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THE FATE OF LEAD IN SOILS CONTAMINATED WITH LEAD SHOT

A thesis

submitted in partial fulfilment

of the requirements for the Degree of

Doctor of Philosophy

at

Lincoln University

by

C.P. Rooney

Lincoln University

2002
In memory of my Grandmothers:

Vivian Dunkley (née Canning)  
1911 – 2001

Mima Rooney (née Kofoed)  
1909 – 2001

The future is not completely beyond our control.
It is the work of our own hands.

Robert F. Kennedy
Abstract of a thesis submitted in partial fulfilment of the requirements for the Degree of Ph.D.

THE FATE OF LEAD IN SOILS CONTAMINATED WITH LEAD SHOT

by C.P. Rooney

A study of the interactions between lead (Pb) shot and the soil, and the fate of Pb at shooting ranges was conducted in order to address the lack of research on these issues at the current time. Surveys of the spatial and vertical distributions of Pb in the soil were carried out at selected Canterbury clay target shooting ranges. These confirmed that maximum soil Pb concentrations at New Zealand ranges are comparable to those reported overseas, which commonly exceed 10,000 mg kg⁻¹, while in New Zealand the guideline limit for Pb in soil is 300 mg kg⁻¹. There was evidence of Pb movement from the contaminated surface-soil zone into underlying soil. While sufficient Pb had been solubilised from the Pb shot to cause substantially elevated soil Pb concentrations, the majority (68-99%) of the total Pb at each site was present as intact Pb shot >2 mm.

An incubation experiment was designed to assess the rate of oxidation of Pb shot and subsequent transfer of Pb to the soil under various environmental conditions. The onset of Pb shot oxidation and subsequent development of the corrosion crust surrounding individual Pb pellets was relatively rapid. Corrosion products in the corrosion crust and precipitated directly onto the soil solid phase readily dissolved over a soil pH range of approximately 4.5-7. Soil solution and fine earth (<1 mm) Pb concentrations became substantially elevated within 6 months, and there was evidence of the development of a quasi-equilibrium within 24 months. Soil pH, moisture content and temperature impacted on these processes.

The data generated by the incubation experiment was used to predict the speciation of Pb in soil solutions using GEOCHEM-PC modelling software. Mechanisms of control of Pb solubility were deduced from equilibrium solubility diagrams constructed with the aid of the speciation calculations. The solubility diagrams were strongly suggestive of Pb solubility regulation by the pH-dependent solubility of corrosion products associated with the corrosion crust or soil solid phase. The dominant mineral controlling Pb solubility appears to be PbCO₃. Thus, the presence of Pb shot in the soil alters the control of solubility from...
Abstract

adsorption mechanisms in uncontaminated soil to precipitation-dissolution mechanisms in contaminated soil. High soil pH reduces, but does not prevent, the solubility of Pb shot corrosion products.

A lysimeter leaching experiment, using intact soil cores collected from three shooting ranges, was carried out to assess the potential for Pb mobility. Leachates from contaminated soil contained elevated Pb concentrations which were sustained over multiple leaching events. Solubility diagrams confirmed that Pb mobilisation was caused by the dissolution of readily soluble Pb shot corrosion products. A large pool of potentially soluble Pb is generated by the readily soluble fine earth Pb and Pb minerals in the corrosion crust. There was a close relationship between leachate Pb concentrations and soluble organic carbon dynamics, indicating the importance of organic complexation on Pb mobility. The results indicate there is a high risk of chronic Pb leaching from contaminated shooting ranges. Natural attenuation by subsoil is expected to delay movement of Pb down the profile, but Pb shot deposition onto young soils with little attenuation capacity could generate substantial movement of Pb.

Management options were considered for soil contaminated with Pb shot. Phosphate addition to Pb-contaminated soil aims to precipitate Pb as relatively insoluble pyromorphite minerals. This study confirmed the effectiveness of phosphate immobilisation of Pb in a preliminary incubation study using fine earth with elevated Pb concentrations. Lysimeters were then collected from three shooting ranges and subjected to leaching following the application of phosphate. Where molar P:Pb ratios were sufficient, substantial reduction in the concentrations of Pb in leachates was observed, confirming that phosphate immobilisation could be used at shooting ranges to reduce Pb mobility. In addition to reducing the mobility of soluble Pb, phosphate addition has the potential to encourage bulk transformations of soluble Pb minerals in the corrosion crust and soil into much less soluble pyromorphite compounds. The use of phosphate immobilisation will be limited by soil vulnerability to phosphorus loss, and environmental sensitivity to the eutrophic effect of phosphorus.

The results of this thesis contribute valuable information on the fate of Pb at CTS ranges. With this new knowledge, the effectiveness of range and contamination management techniques currently suggested in the literature is discussed.

**KEYWORDS**

Lead shot, shooting ranges, soil contamination, lead shot transformation, lead carbonate, lead mobility, phosphate immobilisation, range management.
Name of Candidate: Corinne P. Rooney

DECLARATION

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- which sections have been submitted, which have been accepted and which have appeared;
- which journals they have been submitted to;
- who are the co-authors.

