($P <0.1$), whereas log$_{10}$ Al$_{ox}$ had no effect ($P >0.1$). However, there was not enough residual variation in Model 4.6 to adequately test additional properties.

et al. (1999), Schug et al. (1999), Sauvé et al. (2000a) and Degryse et al. (2003)—only the five in bold reported effects of (hydrous) Fe, Mn and Al oxides on Cd behaviour. As noted by Tessier et al. (1996) and Sauvé et al. (2000a), some of the reported effects are counter to the known sorption properties of these hydrous oxides. Consequently, I sequentially culled studies that were likely to be procedurally unreliable, i.e. where:

1. a common value was used for a key property for more than one sample, e.g. for samples drawn from different plots within a field trial; and
2. the range of concentrations of the (hydrous)oxide(s) was small.

The merits of this subjective process were that the studies that survived the cull were those of Bolton & Evans (1996) and Schug et al. (1999), and both showed mechanistically consistent effects of (hydrous)Fe oxides.

No multiple regression studies of the effects of Mn and Al (hydrous)oxides on Cd behaviour in soils survived the cull. In the case of Al the reason may be that the sorption edge occurs at too high a pH value (7–8) (Spark et al. 1995) for an effect to have been observed in most studies. In contrast, if hausmannite is an appropriate model for the (hydrous)oxides of Mn in soils one might have expected effects to have been observed, given that the sorption edge is pH 3–4 (Backes et al. 1995).

I suggest that the effects of the hydrous oxides on Cd partitioning ought only be explored if the signs of the coefficients of the major variables, e.g. Cd, pH, and ECEC or OM, are consistent with mechanistic expectations. I also suggest that:

1. selective methods be used to extract the hydrous oxide fractions;
2. modelling proceed only if the hydrous oxide data are sufficiently varied and do not cause excessive variance inflation;

3. the studies test the sorption edge concept;

4. the mixed hydrous oxides that occur in soils be characterised, because their effects may well differ from those of the pure synthetic materials (Mann 1985; Cowan et al. 1992; Zachara et al. 1992; Zachara et al. 1994; Spark et al. 1995; Liu & Huang 2000; Spathariotis & Kallianou 2007).

### 4.5.2.3 Effects of the background electrolyte

There were large natural variations in the concentrations of Cl and exchangeable Ca among my samples (Appendix 1) that might have had significant effects in Model 4.6 (McLaughlin et al. 1997b; Elzinga et al. 1999) had not 10 mM CaCl$_2$ been used as the background electrolyte.

The concentration of Ca in the background electrolyte (10 mM) would also have limited the concentration of DOM in the extracts (Römkens & Dolfing 1998) and presumably, the formation of complexes between DOM and Cd (Holm et al. 1995a, b; Xia 1997). This might partly explain the lack of significance of log$_{10}$ DOM as an independent variable when added to Model 4.6 ($P > 0.1$); however, as noted in the preceding paragraph, the residual variation in Model 4.6 was too small to adequately test the effects of additional properties such as DOM. One should also note that the effects of DOM may be more readily observed for soils in which organic matter dominates metal binding (del Castilho et al. 1993a,b; Kalbitz & Wennrich 1998; Römkens & Salomons 1998; Impellitteri et al. 2002).
4.5.2.4 Soil type and land-use

These factors were part of the data structure, and when significant effects were found in the base model it was necessary to continue checking in later models, because these effects may have been eliminated by the additional variables. The inclusion of $\log_{10}$ ECEC made the effects of soil type not significant in Model 4.3, i.e. the principal effect of soil type was associated with surface charge. If this were to prove generally true ECEC would be an extremely useful variable in models of Cd partitioning (see above). In contrast, the effects of land-use persisted throughout the modelling (see Model 4.6).

To further explore the effects of land-use I sought modelling studies in which the effects of this factor had been considered. I found only one study which explicitly declared that the samples had been drawn from both farmed and unfarmed sites, and it was not stated whether the regression analysis tested for land-use effects (Römkens & Salomons 1998). Consequently, I was thrown back on an analysis of my data.

A possible effect of land-use on the coefficient of $\log_{10}$ ECEC in Model 4.4 was resolved in Model 4.6 by the inclusion of $\log_{10}$ Fe$_{ox}$ as an explanatory variable. Nevertheless, in Model 4.6 the coefficient of $\log_{10}$ Cd$_{l}$ was greater ($P < 0.01$) for the farmed than unfarmed soils, i.e. 1.33 ($\pm$ 0.05) and 1.01 ($\pm$ 0.04). Even when Model 4.6 was extended to allow for the amount of Cd desorbed this difference remained strong. Put simply, $\log_{10}$ Cd$_{Ca}$ changed more rapidly with changes in $\log_{10}$ Cd$_{l}$ for the farmed than the unfarmed soils. A similar effect occurred for soils from field plots that had been managed differently for 44 y (Lair et al. 2007).
There are a number of possible explanations for the land-use effect on the partial regression coefficient of $\log_{10} \text{Cd}_t$ in Model 4.6. First, farming may have affected the Cd-complexing properties of OM (McArthur et al. 2001). Second, there were differences in contact time and Cd load, and the direction of the effect is consistent with slow ‘fixation’ reactions, such as occur with synthetic goethite (Barrow 1993; Axe & Anderson 1997), and with specific binding to oxides (Rudzinski et al. 1993) and to DOM (Xia 1997). An effect of Cd load similar to mine is also evident in a large compilation of data from studies of Cd sorption (Fig. 1 of Elzinga et al. 1999). Therefore, contact time and Cd load may be factors; however, direct evidence of Cd fixation in soils is limited (Hamon et al. 1998).

4.6 Conclusion

The large $R^2$ and small rsd values for Model 4.6 (0.974 and 0.121 $\log_{10}$ units) support the hypothesis that mechanistically-informed empirical modelling may accurately describe the behaviour of Cd in aerobic, acidic mineral soils. This result justifies validation of the model as a tool to guide Cd management on the soils of Greater Sydney.

It appears that the application of mechanistic principles may allow the development of a general, empirical model of Cd behaviour that describes the effects of soil properties on Cd partitioning. Further argument in support of this speculation is presented in Chapter 7. When presenting the results of such studies, the models should include error estimates for the partial coefficients, and both $R^2$ and rsd values. Finally, further study is merited of the relative merits of: $\text{Cd}_E$ and $\text{Cd}_t$, ECEC and OM as explanatory variables.
CHAPTER 5—LABILE AND EXTRACTABLE Cd

5.1 Summary

- ICP-MS conditions were established for the measurement of $^{110/111}$Cd.
- Labile Cd (Cd$_E$) was estimated by the dilution of additions of $^{110}$Cd for 23 soils with Cd$_i$ of 0.02–6.4 mg/kg.
- Three electrolytes were used during the isotope exchange: 10 mM CaCl$_2$, 1 M NH$_4$NO$_3$ and 1 M NH$_4$Cl. Electrolyte affected the time to “equilibrium” but not the dilution at equilibrium, and Cd$_E$ constituted 40–102% of Cd$_i$.
- The concentration of Cd was also measured in all three electrolytes. The median concentrations of Cd extracted into the three salt solutions were: 0.057 mg/kg (10 mM CaCl$_2$), 0.059 mg/kg (1 M NH$_4$NO$_3$), and 0.55 mg/kg (1 M NH$_4$Cl) respectively.
- Cd$_E$ was strongly related to Cd$_{NH4Cl}$ with an effect of pH.
- These and other data show that further research is needed to find a universal extractant for Cd$_E$ to make this index of Cd risk more readily accessible.

5.2 Introduction

Plants take up Cd from the soil, which is this main route of Cd entry to the human food chain. Thus the risk of excessive Cd in plant foods could be minimised if soil tests were able to predict Cd uptake by plants; however, Cd$_i$ is poorly related to uptake (Whitten & Ritchie 1991; Rayment 1994; Houba et al. 1996). In contrast, the reservoir of soil Cd that exchanges rapidly with and therefore
“dilutes’ an added Cd isotope, i.e. ‘labile’ Cd (Cd\textsubscript{E}), is a rational index of Cd risk that has not been widely evaluated (Gérard \textit{et al.} 2000; Degryse & Smolders 2006). This circumstance reflects the reliance of estimates of Cd\textsubscript{E} on isotopic methods. The traditional procedures used radioisotopes (Nakhone & Young 1993; Hamon \textit{et al.} 1998; Young \textit{et al.} 2000; Petroni \textit{et al.} 2001; Degryse \textit{et al.} 2003); although, more recently, stable isotopes and inductively coupled plasma-mass spectrometry (ICP–MS) have become an alternative (Mota \textit{et al.} 1999; Ahnstrom & Parker 2001; Gray \textit{et al.} 2003; Gäbler \textit{et al.} 2007). Nevertheless, Cd\textsubscript{E} measurements remain technically demanding; consequently, there is interest in developing a proxy measure for use in assessing environmental risk (Esnaola & Millán 1998; Young \textit{et al.} 2000; Gray \textit{et al.} 2003).

Information from diverse sources points towards chloride (Cl) salts as candidate extractants for Cd\textsubscript{E}. First, Cl salts enhance Cd desorption from soils and soil separates (Zachara \textit{et al.} 1992; Boekhold \textit{et al.} 1993) and increase Cd uptake by plants (Grant \textit{et al.} 1996; McLaughlin \textit{et al.} 1997\textsubscript{b}). Second, plant uptake is usually better related to the concentration of Cd extracted by solutions of Cl rather than stronger complexing agents or strong acids (Whitten & Ritchie 1991; Rayment 1994; Houba \textit{et al.} 1996; Krishnamurti \textit{et al.} 2000; Adiloglu 2003). Third, 1 M CaCl\textsubscript{2} may selectively extract Cd\textsubscript{E} from soils contaminated with Cd in sewage sludge or mine spoil (Young \textit{et al.} 2000; Gray \textit{et al.} 2003); however, no equivalent study has focussed on soils not contaminated with Cd from these sources.
Extraction of Cd by 1 M CaCl₂ (Young et al. 2000; Gray et al. 2003) relies primarily on the formation of relatively weak chlorocomplexes; although Ca too participates by competing with Cd for sorption sites (Cowan et al. 1991; Boekhold et al. 1993; Tipping 1994; Temminghoff et al. 1995). Substituting a monovalent cation for Ca should therefore weaken Cd extraction, as should decreasing the Cl concentration (Homann & Zasoski 1987; Tipping 1994). However, the preferred method of measurement for Cd at low concentrations, ICP–MS, is not highly salt tolerant, and accommodates NH₄Cl better than CaCl₂ (pers. comm. Ross Wenzel). Therefore, 1 M NH₄Cl was evaluated as an extractant for Cd. Stable Cd isotopes were added and the perturbations of the natural isotopic abundances, measured using ICP–MS, were used to calculate Cd. These measurements were made using a protocol established during a series of pilot studies. The Cd extracted by 1 M NH₄Cl (CdNH₄Cl) was also measured using ICP–MS, and the relation between Cd and CdNH₄Cl compared.

5.3 Materials and methods

5.3.1 The soils

This study used 23 of the 41 samples from the partitioning study (see Chapters 2–4). Nineteen of the soils were from vegetable farms, and four from unfarmed sites, i.e. there were different land-use patterns. The soils were acidic and had a diverse range of other properties that were of interest, because of their effects on Cd partitioning (see Section 4.4.1), vis.: Cd₀ 0.02–6.4 mg/kg, pH 4.0–6.8, Cₜ 8–32 g/kg, ECEC 1–34 cmolc/kg and Feox 410–6800 mg/kg. The methods of measurement are detailed in Chapter 3 and the data are presented in Appendix 1.
5.3.2 Reagents

Water and all the chemicals were of at least reagent quality. One percent HNO₃ was made by diluting 10 mL of concentrated nitric acid (69%, Analar, BDH) to 1 L. Where practicable, solutions were prepared and diluted by mass rather than volume, and volumetric dilutions were confirmed gravimetrically. The primary Cd standard for concentration measurements was 20 mg/L and the internal standard was 100 mg/L (Alpha Resources Inc., USA). The stable Cd isotopes were highly enriched $^{116}$Cd or $^{110}$Cd with certified isotopic ratios (Trace Sciences International Corp., Canada) from which ‘spiking’ solutions of ~100 mg Cd/L were prepared in dilute HNO₃. Extracts and standard solutions contacted only plastic-ware that had been soaked for at least 16 h in 5% v/v HNO₃ and rinsed just before use.

5.3.3 Pilot studies

Protocols for stable Cd isotope dilution and reliable measurement of isotopic ratios using ICP–(quadruple) MS are not well established, so this was the focus of the pilot studies. The three isotopes of direct interest, and their natural abundances, are: $^{110}$Cd (12.49%), $^{111}$Cd (12.80%) and $^{116}$Cd (7.49%) (Rosman & Taylor 1997). Possible effects of the supporting electrolyte were investigated by suspending soils in either 0.01 M CaCl₂, 1 M NH₄NO₃ or 1 M NH₄Cl, and conditioning the suspensions by shaking end-over-end at 30 rpm and ~25°C for 2 h. Small volumes of solutions enriched in $^{116}$Cd or $^{110}$Cd were then added to give enrichments of 20–100%, assuming that Cdₙ would completely exchange. Shaking and sampling were resumed, with aliquots being removed after 2, 24 and 48 h. Five soils were used, namely 5, 10, 13, 15 and 28 (Table 5.1).
Supernatants were analysed for either $^{110}$Cd or $^{116}$Cd and $^{111}$Cd using an ICP–quadrupole MS (Varian Ultramass, Australia running WinMass software, ICP Expert Version 4.0, build 425). To establish optimum conditions for the measurements using the ICP–MS, the number of scans/replicate, replicates/sample, peak dwell times and points/peak were varied. The effect of varying these parameters on the stability of the isotope ratios $^{116/111}$Cd and $^{110/111}$Cd was evaluated at 1 µg Cd/L, which was the lowest Cd concentration expected. Isotopic data were adjusted for any Cd removed in preceding aliquots of the supernatant. The protocol included frequent measurement of a solution containing 10 µg Cd/L, with either natural isotopic abundance or with ~50% enrichment of either $^{116}$Cd or $^{110}$Cd. This study showed that Cd isotope data were reliably collected using 1 point/peak, 15 scans/replicate and a dwell time of 1 s. In addition, $^{103}$Rh, $^{109}$Ag and $^{115}$In were trialled qualitatively as internal standards.

### 5.3.4 Major study

**Concept**—batch Cd extraction for acidic soils is well documented and robust, provided that at least 5 g of soil is used and suspensions are shaken for 1–2 h (see Sections 3.3.5 and 3.4.1). I compared the amount of Cd extracted by 1 M NH$_4$Cl under such conditions with ‘equilibrium’ values of Cd$_E$, measured in the same suspensions, using a stable isotope dilution protocol based on the results of the pilot studies.

**Extraction and isotopic labelling**—soil (20 g) was shaken with 40 mL of a 1 M solution of NH$_4$Cl, end-over-end at 30 rpm and ~25°C for 2 h in 75 mL, screw-capped, polypropylene centrifuge tubes, and 1 mL aliquots of supernatant were removed for Cd analysis (Young et al. 2000; Milham et al. 2004). Cadmium was
determined using the ICP–quadrupole MS described above. Additions of highly enriched $^{110}\text{Cd}$ were made to these preconditioned suspensions and the size of each addition was adjusted to increase the natural abundance of $^{110}\text{Cd}$ by ~50%. Shaking was resumed for 24 h, after which the suspensions were centrifuged and 1 mL aliquots of the supernatant were removed for Cd isotope analysis.

**ICP–MS measurements**—the instrument and software were as described above. Plasma and ion optics were optimised for Cd sensitivity while maintaining CeO/Ce and Ba$^{2+}$/Ba ratios below 3% to minimise potential oxide interference, e.g. from MoO$^{2+}$. Typical optical conditions were: extraction lens –600 V, first lens – 200 V, second lens –9.6 V, third lens + 1.4 V, fourth lens – 118 V, photon stop – 13.6 V, entrance and exit plates 0 V. The quadrupole conditions were: detector 2800 V; delta high resolution 0.757 V; high resolution 0.00 AMU; pole bias 0.000 V. The instrument was operated in the peak hopping mode. Using the run conditions described above, instrument time/solution was 2.5 min. A 60 s rinse and a 15 s stabilisation time were allowed between solutions.

Extracts were diluted 10-fold with 1% HNO$_3$ before measurement and analysed within 24 h. Samples were introduced into the argon plasma via a micro-concentric glass nebuliser and a cyclonic glass spray chamber (Glass Expansion, Australia). The concentrations of $^{110}\text{Cd}$ and $^{111}\text{Cd}$ were measured against a calibration curve 1–100 µg (natural) Cd/L. Extracts were diluted further if required to bring them within the calibrated range. Measurements alternated between extracts and a solution that contained ~10 µg Cd/L, which had been enriched by ~50% in $^{110}\text{Cd}$. When the measured $^{110}/^{111}\text{Cd}$ ratio for this solution deviated by more than 10% from the known value, the group of measurements
was repeated, and when duplicate extracts differed by more than ±10%, the sample was re-extracted. Consequently, the data presented are means of at least duplicates. Values of Cdₐ were calculated from the observed isotopic ratios and the added amounts of ¹¹⁰Cd and accompanying isotopes (Ahnstrom & Parker 2001; Gray et al. 2003).

Labile Cd was calculated after Fassett and Paulsen (1989):

\[
C_x = \left( \frac{C_s W_s}{W_x} \right) \left[ \frac{(A_s - R_m B_s)/(R_m B_x - A_x)}{\Delta R} \right]
\]

Equation 5.1

where respectively: \(A_x\) and \(B_x\) are the atom fractions of isotopes A and B in the sample (given above for \(^{110}\)Cd, \(^{111}\)Cd and \(^{116}\)Cd); \(A_s\) and \(B_s\) are the atom fractions in the “spike”; \(C_x\) and \(C_s\) are the concentrations of the element in the sample and spike; and \(W_x\) and \(W_s\) are the weights of the sample and spike, and \(R_m\) is the measured ratio of isotope A to isotope B.

Estimates of \(C_x\) from Eqn 1 are presented as Cdₐ values, which like those of Cdₐ₄Cl, are expressed in mg/kg of soil.

**Statistics**—to homogenise the variance, the log₁₀ scale was used for all properties other than pH and stepwise multiple linear regression modelling was performed using the statistical package ASReml (Gilmour et al. 2002).

### 5.4 Results and discussion

#### 5.4.1 Pilot studies

There was substantial isobaric interference from \(^{116}\)Sn on \(^{116}\)Cd for some samples. This isobaric interference is well documented, and can be of substantial proportions because the continental crustal abundance of Cd is ~0.15 mg/kg,
whereas that of Sn is an order greater (CRC Handbook of Chemistry and Physics 2006). Isobaric interferences can be corrected (Gray et al. 2003), but this increases the complexity of the measurement and may increase the uncertainty. In contrast, $^{110}$Pd is the isobaric interferent for $^{110}$Cd and the crustal abundance of Pd is about one hundredth that of Sn (CRC Handbook of Chemistry and Physics 2006). Therefore, the likelihood of appreciable Pd interference was small and no Pd was detected. These are the reasons $^{110}$Cd, rather than $^{116}$Cd, was added during the major study.

Both insufficient and excessive isotope additions may prejudice the estimation of Cd$_E$ (Gäbler et al. 2007). My Cd$_E$ values were similar when $^{110}$Cd additions were 20–100% of $^{110}$Cd. An increase of ~50% in the abundance of $^{110}$Cd gave robust estimates of $^{110/111}$Cd and, hence, of Cd$_E$; consequently, this procedure was used in the major study. For example, the estimated rsd of $^{110/111}$Cd measurements was ~3% for a 50% enrichment of $^{110}$Cd in a solution that contained 1 µg of natural abundance Cd/L. The measured $^{110/111}$Cd ratio for natural Cd was 0.959, which is less than the value of 0.976 calculated from the natural abundances (see Section 5.3.3). This bias was independent of Cd concentration (1–100 µg/L) and of $^{110}$Cd enrichment (20–100%), so the data were not corrected. The qualitative comparison of the efficacy of $^{103}$Rh, $^{109}$Ag and $^{115}$In as internal standards indicated that $^{115}$In may reward further investigation: however, none of the Cd data were adjusted because of uncertainty about reliability.

The five samples used in the pilot studies were part of the complete suite of 23 samples in the major study; therefore, the effects of electrolyte, shaking time and pH on isotope exchange are presented in the major study.
5.4.2 Major study

Suspension pH differed little between electrolytes; consequently, a mean pH (pH<sub>s</sub>) is presented for each soil, where the subscript ‘s’ denotes measurements made in salt solutions (Table 5.1). The Cd<sub>s</sub> range was wide (0.02–6.4 mg/kg, Table 5.1), encompassing that of many agricultural soils (Sillanpää & Jansson 1992). Median Cd<sub>s</sub> values for the unfarmed and farmed soils were 0.04 mg/kg and 1.12 mg/kg respectively. Much of this difference in the medians is due to land-use: principally the inadvertent addition of Cd to the farmed soils as a constituent of phosphate fertilisers (Jinadasa et al. 1997). Not surprisingly, the ranges for Cd<sub>E</sub> and Cd<sub>NH4Cl</sub> were also large (Table 5.1).

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Shaking 2 h</th>
<th>Shaking 24 h</th>
<th>Shaking 48 h</th>
<th>Mean (48 h)</th>
<th>Cd&lt;sub&gt;E&lt;/sub&gt; (2 h)</th>
<th>Cd&lt;sub&gt;NH4Cl&lt;/sub&gt;</th>
<th>Cd&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>35 28 55</td>
<td>50 46 59</td>
<td>60 59 62</td>
<td>5.8</td>
<td>0.14</td>
<td>0.12</td>
<td>0.24</td>
</tr>
<tr>
<td>*5</td>
<td>53 42 62</td>
<td>64 61 71</td>
<td>71 70 69</td>
<td>6.4</td>
<td>1.29</td>
<td>0.55</td>
<td>1.84</td>
</tr>
<tr>
<td>6</td>
<td>21 27 35</td>
<td>34 36 38</td>
<td>41 39 40</td>
<td>6.5</td>
<td>0.136</td>
<td>0.085</td>
<td>0.34</td>
</tr>
<tr>
<td>7</td>
<td>30 29 35</td>
<td>36 36 35</td>
<td>37 40 37</td>
<td>6.1</td>
<td>0.32</td>
<td>0.24</td>
<td>0.85</td>
</tr>
<tr>
<td>9</td>
<td>63 51 70</td>
<td>71 72 76</td>
<td>80 78 79</td>
<td>5.2</td>
<td>1.11</td>
<td>0.98</td>
<td>1.41</td>
</tr>
<tr>
<td>*10</td>
<td>30 40 50</td>
<td>41 46 48</td>
<td>48 49 51</td>
<td>4.2</td>
<td>0.093</td>
<td>0.091</td>
<td>0.19</td>
</tr>
<tr>
<td>12</td>
<td>58 43 76</td>
<td>66 69 78</td>
<td>80 76 78</td>
<td>5.9</td>
<td>1.52</td>
<td>1.03</td>
<td>1.95</td>
</tr>
<tr>
<td>*13</td>
<td>47 54 67</td>
<td>55 59 70</td>
<td>65 66 68</td>
<td>4.5</td>
<td>0.74</td>
<td>0.70</td>
<td>1.12</td>
</tr>
<tr>
<td>14</td>
<td>49 69 81</td>
<td>68 81 84</td>
<td>79 81 80</td>
<td>4.2</td>
<td>1.28</td>
<td>1.1</td>
<td>1.59</td>
</tr>
<tr>
<td>*15</td>
<td>58 73 80</td>
<td>72 76 80</td>
<td>83 80 81</td>
<td>4.9</td>
<td>1.58</td>
<td>1.4</td>
<td>1.95</td>
</tr>
<tr>
<td>16</td>
<td>82 81 102</td>
<td>100 103 103</td>
<td>103 100 102</td>
<td>5.4</td>
<td>1.14</td>
<td>0.87</td>
<td>1.12</td>
</tr>
<tr>
<td>17</td>
<td>39 37 54</td>
<td>53 54 59</td>
<td>66 65 64</td>
<td>6.0</td>
<td>4.16</td>
<td>2.75</td>
<td>6.4</td>
</tr>
<tr>
<td>18</td>
<td>87 68 87</td>
<td>94 100 98</td>
<td>98 100 99</td>
<td>4.7</td>
<td>0.22</td>
<td>0.19</td>
<td>0.22</td>
</tr>
<tr>
<td>20</td>
<td>47 64 74</td>
<td>64 75 75</td>
<td>75 77 75</td>
<td>4.7</td>
<td>0.37</td>
<td>0.35</td>
<td>0.49</td>
</tr>
<tr>
<td>23</td>
<td>60 53 66</td>
<td>70 69 74</td>
<td>74 73 73</td>
<td>5.3</td>
<td>0.50</td>
<td>0.41</td>
<td>0.68</td>
</tr>
<tr>
<td>24</td>
<td>34 25 41</td>
<td>52 51 59</td>
<td>60 59 60</td>
<td>6.3</td>
<td>0.21</td>
<td>0.12</td>
<td>0.35</td>
</tr>
<tr>
<td>25</td>
<td>34 20 57</td>
<td>56 57 66</td>
<td>68 72 70</td>
<td>6.5</td>
<td>1.32</td>
<td>0.41</td>
<td>1.88</td>
</tr>
<tr>
<td>26</td>
<td>37 26 65</td>
<td>64 56 68</td>
<td>69 70 69</td>
<td>6.5</td>
<td>0.27</td>
<td>0.17</td>
<td>0.39</td>
</tr>
<tr>
<td>*28</td>
<td>39 46 53</td>
<td>55 60 68</td>
<td>66 70 70</td>
<td>6.8</td>
<td>4.35</td>
<td>1.00</td>
<td>6.30</td>
</tr>
<tr>
<td>6A</td>
<td>40 53 58</td>
<td>58 62 57</td>
<td>60 59 60</td>
<td>4.2</td>
<td>0.036</td>
<td>0.035</td>
<td>0.060</td>
</tr>
<tr>
<td>18A</td>
<td>52 41 56</td>
<td>55 53 56</td>
<td>59 55 56</td>
<td>4.1</td>
<td>0.011</td>
<td>0.011</td>
<td>0.020</td>
</tr>
<tr>
<td>20A</td>
<td>46 27 50</td>
<td>52 38 53</td>
<td>51 48 52</td>
<td>4.0</td>
<td>0.020</td>
<td>0.020</td>
<td>0.040</td>
</tr>
<tr>
<td>25A</td>
<td>61 65 81</td>
<td>76 76 83</td>
<td>80 78 80</td>
<td>4.2</td>
<td>0.032</td>
<td>0.031</td>
<td>0.040</td>
</tr>
</tbody>
</table>
The median concentrations of Cd extracted into the three salt solutions were: 0.057 mg/kg (10 mM CaCl₂), 0.059 mg/kg (1 M NH₄NO₃), 0.55 mg/kg (1 M NH₄Cl)—data for individual soils are not presented. That is, 1 M NH₄Cl extracted much more Cd than did 1 M NH₄NO₃. Therefore, application to the Cd data of the operational definition for exchangeable major cations, such as Ca, would classify much of Cd_{NH₄Cl} and consequently too of Cd_{E}, as non-exchangeable. These results therefore challenge the usual practice of ascribing the Cd extracted by concentrated solutions of chloride salts to the exchangeable fraction.

The isotopic ratio, \(^{110}/^{111}\)Cd, following \(^{110}\)Cd additions stabilised more quickly in 1 M NH₄Cl than in 0.01 M CaCl₂ and 1 M NH₄NO₃, presumably because, as noted in the preceding paragraph, 1 M NH₄Cl displaced a much greater proportion of Cd_{E} into solution than the other electrolytes. The difference in time to ‘equilibrium’ is evident in the estimates of Cd_{E}, expressed as a proportion of Cd_t (E values), observed during isotope dilution (Table 5.1). However, the ‘equilibrium’ E values were unaffected by the different electrolytes (Table 5.1), which is consistent with earlier reports (Young et al. 2000; Gray et al. 2003). The isotopic ratios also took longer to stabilise as pHₖ increased from 4.0 towards near-neutral values (Table 5.1). Cadmium desorption and exchange reactions are fast for soils and minerals under acidic conditions, and slower under alkaline conditions (O’Connor et al. 1984; Barrow et al. 1989; McLaren et al. 1998; Ramachandran and D’Souza 1999; Biškup & Subotić 2004; Zhang et al. 2006). Nonetheless, the longer ‘equilibration’ time at the higher values of pHₖ may signal the occurrence of processes other than exchange, e.g. the release of occluded Cd (Harper et al. 1998; Hamon et al. 2002b; Lombi et al. 2003).
There was a strong relation between Cd\textsubscript{t} and Cd\textsubscript{E} (Fig. 5.1), which was linear (R\textsuperscript{2} = 0.986, rsd = 0.14). The strength of the relation is not surprising, since measured values of Cd\textsubscript{E} constituted 40–102\% of Cd\textsubscript{t}. Regression analysis using the model:

\[
\log_{10} \text{Cd}_E = a + b \log_{10} \text{Cd}_t + c \text{pH}_s + \ldots
\]

Model 5.1 showed that the properties pH\textsubscript{s}, ECEC and Fe\textsubscript{ox}, and their interactions with land-use, did not affect the relation between Cd\textsubscript{t} and Cd\textsubscript{E} (P > 0.1). The lack of an effect of pH\textsubscript{s} is noteworthy, because pH\textsubscript{s} was correlated with log Cd\textsubscript{E} (r = 0.546, P < 0.01) and with log Cd\textsubscript{t} (r = 0.597, P < 0.01), and pH\textsubscript{s} strongly affected the relation between Cd\textsubscript{E} and Cd\textsubscript{NH4Cl} (see below).

During the modelling of Cd partitioning into 10 mM CaCl\textsubscript{2} for the 41 soils from which the subset of 23 were drawn for this study I speculated that Cd\textsubscript{t} and Cd\textsubscript{E} may be correlated (see Section 4.5). Such a correlation is likely because the

Figure 5.1 Relation between Cd\textsubscript{t} and Cd\textsubscript{E}.
evidence for appreciable Cd fixation is tenuous (Jensen & Mosbæk 1990; Hamon et al. 1998; Smolders et al. 1999). A linear relation also occurred between Cd$_E$ and Cd$_i$ ($R^2 = 0.67$, rsd = 0.38) for 20 soils from New Zealand that had been contaminated with Cd through the application of sewage sludge (Gray et al. 2003). Linear regression again showed that pH$_s$ did not affect the relation ($P < 0.1$). Note that Gray et al. (2003) measured pH in water and, for comparison with my data, the water pH values (pH$_w$) were decreased by 0.70 units (Conyers & Davey 1988; Bruce et al. 1989).

The range of the E values (40–102%, Table 5.1) is within that for other studies (Nakhone & Young 1993; Ahnstrom & Parker 2001; Gray et al. 2003; Degryse et al. 2004). The median E value for the unfarmed soils was ~60% and for the farmed soils was ~70% ($n = 19$); given that there were only 4 unfarmed soils, it would be imprudent to rely on these data to infer effects of different Cd origins (Degryse et al. 2004), or of Cd fixation (Jensen & Mosbæk 1990; Hamon et al. 1998; Smolders et al. 1999).

**The relation between Cd$_E$ and Cd$_{NH4Cl}$**

At pH$_s$ values near 4.0, Cd$_{NH4Cl} \approx$ Cd$_E$, and as pH$_s$ increased, Cd$_{NH4Cl}$ became a decreasing proportion of Cd$_E$ (Table 5.1). There were insufficient data to model the effects of other soil properties on this relationship; however, the effect of pH$_s$ is readily observed in a plot of (Cd$_{NH4Cl}$/Cd$_E$) against pH$_s$ (Fig. 5.2). Since pH$_s$ was not related to either Cd$_E$ or Cd$_i$ ($P > 0.1$), and pH$_s$ did not affect the relation between Cd$_E$ and Cd$_i$ (Model 5.1), the primary effect of increasing pH$_s$ was to
Figure 5.2. The effect of pH on Cd$_{NH4Cl}$/Cd$_E$.

decrease the efficiency of extraction of Cd$_E$ by 1 M NH$_4$Cl. This inference rests on the reasonable assumption that 1 M NH$_4$Cl extracts predominantly labile Cd.

To ascertain whether the effect of pH illustrated in Fig. 5.2 was peculiar to my data, I examined the results of both the earlier studies of selective Cd$_E$ extraction (Young et al. 2000; Gray et al. 2003). Analysis of these data revealed that there was a pH effect in only one study, vis. that of Gray et al. (2003). Now Gray et al. (2003) had added $^{114}$Cd, measured $^{114/111}$Cd using ICP–MS, and used 1 M CaCl$_2$ as the extractant. For comparison with the data in the present study, (Cd$_E$/extracted Cd) was plotted against pH$_s$ (Fig. 5.3). The illustrated effect of pH$_s$ was previously undetected.
Figure 5.3 The effect of pH$_s$ on Cd$_{extracted}$/Cd$_E$. The Cd was extracted in 1 M NH$_4$Cl (this study, open circles) or in 1 M CaCl$_2$ (Gray et al. (2003), solid circles). Gray et al. (2003) measured the pH of soil suspensions in water (pH$_w$) and for this comparison, values of pH$_w$ were decreased by 0.70 units (Conyers & Davey 1988; Bruce et al. 1989).

A quantitative comparison of the effects of pH$_s$ in the current study and that of Gray et al. (2003) was not possible due to the paucity of data. Nonetheless, Fig. 5.3 shows that neither 1 M NH$_4$Cl nor 1 M CaCl$_2$ efficiently extracted Cd$_E$ from soils of pH$_s$ > (say) 5.5. This finding contrasts with the lack of a pH effect (pH$_s$ range 4.0–7.3) in the study of selective Cd$_E$ extraction by Young et al. (2000). In that study, $^{109}$Cd was added to soils that were highly contaminated from mine spoil or sewage sludge, the extractant was 1 M CaCl$_2$, and Cd in solution was measured using furnace AAS.

The simplest hypothesis that would encompass the results from all three studies is that the efficiency of Cd$_E$ extraction by concentrated solutions of chloride salts
declines with increasing pH for some soils, i.e. the ‘pH-effect’ is multi-factorial. The ‘pH-effect’ may also be independent of whether the extractant is 1 M NH$_4$Cl or CaCl$_2$, and the Cd is ‘natural’ or a contaminant. The extraction efficiency hypothesis is well-founded, although the literature pertains to more dilute solutions of chloride salts (Kinniburgh et al. 1976; Johnson 1990; Tipping 1994; Lee et al. 1996; Trivedi & Axe 2000; see Section 4.4.1). Again, taking the simplest approach, the second factor should have the characteristic that little Cd is bound at low pH, with binding that increases strongly above pH (say) 5.5 to 6.0. At least two common classes of constituents would fit this description, i.e. basic phases such as calcite, which are unstable under acidic conditions, and hydrous oxides such as those of iron, for which the Cd sorption edge occurs near pH 6 (Cowan et al. 1991). Empirical support for the latter speculation comes from two directions. New data are needed to test this hypothesis.

5.5 Conclusion

The efficiency of Cd extraction by 1 M NH$_4$Cl and 1 M CaCl$_2$ diminished as pH$_s$ values increased from 4.0–6.8. Elucidation of the cause(s) of this discrepancy may lead to a universally applicable method for the selective extraction of Cd$_E$ and improve understanding of Cd binding to different soil constituents.
6.1 Summary

- Synchrotron micro-x-ray fluorescence spectroscopy (micro-XRFS) was tested in an attempt to map the distribution of Cd.
- The soils examined contained 0.3–6.4 mg Cd/kg, i.e. were typical agricultural soils, except that one was spiked to ~100 mg Cd/kg.
- Cd was mapped in one particle of one soil and the in the spiked soil.

6.2 Introduction

The approach taken in Chapters 2–5 relied on samples of soil that had been ground and mixed to minimise natural heterogeneity that would otherwise have caused unacceptable variation between replicate analyses. This high degree of homogeneity stands in stark contrast with the situation for soils in situ, in which the behaviour of Cd and its impact on biota exhibit considerable spatial variation (Boekhold & van der Zee 1991; Böttcher 1997; Seutjens et al. 2002; Wu et al. 2002). It is reasonable to assume that spatial variation also occurs at the microscopic scale and impacts on Cd partitioning and bioavailability; however, it has not been possible to observe Cd distributions at this scale in agricultural soils because of the low concentrations of Cd they contain (<1 to 10 mg/kg) (Sillpanää & Jansson 1992; Sánchez-Camazano et al. 1994).
The brilliance of 4th generation synchrotron x-ray sources and the sensitivity of energy dispersive x-ray fluorescence spectroscopy (XRFS), have revealed the average atomic environment of heavy atoms in various materials (Xia, 1997; Xia et al. 1997; Rouff et al. 2004; Bohic et al. 2005), including Cd in plant roots, OM and biosolids (Naftel et al. 2001; Karlsson et al. 2005; Hettiarachchi et al. 2006). However, the concentrations of Cd in the preceding studies were high compared with those of Cd in typical agricultural soils, and no XRFS study had been reported for them. Consequently, to learn more about the Cd distribution in agricultural soils, I tested whether synchrotron micro-XRFS was sufficiently sensitive to map the distribution.

6.3 Materials and methods

The samples—were five of the 41 soils (Table 6.1) used in the modelling study (Chapters 2–4).

Table 6.1 Some properties of the soils examined using the x-ray microprobe. The data are drawn from Appendix 1.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Soil properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_t</td>
</tr>
<tr>
<td></td>
<td>(g/kg)</td>
</tr>
<tr>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>28</td>
</tr>
<tr>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>17A</td>
<td>21</td>
</tr>
<tr>
<td>25</td>
<td>22</td>
</tr>
</tbody>
</table>
Four of the soils were from farms: one (#17) was of the same soil type as that from an unfarmed site nearby (#17A). The samples had a wide range of Cd concentrations. To increase that range, a sub-sample of soil #17A was shaken with a solution of Cd(NO$_3$)$_2$ to increase the Cd concentration to ~100 mg/kg, after which the soil was dried. A sample of phosphorite from Nauru was also finely ground: Nauru phosphorite had been used to manufacture much of the P-fertiliser that was the main source of Cd accessions to the soils on vegetable farms in Greater Sydney during the 20$^{th}$ Century (Jinadasa et al. 1997). This sample contained ~100 mg Cd/kg.

**Grain mounts**—5–10 mg of dry powdered sample was placed into an ~20 mm diameter mould in a chamber that could be evacuated. About 2 mL of a low viscosity, low volatility epoxy resin (Epo-thin®, Buehler Pty Ltd, USA) was injected onto the powder. The chamber was evacuated for ~30 s then air was allowed to return. This process infiltrated and suspended the sample in the resin, which was allowed to cure as a block. The resin blocks were thinned to 150–200 μm and the surface polished: the resulting grain mount contained at most 1 mg of sample.

**Synchrotron micro-XRFS**—measurements were performed at beam-line 2-ID-D of the Advanced Photon Source, Argonne (Yun et al. 1999; Cai et al. 2000). The electron current in the storage ring was ~100 mA, and an undulator source produced a broad x-ray spectrum, from which a narrow band was selected by using a pair of Si(111) crystals (27.0 ± 0.003 keV). This was the incident radiation for the experiment, which is represented schematically in Figure 6.1. The radiation was focussed to ~1 μm diameter using a gold zone plate of 150 μm
diameter with a focal length of 337.5 mm. A pin hole of 25 x 25 µm, in polished tungsten blades, was placed ~5 mm upstream of the sample to decrease the zero- and high-order diffraction from the zone plate reaching the sample. A sample holder supported the grain mounts at the focal point, with an angle of ~15º between the incident beam and the normal to the sample plane.

The energy dispersive germanium detector (100 mm² LEGe, Canberra Industries, Canada) was placed upstream, and as close as possible to the grain mount, at 90º to the incident beam, (Fig. 6.1). An ion chamber detector was located downstream of the grain mount to monitor the x-ray flux. The beam exiting the ion chamber was intercepted and visualised using a CdWO₄ scintillator crystal (~500 µm thick). The downstream monitoring locations were satisfactory because the samples did not appreciably absorb/scatter the incident beam. The incident beam, sample and detectors were enclosed in a hood that was continuously purged with helium gas.

Small areas of the grain mounts were scanned. A scan consisted of a set of stepwise fluorescence intensity observations at points on a rectangular grid. The
sample holder, with grain mount attached, was driven in the X-Y plane, using computer controlled motors with linear encoder feedback. The range of a scan could extend to several mm, while the step size within the selected range could be adjusted in 0.05 µm increments. The counting time could be varied between scans, but was fixed within a scan. Typically, the initially scan of a grain mount used short counting times and relatively large steps to identify particles of potential interest: the more detailed scans of these particles used longer counting times and smaller steps. Counting times and step sizes are presented with the images.

During a scan, the signal from the fluorescence detector was processed through a shaping amplifier and pulse height analyser. The resulting spectrum at each observation point (pixel) was stored in a computer file. Spectral regions characteristic of particular elements were examined, giving fluorescence intensity data for the elements: silicon (Si), potassium (K), calcium (Ca), titanium (Ti), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), lead (Pb), strontium (Sr), yttrium (Y) and Cd. The data for Pb contain a contribution from As; however, the effect was small because the As concentrations in the soils were low. This list of elements contains some that are geochemically associated and others that are either natural soil constituents or contaminants.

Data processing—a map was constructed for each element in a scan from the stored intensity data. In each map, the relative intensity of all the pixels is represented on an artificial colour scale: red (greatest intensity) >orange >yellow >green >blue >grey (least intensity). The numeric scales on the axes are distances (µm) in the X–Y plane from an arbitrary reference position.
In interpreting the images it should be kept in mind that:

- the intensities are relative not absolute;
- for small spherical particles of uniform composition, the fluorescence intensity for an element increases from background to a local maximum as the particle is scanned radially from the edge to the centre. Scans that deviate from this pattern indicate deviations from either spherical geometry or uniform distribution, or both; and
- clay-sized particles are <2 µm in diameter.

6.4 Results and discussion

The soil properties—were described in Chapter 3. Of note here is that Cd, was 0.3–6.4 mg/kg, which is typical of intensively managed agricultural soils worldwide (Sillpanää & Jansson 1992; Sánchez-Camazano et al. 1994).

Source intensity—was monitored by the downstream ionisation chamber (Fig. 6.1) during the 72 h of synchrotron measurements. The count rate was \( \sim 1 \times 10^5 \) counts/s with a range of ±5%; insufficient variation to affect data interpretation.

Micro-XRFS data for natural soils—a strong Cd K\(_\alpha\) signal was obtained for one particle in #6 (Fig. 6.2). The scan was in 0.5 µm steps with a counting time of 5 s/step (pixel). The particle was \( \sim 10 \) µm in diameter, and the peak intensity of the fluorescence signal for Cd was \( \sim 0.5 \times 10^3 \) counts/s. The peak signals for Cd and Zn both occurred near the assumed centre of the particle at approximate X, Y coordinates of (823, 278). Peak signal intensities for Y, Ti and Ca also occurred nearby (not shown). In contrast, the strongest signals for Fe, Pb and Cu occurred
Figure 6.2. Cd, Cu, Fe, Zn, Pb and K distributions in a small particle in the mount prepared from #6. The scanning step was 0.5 µm and the counting time 5 s/pixel. The artificial colour scale indicates the relative count rates for an element (white > red> orange> yellow> green> pale blue> dark blue >grey ≈ background). The scales on the axes are distances from an arbitrary reference position.
close to the putative rim (Fig. 6.2), as they did for Si and Mn. These data are not shown because of concern over the origin of this unusual particle and, consequently, about how typical or otherwise the elemental associations may be (see the following paragraph). The distribution of the signal for K was bimodal, with a major peak located centrally and a smaller peak towards the upper centre of the image. Therefore, if the particle was approximately spherical, only Cd, Zn, Y, Ti and Ca were distributed relatively uniformly throughout (see Section 6.3). No other observed particle in the grain mounts of the natural soils had sufficient Cd signal to be mapped; however, only <1% of the area of the grain mounts was scanned and each mount contained at most 1 mg of soil, i.e. the effective sample size was small.

It was surprising that the only Cd-rich particle found was in the grain mount of #6, which had the lowest bulk Cd concentration of the 5 soils sampled (0.3 mg/kg, Table 6.1). One can only speculate on the origin of this Cd-rich particle, e.g. it could be geogenic, because the soil at location 6 developed on shale, and shale soils in Greater Sydney can have appreciable Cd concentrations (Jinadasa et al. 1997). The alternative is contamination, which is unlikely because of the precautions taken to maintain integrity (see Section 3.3). Farming too seems an unlikely cause because no similar particles were observed in the mounts of the other farmed soils; however, this argument must be tempered with caution because of the small quantity of soil examined (see above). Site 6 is within 100 m of a minor road, therefore road dust is a credible source of this Cd-Pb rich particle (Adachi et al. 2004).
Figure 6.2 has areas where none of the 12 monitored elements had count rates >5/s. These low count rates show that the resin itself was relatively free of these elements, and that there had been little ‘leakage’ from the soil into the resin.

**Observations for sample #17A amended with Cd**

To estimate the increase in sensitivity that may be needed to allow Cd mapping for agricultural soils, I scanned a number of areas of the grain mount of the Cd-enriched sub-sample of soil #17A, e.g. an area of about 120 x 120 µm was scanned with a step size of 1 µm and a counting time of 2 s/pixel. Towards the centre-left of the images (Fig. 6.3) is a large, crescent-shaped assemblage of particles (X coordinate approximately –140 µm, Y coordinates –220 to –160 µm). The Cd and Pb maxima are closely associated and occur away from the apparent rim of the crescent. In the same region, there is also an elevated Ca signal, which is not obvious due to the scaling effect caused by an even greater Ca intensity in the upper right corner of the map (Fig. 6.3). This crescent shaped object also includes intense signals or Fe at locations different from those for Cd and Pb (Fig. 6.3). In addition, the area of local, high signal intensity for Fe overlaps with that for Ti, and a similar pattern occurs for Cd and Zn (not shown). The complex distribution of elements in this object, and its large size relative to clay particles, indicate that it may be an assemblage of organic matter, clay and other minerals, as reported for particles in groundwater (Bertsch & Seaman 1999; Dolfing *et al.* 1999). The distribution of elements among particles of the assemblage is highly heterogeneous (Fig. 6.3).
Figure 6.3  Localisation of Cd, Fe, K and Pb in an assemblage of particles in the grain mount of soil #17A that contained ~100 mg Cd/kg. The scanning step was 1 µm and the counting time 2 s/pixel. The artificial colour scale indicates the relative count rates for an element (Fig. 6.2). The scales on the axes are distances from an arbitrary reference position.

Agricultural soils typically contain <10 mg Cd/kg (Sillpanää & Jansson 1992; Sánchez-Camazano et al. 1994) and there is a concern that Cd distribution may vary with load (Nirel & Morel 1990; Xia et al. 1997; Ho & Evans 2000; Milham et al. 2004). Consequently, the detailed associations of Cd with other elements were not explored since they may have been misleading.
The images in Fig 6.3 also illustrate how scanning was used to locate small, Cd-rich particles for more detailed observation. Inspection of the Cd image shows an area of considerable enrichment with approximate coordinates of \((-10, -110)\). The peak Cd intensity was \(\sim 0.5 \times 10^3\) count/s. Typically, it would be necessary to rescan such an area at higher resolution; however, in this case the step size of the initial scan was 1 µm, so images of the area \(X = 0\) to \(-30\), \(Y = -100\) to \(-130\) were simply expanded about 4-fold (Fig. 6.4). These expanded images show the expected Cd/Pb hot spot but do not resolve the locations of these elements, i.e. the Cd and Pb are similarly distributed within and between particles in this grain mount (Figs 6.3 and 6.4). An association between Cd and Pb is not unreasonable, because both bind to soil organic matter and hydrous metal oxides (Adriano 2001): however, the Cd-Pb hot spot occurs at a location separate from several strong localisations of Fe. That is, there was no consistent co-location of strong signals for Cd and Fe as reported for a sewage sludge (Hettiarachchi et al. 2006).

The sludge studied by Hettiarachchi et al. (2006) had been flocked with basic Fe (hydr)oxide, as evidenced by the percentage concentrations of Fe, i.e. the Fe concentration in the sludge was almost 10 times that of the (hydrous)Fe oxides in my soils (Table 6.1). This difference may have sufficiently affected the Cd and Fe distributions to make the association observable in one study and not the other; alternatively, a Cd-Fe association may not be general in soils, though it has been inferred from desorption studies (Milham et al. 2004).
Figure 6.4  Data for the top right corner of Fig. 6.3 on an ~4x expanded scale. The scanning step was 1 µm and the counting time 2 s/pixel. The artificial colour scale indicates the relative count rates for an element (Fig. 6.2). The scales on the axes are distances from an arbitrary reference position.

**Observations for Nauru phosphorite**

Nauru phosphorite has a Ca, F, O and P matrix, and the typical concentration of Cd is ~100 mg/kg (McLaughlin et al. 1996). The $K_{\alpha}$ fluorescence energies
for F, O and P were too weak to be detected in my study; however, the Ca was readily detected, and differences in the Ca signal intensity related to particle thickness (Fig. 6.5). Therefore, the similarity of the relative intensity patterns for Ca and Cd shows that Cd too was relatively uniformly distributed through the matrix. This result is consistent with that for an apatite from Africa (Séry et al. 1996); consequently, Cd may generally be relatively uniformly distributed in such minerals.

6.5 Conclusion

Grain mounts proved satisfactory for observing Cd distributions in small soil particles by micro-XRFS and the resolution was adequate for Cd mapping. The Cd sensitivity achieved would have been sufficient to characterise the average Cd binding site, but fell at least 10-fold below that needed to readily map the Cd distribution in agricultural soils: such an increase is technically feasible.
CHAPTER 7—GENERAL DISCUSSION

7.1 Towards a general model of Cd partitioning

The mechanistically-informed approach taken to empirical modelling of the effect of soil properties on Cd partitioning was so successful that I postulated that it may lead to a general model of Cd partitioning (see Section 4.6). Discussion of this topic is extended here to include the important issue of the relative effects of soil properties on Cd partitioning during Cd sorption and desorption phenomena. Finally the importance of the choice of the dependent variable in the development of a general model is addressed.

The following arguments involve comparisons of the values of partial coefficients of explanatory variables between models; therefore, before proceeding, I reiterate that the values of such coefficients may be affected by the other properties used as explanatory variables. In addition, the signs of the coefficients are affected by the property used as the dependent variable; consequently, it is the absolute values of the coefficients that are compared between models.

First, the absolute value of the pH coefficient in Model 4.6 was 0.49 ± 0.03. This value is similar to the mean of 0.56 for the following multiple regression studies (de Haan et al. 1987; Anderson & Christensen 1988; del Castilho et al.1993a; Springob & Böttcher 1998b; Jopony & Young 1994; Celardin 1999; Römkens & Salomons 1998; Elzinga et al. 1999; Gray et al.1999; Sauvé et al. 2000a;
Degryse et al. 2003). In these 11 studies, there were no discernable effects on the value of the pH coefficient, whether the range of pH values was ‘natural’, or had been extended by adjustment either in the field or laboratory. Neither was there an effect of whether the data were from desorption or sorption studies.

The lack of effect of pH adjustment on the value of the Cd coefficient in the partitioning models may be no coincidence, since proton stoichiometry for sorption by goethite is determined by the sorbate (Spark et al. 1995). That is, the soil data indicate that the average proton coefficient for Cd complexation may also have a narrow range of values. Conclusive evidence that the value of the pH coefficient in empirical models of Cd partitioning in soils is effectively a constant would be of fundamental interest. Such a finding would also greatly simplify the modelling of Cd partitioning, on which pH has so strong an impact, e.g. in my data, the partial correlation was −0.93 (see Section 4.5.2.2).

Second, consider the effect of the choice of dependent variable on the values of the partial coefficients of the explanatory variables. Had my primary interest been in the effects of soil properties on the amount of Cd bound to the solid phase, I would have used \( \log_{10} \text{Cd}_i \), not \( \log_{10} \text{Cd}_{\text{Ca}} \), as the dependent variable. When the modelling was repeated with \( \log_{10} \text{Cd}_i \) as the dependent variable, the main effect of this change, e.g. in a recast Model 4.6, was to change the signs of the coefficients of the explanatory variables, with little effect on their absolute values, or on the \( R^2 \) and rsd for the model. That is, the effect was benign.
In many other studies, the dependent variable is a partition coefficient, such as \( \log_{10}(Cd_t/Cd_{Ca}) \), or its inverse (Gerritse & van Driel 1984; Buchter et al. 1989; Houba et al. 1996; Sauvé et al. 2000a). To provide a direct link with such studies, I also used \( \log_{10}(Cd_t/Cd_{Ca}) \) as the dependent variable and, conforming with tradition, expressed \( Cd_t \) in units of mg/kg and \( Cd_{Ca} \) in units of mg/L. Otherwise the following model corresponds to Model 4.6:

\[
\log_{10}(Cd_t/Cd_{Ca}) = [-1.15 (\pm 0.18) \text{ for } pH \leq 5.6] \text{ or } [-2.38 (\pm 0.58) \text{ for } pH > 5.6] \\
+ 0.53 (\pm 0.04) pH_{Ca} + 0.48 (\pm 0.10) \log_{10} ECEC \\
+ 0.35 (\pm 0.16) \log_{10}^{pH>5.6} Fe_{ox}
\]

\((n = 41, R^2 = 0.919, rsd = 0.169) \quad \text{Model 7.1}\)

The effect of using \( \log_{10}(Cd_t/Cd_{Ca}) \) as the dependent variable was not benign, e.g. the absolute value of the coefficient for \( \log_{10} ECEC \) in Model 4.6 was 0.69 (± 0.08), whereas in Model 7.1 it was 0.48 (± 0.10). Investigation showed that this difference was caused by the use of \( Cd_t/Cd_{Ca} \) as the dependent variable and a lack of strict proportionality between \( \log_{10} Cd_t \) and \( \log_{10} Cd_{Ca} \) in the data. Explicitly, in Model 4.6 the coefficient of \( \log_{10} Cd_t \) for the farmed soils had a value of 1.33 ± 0.05, rather than exactly 1.0 (strict proportionality). Therefore, the value of 0.48 (± 0.10) for the coefficient of \( \log_{10} ECEC \) in Model 7.1 is a biased estimate of the effect of this variable on Cd partitioning. That is, in the interest of developing general models of Cd behaviour in soils, the use of partition coefficients as dependent variables can be justified only if it is first demonstrated that \( \log_{10} Cd_t \) and \( \log_{10} Cd_{Ca} \) vary in strict proportion. Strict proportionality is atypical of partitioning reactions in which the range of sorbate concentration extends over two or more orders of magnitude (Barrow 1999). Therefore, it is reasonable to infer that partition coefficients confer no benefits to the partitioning modelling.
and are rarely suitable as the dependent variable, whether the sorbate is Cd or another substance.

Third, in Section 2.4, I questioned whether soil properties may affect Cd partitioning differently during sorption and desorption. This question was beyond the empirical scope of my study, but it is addressed inferentially here, initially by comparing my modelling with that of Elzinga et al. (1999). The latter study modelled the effects of pH, log\(_{10}\) ECEC and log\(_{10}\) Ca (in solution) on sorbed Cd, using the data from 26 Cd sorption studies. Model 7.2 is after Elzinga et al. (1999), except that the notation for sorbed Cd is (Cd\(_{t}\) – Cd\(_{Ca}\)):

\[
\log_{10}(Cd_{t} – Cd_{Ca}) = -3.22 (± 0.10) + 0.87 (± 0.01) \log_{10}Cd_{Ca} + 0.45 (± 0.01) pH \\
+ 0.63 (± 0.03) \log_{10} ECEC - 0.47 (± 0.02) \log_{10} Ca
\]

\((n = 1125, R^2 = 0.78, \text{rsd not given})\)  \hspace{1cm} \text{Model 7.2}

where Ca represents the concentration of Ca\(^{2+}\) in solution. Model 7.2 also fitted my data well \((R^2 = 0.946, \text{rsd} = 0.170)\), and the coefficients of pH\(_{Ca}\) and log\(_{10}\) ECEC were 0.49 (± 0.04) and 0.67 (± 0.09), respectively, i.e. not different from those in Model 7.2 \((P < 0.05)\).

The similarities between the coefficients above are noteworthy for three reasons. First, the data compiled by Elzinga et al. (1999) were for the sorption of added Cd, whereas mine were for desorption of ‘native’ Cd. Second, the data compiled by Elzinga et al. (1999) had a wide range of concentrations of Ca and Cl, whereas in my study, the concentrations of both ions were relatively constant, due to the use of 10 mM CaCl\(_2\) as the background electrolyte. Third, for my data, the modelling showed that the value of the coefficient for log\(_{10}\) ECEC was slightly affected by land-use, as it was in Model 4.4. The similarity of the coefficients
between these two studies may have resulted from chance; consequently, I sought to compare the coefficients with those from another modelling study that also included both pH and \( \log_{10} \) ECEC among the explanatory variables.

Fortunately, an independent comparison was possible because Degryse et al. (2003) had used a model that included both pH and \( \log_{10} \) ECEC among the explanatory variables to describe the partitioning of Cd under desorption conditions for 74 polluted European soils \( (R^2 = 0.87, \text{ no rsd reported}) \). The estimated values of the coefficients for pH and \( \log_{10} \) ECEC were 0.45 and 0.63 (no uncertainties reported): again the values are very similar to the preceding ones. Again, there was also a strong likeness to the absolute values in Model 4.6, i.e. 0.49 \((\pm 0.03)\) for \( \text{pH}_{\text{Ca}} \) and 0.69 \((\pm 0.08)\) for \( \log_{10} \) ECEC.

Importantly, the coefficients of pH and \( \log_{10} \) ECEC in the preceding models appear independent of whether they were derived from data acquired under conditions of Cd sorption or desorption, and whether or not the pH was adjusted. This independence supports two inferences. First, it seems feasible that general models of the effects of soil properties on Cd partitioning could be developed. Second, the data from both sorption and desorption studies might reasonably be combined for meta-analysis.

### 7.2 Does colloidal Cd contribute to measures of Cd in solution?

During the partitioning study, I found that ultra-filtration using 10 kDa cut-off filters had no effect on \( \text{Cd}_{\text{Ca}} \) (see Chapter 3). As noted there, this was not sufficient to prove that the extracts did not contain appreciable amounts of Cd associated with colloids, especially given the wealth of contrary information from
other studies. However, in Chapter 4 it was argued that the background electrolyte may have minimised the contribution from colloids; nevertheless, no firm conclusion could be drawn and I had intended no further comment on the matter. However, the following information caused me to reconsider:

- there was a small pH effect in the relation between \( \text{Cd}_E \) and \( \text{Cd}_{\text{NH}_4\text{Cl}} \) \( (P < 0.01) \) (Model 5.1);
- I found a similar effect in data published by Gray et al. (2003) (Model 5.2); and
- Lombi et al. (2003) reported an effect of pH on the amount of slowly dissociable Cd associated with colloids in soil extracts.

Models 5.1 and 5.2 were discussed at length (see Chapter 5); however, this is the first time I have discussed the study by Lombi et al. (2003), who measured the effects of “colloidal” Cd on estimates of \( \text{Cd}_E \). The definition of colloidal Cd was that it passed 0.2 \( \mu \text{m} \) filters and exchanged slowly with added label. The procedure used isotope dilution, in association with ion exchange by a chelating resin Chelex (Bio-Rad Laboratories), to discriminate between two Cd pools, namely: rapidly and slowly labelled. That is, it was a kinetic discrimination. The resin efficiently recovered free Cd and Cd in labile complexes from synthetic solutions, and the labelling was complete. However, in the soil extracts, the label equilibrated with only part of the Cd: the other Cd component was at best partially labelled. The duration of isotope exchange was 3 days, which may have permitted slow concomitant processes to occur. Therefore, if anything, the size of the non-labile Cd pool may have been underestimated. (This assumes that the resin was not “fouled” in the process.) Therefore, it is likely that my measured
values of Cd_{Ca} and Cd_{E} had some contribution from "colloidal" Cd (see Chapters 3 and 5). However, the large R^2 and small rsd for (say) Model 4.6 (R^2 = 0.974, rsd = 0.121) indicate that the contribution was either small or relatively uniform.

### 7.3 Cadmium fractionation, binding and distribution

One M NH₄Cl failed to completely extract Cd_{E} (Model 5.1), and 1 M NH₄NO₃ and 10 mM CaCl₂ extracted much less Cd again (Table 7.1). The latter data were not presented in Chapter 5 because they would have detracted from the focus on labile Cd. In this context, 0.1 M solutions of Ba^{2+} or NH₄⁺ efficiently displace the major "soluble plus exchangeable" fractions of cations such as Ca^{2+} from soils (Gillman 1979). Therefore, by definition, 1 M NH₄NO₃ displaces soluble plus exchangeable Cd. The additional amount of Cd displaced by the chloride salt must therefore mainly have come from components of the labile pool, other than the soluble and exchangeable fractions, and was accessed by the formation of chloro complexes. There has been much speculation about the contributions of soluble, exchangeable and other Cd fractions to the

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Cd_{NH₄NO₃} (mg/kg)</th>
<th>Cd_{NH₄Cl} (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0038</td>
<td>0.12</td>
</tr>
<tr>
<td>7</td>
<td>0.096</td>
<td>0.24</td>
</tr>
<tr>
<td>9</td>
<td>0.046</td>
<td>0.98</td>
</tr>
<tr>
<td>10</td>
<td>0.059</td>
<td>0.091</td>
</tr>
<tr>
<td>12</td>
<td>0.059</td>
<td>1.03</td>
</tr>
<tr>
<td>13</td>
<td>0.17</td>
<td>0.70</td>
</tr>
<tr>
<td>14</td>
<td>0.54</td>
<td>1.10</td>
</tr>
<tr>
<td>15</td>
<td>0.17</td>
<td>1.40</td>
</tr>
<tr>
<td>16</td>
<td>0.086</td>
<td>0.87</td>
</tr>
<tr>
<td>18</td>
<td>0.088</td>
<td>0.19</td>
</tr>
<tr>
<td>20</td>
<td>0.074</td>
<td>0.35</td>
</tr>
<tr>
<td>23</td>
<td>0.045</td>
<td>0.41</td>
</tr>
<tr>
<td>6A</td>
<td>0.017</td>
<td>0.035</td>
</tr>
<tr>
<td>18A</td>
<td>0.0058</td>
<td>0.011</td>
</tr>
<tr>
<td>20A</td>
<td>0.0028</td>
<td>0.020</td>
</tr>
<tr>
<td>25A</td>
<td>0.0080</td>
<td>0.031</td>
</tr>
</tbody>
</table>
labile pool. However, for the soils in this study, the labile pool appears to have been largely weakly complexed, because although the binding between Cd and Cl\(^-\) is weak, Cl\(^-\) broke a considerable proportion of the soil complexes.

Fractionation of soil Cd has been strongly criticised (Nirel & Morel 1990; Jeng & Singh 1993; Ma & Uren 1998; Benitez & Dubois 1999; Ho & Evans 2000), and the difficulty of inferring environmental behaviour from the results of soil extractions has been exhaustively reviewed (Kennedy et al. 1997; Sauvé 2002; Ure & Davidson 2002). My results show that the sequential extraction schemes commonly applied to fractionate soil Cd, and evaluate environmental risk, or the interpretation of the data from such fractionations, should be modified.

Prior to the x-ray-microprobe study, the sensitivity of the technique was thought to be insufficient to map the Cd distribution in soil particles, unless the soils contained a bulk Cd concentration of ~1000 mg/kg. In the event, images were readily obtained at 100 mg Cd/kg, but not at <10 mg Cd/kg. Since typical agricultural soils contain <1 mg Cd/kg, the answer to supplementary question 2 (see Section 1.8) was that at least a 10-fold sensitivity increase would be needed to readily map the Cd distribution in typical agricultural soils. Advances in x-ray optics and detectors are in train that will deliver the required increase in sensitivity. The data also showed that the sensitivity of x-ray fluorescence spectroscopy achieved during the study would have been sufficient to characterise the average Cd binding site in agricultural soils.
7.4 Conclusion

Each of the three strands of the study used innovative approaches to challenge and extend knowledge of Cd behaviour in soils. The results of the partitioning study (see Chapter 4) supported the hypothesis that mechanistically-informed empirical modelling may accurately describe the effects of soil properties on Cd partitioning (see Section 1.8). The first supplementary question was: can labile Cd be measured without isotope addition (see Section 1.8)? Comparison of Cd extracted in 1 M NH₄Cl and an isotope dilution measure of labile Cd show that labile Cd can indeed be selectively extracted, at least for soils of pH ≤6.1 (see Chapter 5). The second supplementary question was: can an x-ray microprobe map the distribution of Cd in soil particles (see Section 1.8)? The micro-x-ray fluorescence data presented in Chapter 6 show that a sensitivity increase of at least ten-fold is needed to make this application feasible: technical innovations will soon make this achievable.

The study also produced new insights into the behaviour of Cd in soil, its modelling and measurement, notably:

1. it is likely that general models of the effects of soil properties on Cd partitioning can be developed;
2. the data for the effects of soil properties on Cd partitioning, from both sorption and desorption studies, could be combined for meta-analysis;
3. the use of partition coefficients as dependent variables is problematic, and unnecessary, so their use should be discontinued;
4. partitioning models should include estimates of the standard errors of the coefficients, and both the R² and the rsd values should be reported; and

5. labile Cd is not displaced quantitatively from some acidic soils by 1 M NH₄Cl or 1 M CaCl₂.

6. Finally, by analogy to the result for chloride and Cd, weak complexing agents may selectively extract the labile fractions of other trace metals.

This study improves the prospect of using soil properties to predict Cd partitioning. If it is assumed that plant uptake is principally controlled by the concentration of Cd in solution, then predictable Cd partitioning may, in turn, lead to prediction of Cd uptake by plants. This possibility may be strengthened by the readier access to estimates of labile Cd promised by my novel extraction method. Such developments would make it feasible to manage soils to decrease Cd in plant foods and consequently human exposure to Cd.

Modelling Cd uptake by plants will almost certainly require the inclusion of variables additional to those needed to model Cd partitioning. For example, chloride affects Cd partitioning in the laboratory and the uptake of Cd by plants. Finally, the distribution of Cd in field soils is heterogeneous, and the effect of this heterogeneity, on the predictability of Cd uptake by plants, remains unknown.

7.5 Research leads

1. The amount of Cd extracted by 1 M solutions of NH₄Cl or CaCl₂ could be evaluated as an index of Cd risk for soils of pH <5.5.
2. The role of measures of labile Cd in descriptions of Cd partitioning, such as Model 4.6, should be tested and the models validated.

3. The cause(s) of the effect of pH, at values >5.5, on the relation between Cd$_E$ and Cd extracted by 1 M solutions of NH$_4$Cl and CaCl$_2$, should be elucidated to minimise the pH effect, especially.

4. The contribution of slowly-labile, soluble Cd complexes to the concentration of Cd in soil extracts should be investigated.

5. The typical Cd binding site in agricultural soils should be characterised.
LITERATURE CITED


Anonymous (2005) Australia New Zealand Food Standards Code, Standard 1.4.1, Contaminants and Natural Toxicants. (Australia and New Zealand Food Authority: Canberra, Australia)


Burgess J (1994) Annual List of Registered Fertilisers ISSN 1038-7927. (New South Wales Agriculture, Biological and Chemical Research Institute: Rydalmere, Australia)


Hawkins CA, Haddad NI (2005) Soils of the Plateau of the Central Coast of New South Wales. (New South Wales Department of Primary Industries)


Kennedy VH, Sanchez AL, Oughton DH, Rowland AP (1997) Use of single and sequential chemical extractants to assess radionuclide and heavy metal availability from soils for root uptake. *Analyst* **122**, 89R-100R.


Long SE, Martin TD (1989) Determination of trace elements in water and wastes by ICP-MS, version 4.0. (Office of Research and Development, USEPA: Cincinnati, Ohio)


Northcote KH (1979)  A Factual Key for the Recognition of Australian Soils.  
(Rellim Technical Publications: Glenside, South Australia)

Nriagu JO (1980a)  Human Influence on the Global Cadmium Cycle.  In  
‘Cadmium in the Environment’ (Ed. JO Nriagu) pp. 1-12.  (John Wiley and  
Sons: New York)

Nriagu JO (1980b)  Production, Uses and Properties of Cadmium.  In ‘Cadmium in  
the Environment’ (Ed. JO Nriagu) pp. 35-70.  (John Wiley and Sons: New  
York)

Nriagu JO (1980c)  Cadmium in the Atmosphere and Precipitation.  In ‘Cadmium  
in the Environment’ (Ed. JO Nriagu) pp. 71-114.  (John Wiley and Sons: New  
York)

York)

O’Connor GA, O’Connor C, Cline GR (1984)  Sorption of cadmium by calcareous  
48, 1244-1247.

blood and urine—impact of sex, age, dietary iron intake, iron status and former smoking—association of renal effects.  Environmental  
Health Perspectives 110, 1185-1190.

production systems: a health risk for sensitive population groups.  Ambio 34, 344-351.

variations.  In ‘International Symposium on Manganese in Soils and Plants’  
(Eds MJ Webb, RD Graham, RJ Hannam) pp. 11-13.  (Manganese  
Symposium 1988 Inc.: Adelaide, Australia)

Palm V (1994)  A model for sorption, flux and plant uptake of cadmium in a soil 
profile: model structure and sensitivity analysis.  Water, Air and Soil  
Pollution 77, 169-190.

Parfitt RL, Childs CW (1988)  Estimation of forms of Fe and Al: a review and 
analysis of contrasting soils by dissolution and Moessbauer methods.  
Australian Journal of Soil Research 26, 121-144.

Parker DR, Norvell WA, Chaney RL (1995) GEOCHEM-PC-a chemical


### APPENDIX 1. SITE AND SOIL PROPERTIES†

| Site # | Farmed (y) | Texture | Clay content (g/100 g) | EC (ds/m) | Cl (mg/L) | DOC (mg/kg) | pHcs | Cdcs (mg/kg) | Cd (mg/kg) | Pt (mg/kg) | Zn (mg/kg) | Ct g/kg | ECEC cmol/kg | Excs mg/kg | Feox mg/kg | Alox mg/kg | Pox mg/kg | Mnox mg/kg |
|--------|------------|---------|------------------------|-----------|----------|-------------|-------|--------------|-----------|-----------|------------|--------|---------------|------------|------------|-------------|-----------|
| 4      | ~20        | CL (with grit) | 30                     | 0.50      | 300      | 83          | 5.4   | 0.0012       | 0.36      | 2400      | 82         | 28     | 22.4          | 16         | 6300       | 2300       | 1500      | 520        |
| 6      | ~20        | CL to LC     | 38                     | 0.30      | 120      | 85          | 6.6   | 0.0002       | 0.34      | 3600      | 110        | 23     | 33.7          | 24         | 6000       | 1500       | 1500      | 280        |
| 7      | ~50        | CL           | 35                     | 0.20      | 73       | 70          | 6.0   | 0.0012       | 0.85      | 2600      | 77         | 29     | 20.4          | 14         | 5900       | 1500       | 1400      | 620        |
| 8      | ~20        | CL to LC     | 38                     | 0.20      | 100      | na          | 5.2   | 0.0002       | 0.14      | 1400      | 74         | 25     | 19.5          | 11         | 7300       | 1700       | 820       | 890        |
| 17     | ~20        | gravelly LC  | 38                     | 0.90      | 300      | 51          | 5.7   | 0.0372       | 6.37      | 1900      | 60         | 18     | 22.2          | 16         | 3200       | 960        | 1000      | 99         |
| 25     | ~20        | CL to LC     | 38                     | 0.36      | 200      | 67          | 6.4   | 0.0014       | 1.88      | 3600      | 90         | 22     | 26.6          | 18         | 6700       | 1300       | 1900      | 790        |
| 27     | ~20        | SCL          | 30                     | 0.54      | 83       | 54          | 4.4   | 0.0542       | 3.15      | 520       | 27         | 19     | 13.6          | 9.1        | 5600       | 950        | 300       | 1300       |
| 28     | ~20        | LC           | 40                     | 0.42      | 53       | na          | 6.8   | 0.0040       | 6.30      | 7500      | 200        | 31     | 38.8          | 28         | 5200       | 1300       | 3300      | 170        |
| 29     | 1          | LC           | 40                     | 0.63      | 460      | 41          | 4.9   | 0.0400       | 2.25      | 830       | 33         | 18     | 15.1          | 8.7        | 4200       | 1400       | 270       | 34         |
| 6A     | 0          | CL           | 35                     | 0.10      | 90       | 107         | 4.3   | 0.0020       | 0.06      | 560       | 55         | 30     | 10.8          | 3.3        | 5900       | 1400       | 200       | 540        |
| 7A     | 0          | CL           | 35                     | <0.01     | 70       | 54          | 4.7   | 0.0004       | 0.04      | 800       | 78         | 22     | 14.3          | 4.8        | 5400       | 1500       | 67        | 1140       |
| 17A    | 0          | CL           | 35                     | 0.04      | 23       | na          | 4.6   | 0.0598       | 1.93      | 140       | 11         | 22     | 5.3           | 3.1        | 2600       | 780        | 61        | 150        |
| 25A    | 0          | CL           | 35                     | <0.01     | 43       | 62          | 4.3   | 0.0014       | 0.04      | 270       | 35         | 26     | 6.5           | 3.0        | 3000       | 1500       | 71        | 150        |
| 29A    | 0          | LC           | 40                     | 0.04      | 18       | na          | 5.0   | 0.0004       | 0.04      | 270       | 19         | 19     | 8.7           | 6.4        | 3400       | 1100       | 42        | nt         |

Strongly weathered soils on Triassic shale; gently sloping topography

| Site # | Farmed (y) | Texture | Clay content (g/100 g) | EC (ds/m) | Cl (mg/L) | DOC (mg/kg) | pHcs | Cdcs (mg/kg) | Cd (mg/kg) | Pt (mg/kg) | Zn (mg/kg) | Ct g/kg | ECEC cmol/kg | Excs mg/kg | Feox mg/kg | Alox mg/kg | Pox mg/kg | Mnox mg/kg |
|--------|------------|---------|------------------------|-----------|----------|-------------|-------|--------------|-----------|-----------|------------|--------|---------------|------------|------------|-------------|-----------|
| 5      | ~50        | CL      | 35                     | 0.20      | 90       | 40          | 6.4   | 0.0028       | 1.84      | 1900      | 72         | 16     | 20            | 16         | 6800       | 800        | 1300      | 2004       |
| 9      | ~50        | L (fat) | 28                     | 0.40      | 170      | 21          | 4.6   | 0.0274       | 1.41      | 1300      | 43         | 9.6    | 8.8           | 6.7        | 2500       | 660        | 830       | 120        |

Mildly weathered soils on a recent river terrace
| 10 | -100  | S    | 5   | 0.13 | 93   | 23   | 4.2  | 0.0086 | 0.19 | 680  | 30   | 8.0  | 3.0  | 1.5  | 1500  | 540  | 450  | 25    |
| 12 | -100  | LS or SL | 20  | 0.27 | 130  | 24   | 5.9  | 0.0088 | 1.95 | 1300 | 51   | 13   | 14   | 11   | 2800  | 600  | 840  | 130   |
| 13 | -100  | CL   | 35  | 0.54 | 220  | 35   | 4.4  | 0.0200 | 1.12 | 1100 | 80   | 17   | 13   | 9.1  | 5100  | 990  | 750  | 170   |
| 14 | -100  | L    | 25  | 0.39 | 250  | 24   | 4.1  | 0.0584 | 1.59 | 670  | 53   | 14   | 9.4  | 6.0  | 4500  | 820  | 470  | 120   |
| 15 | -100  | CL   | 35  | 0.20 | 140  | 19   | 4.9  | 0.0218 | 1.95 | 1100 | 63   | 17   | 15   | 11   | 4400  | 800  | 720  | 180   |
| 16 | -100  | SL to LS | 20  | 0.10 | 80   | 28   | 5.1  | 0.0130 | 1.12 | 890  | 54   | 11   | 11   | 7.5  | 2900  | 560  | 590  | 89    |
| 5A | 0     | CL   | 35  | 0.04 | 160  | 98   | 5.7  | 0.0004 | 0.12 | 610  | 87   | 31   | 18   | 12   | 5700  | 790  | 410  | 200   |
| 9A | 0     | L    | 25  | 0.10 | 50   | na   | 5.2  | 0.0046 | 0.67 | 800  | 78   | 29   | 18   | 12   | 3500  | 640  | 290  | nt    |
| 20 | ~50   | SL to L | 20  | 0.40 | 220  | 35   | 4.7  | 0.0084 | 0.49 | 1100 | 44   | 22   | 9.0  | 5.9  | 3900  | 1100 | 790  | 11    |
| 24 | ~50   | L with KS | 25  | 0.20 | 60   | 46   | 6.0  | 0.0012 | 0.35 | 1300 | 20   | 18   | 11   | 8.3  | 2400  | 1000 | 980  | 14    |
| 20A| 0     | LS   | 10  | <0.01| 68   | 119  | 4.3  | 0.0010 | 0.04 | 180  | 16   | 39   | 7.4  | 2.8  | 1800  | 1500 | 64   | 28    |
| 24A| 0     | LS   | 10  | <0.01| 70   | 118  | 4.3  | 0.0010 | 0.02 | 220  | 12   | 32   | 6.7  | 3.1  | 2500  | 1300 | 79   | 19    |

**Strongly weathered soils on Triassic interbedded shales and sandstone; hilly topography**

| 1  | ~100  | M-K S | 5   | 0.90 | 12   | 29   | 5.8  | 0.0016 | 0.24 | 990  | 44   | 19   | 5.6  | 4.3  | 1000  | 530  | 710  | 580   |
| 2  | <20   | M-K S | 5   | 0.06 | 50   | Na   | 5.6  | 0.0006 | 0.11 | 320  | 11   | 7.1  | 3.1  | 2.5  | 720   | 470  | 250  | nt    |
| 3  | ~50   | S    | 5   | 0.10 | 65   | 25   | 4.6  | 0.0034 | 0.24 | 1300 | 27   | 9.2  | 3.9  | 2.8  | 1100  | 650  | 1100 | 200   |
| 11 | ~50   | SL   | 15  | 0.10 | 90   | 22   | 5.9  | 0.0214 | 2.15 | 1100 | 34   | 5.5  | 7.8  | 5.0  | 1700  | 520  | 600  | 180   |
| 26 | ~20   | KSC  | 38  | 0.46 | 210  | 30   | 6.4  | 0.0008 | 0.39 | 1400 | 28   | 9.3  | 12   | 8.7  | 2200  | 690  | 870  | 640   |
| 11A| 0     | SL   | 15  | 0.08 | 50   | na   | 4.7  | 0.0024 | 0.07 | 160  | 13   | 16   | 4.0  | 2.4  | 1200  | 510  | 57   | 870   |

**Moderately weathered soils on a late Pleistocene river terrace**
Strongly weathered soils on Triassic sandstone and sandy early Pleistocene alluvium

<p>| | | | | | | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>50</td>
<td>S</td>
<td>5</td>
<td>&lt;0.01</td>
<td>28</td>
<td>18</td>
<td>4.5</td>
<td>0.0114</td>
<td>0.22</td>
<td>880</td>
<td>16</td>
<td>8.5</td>
<td>2.1</td>
<td>0.89</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
<td>S</td>
<td>5</td>
<td>&lt;0.01</td>
<td>30</td>
<td>33</td>
<td>5.8</td>
<td>0.0026</td>
<td>0.31</td>
<td>920</td>
<td>17</td>
<td>13</td>
<td>5.4</td>
<td>4.7</td>
</tr>
<tr>
<td>21</td>
<td>50</td>
<td>KS to KLS</td>
<td>8</td>
<td>0.10</td>
<td>28</td>
<td>19</td>
<td>4.6</td>
<td>0.0160</td>
<td>0.56</td>
<td>910</td>
<td>12</td>
<td>11</td>
<td>3.3</td>
<td>2.2</td>
</tr>
<tr>
<td>22</td>
<td>50</td>
<td>KS</td>
<td>5</td>
<td>&lt;0.01</td>
<td>25</td>
<td>20</td>
<td>4.5</td>
<td>0.0048</td>
<td>0.14</td>
<td>450</td>
<td>8</td>
<td>11</td>
<td>1.9</td>
<td>1.3</td>
</tr>
<tr>
<td>23</td>
<td>20</td>
<td>KS + clay</td>
<td>8</td>
<td>0.10</td>
<td>23</td>
<td>28</td>
<td>5.2</td>
<td>0.0104</td>
<td>0.68</td>
<td>450</td>
<td>12</td>
<td>14</td>
<td>5.9</td>
<td>4.0</td>
</tr>
<tr>
<td>18A</td>
<td>0</td>
<td>S</td>
<td>5</td>
<td>&lt;0.01</td>
<td>25</td>
<td>45</td>
<td>4.3</td>
<td>0.0016</td>
<td>0.02</td>
<td>17</td>
<td>5</td>
<td>13</td>
<td>1.0</td>
<td>0.24</td>
</tr>
<tr>
<td>19A</td>
<td>0</td>
<td>LS</td>
<td>10</td>
<td>&lt;0.01</td>
<td>25</td>
<td>78</td>
<td>4.3</td>
<td>0.0012</td>
<td>0.02</td>
<td>31</td>
<td>5</td>
<td>20</td>
<td>1.9</td>
<td>0.42</td>
</tr>
</tbody>
</table>

†The methods are described in full in Section 3.3, briefly: the soil texture abbreviations are: S = sand, KS = coarse sand, L, loam, LS = loamy sand, SL = sandy loam, CL = clay loam, SC = sandy clay, LC = loamy clay, and MC = medium clay; approximate clay content was estimated after Northcote (1979); EC was measured in 1:5 (w/v) suspensions in water; DOC, pH\text{Ca} and Cd\text{Ca} were measured on 1:5 (w/v) suspensions in 10 mM CaCl$_2$; Cd and P$_t$ were extracted by reverse \textit{aqua regia}; C$_t$ was measured as CO$_2$ after combustion; ECEC is the sum of exchangeable Na, K, Ca, Mg and Al; Fe$_{ox}$, Al$_{ox}$ and P$_{ox}$ are oxalate extractable Fe, Al and P; and M$_{nq}$ is Mn reducible by hydroquinone.

Nt = not tested due to insufficient sample.
APPENDIX 2. LIST OF MANUSCRIPTS THAT ARE EITHER PUBLISHED OR IN PREPARATION