Candidate _______________ Date 12/8/2002

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The data presented in Chapter 4 has been published within:

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Selected data presented in Chapter 4 has also been published as a paper:

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Rooney, C.P. and McLaren, R.G. 2001

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<td>Breakthrough curve(s)</td>
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<td>CTC(s)</td>
<td>Clay Target Club(s)</td>
</tr>
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<tr>
<td>SOC</td>
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</tr>
<tr>
<td>Fine earth</td>
<td>Soil &lt;1mm (Pb shot removed)</td>
</tr>
<tr>
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</tr>
</tbody>
</table>
Chapter One

General Introduction

1.1 Project Rationale

Lead (Pb) has been used frequently by humans from early times to the present day. The beneficial physical properties of the metal have promoted its mining, smelting and various uses, including weather-proofing of buildings, water pipelines, cooking vessels and as an additive to wine. More recent uses include ammunition, pigments for paints, lead-acid batteries and petrol additives. This anthropogenic use of Pb has led to recurring environmental contamination in developing and industrialised areas of the world. Contamination of soil with Pb from the main recognised sources is well documented: mining and smelting, automotive emissions, Pb-based paints, and industrial activity. Recognition as an environmental contaminant has led to the removal of Pb from paint products and petrol.

Accumulation of Pb in surface soils impacts on environmental health and can affect food quality and human health. The diversity of the biological population in soils may be affected (Kabata-Pendias and Pendias, 1992), and biochemical processes including soil organic matter breakdown (Kabata-Pendias and Pendias, 1992) and nutrient cycling (Davies, 1990; Lorenz et al., 1992; Marzadori et al., 1996) have been shown to be influenced by high soil Pb concentrations. Evidence of the impact of elevated soil Pb concentrations on plant growth is inconsistent, but the contribution of plant-Pb to elevated levels of Pb in the food chain is significant. Movement of Pb from contaminated sites may occur via dust, lateral and vertical drainage into surface- and ground-water, plant uptake and uptake by animals and migratory birds (Castrale, 1989). Pica (soil ingestion) is a common cause of Pb poisoning in children. Lead accumulates in the bones and kidneys of humans and other animals, and is carried in red blood cells (Howard, 1985). Poisoning can impact on the nervous system, affecting development and behaviour.
1. Introduction

Relatively limited attention has been given to the contamination of soil by Pb shot deposition onto land. Clay target shooting (CTS) is a popular recreational and sporting activity around the world and Pb is the material of choice for shotgun pellets due to ballistic qualities, availability and cost (Soulsby, 1998). It has become apparent that shooting ranges in dryland environments may be highly contaminated with Pb. Soil containing elevated levels of Pb have been reported at shooting ranges in Scandinavia (Jørgensen and Willems, 1987b; Tanskanen et al., 1991; Manninen and Tanskanen, 1993), England (Mellor and McCartney, 1994; Merrington and Alloway, 1995), Germany (Fahrenhorst and Renger, 1990; Braun et al., 1997), and the United States of America (Murray et al., 1997; Edwards et al., 1999). At CTS sites there is a definable area in which spent Pb shot is deposited, and the Pb shot is readily visible on the soil surface (Plate 1.1). Exposed to soil and atmospheric chemical processes, the Pb shot develops a crust of oxidised Pb compounds which interact with the soil, causing soil Pb concentrations to become elevated.

Plate 1.1. Lead shot deposition on the soil surface of the Motukarara CTC.
The New Zealand Clay Target Association lists 91 clay target shooting clubs in New Zealand (New Zealand Clay Target Association Incorporated, 2001). Clay target shooting is also offered as a recreational activity to clients at various luxury accommodation lodges around New Zealand. Table 1.1 summarises information available on the number of ranges in the country. In addition, a number of businesses throughout the country include CTS in commercial adventure tourism activities. The Moving Target franchises operate with mobile trap units that may be set up anywhere with suitable space.

<table>
<thead>
<tr>
<th>Number of clay target shooting clubs</th>
<th>91</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of individual trap ranges</td>
<td>228</td>
</tr>
<tr>
<td>Number of individual skeet ranges</td>
<td>116</td>
</tr>
<tr>
<td>Number of individual sporting fields</td>
<td>19</td>
</tr>
</tbody>
</table>

Luxury lodges offering on-site clay target shooting | 6

(Sources: Lobb et al., 1997; New Zealand Clay Target Association Incorporated, 2001; Trips and Travel Limited, 2002)

The Canterbury Regional Council has identified 18 sites in Canterbury which are, or have been, used by CTS clubs for varying durations (Lobb et al., 1997). Many sites are significantly contaminated with Pb. Reports of live pigeon shooting matches in issues of The Press circa 1870 confirm the long history of pigeon and clay target shooting in Canterbury. In this region and throughout New Zealand, many clay target shooting sites are located on, and/or shoot onto, land used for agricultural production. This appears to be a continuation of historical practice, where paddocks were offered as sites to hold pigeon shooting matches (News of the Day, 1876). Decades of shooting at the present sites has led to accumulation of Pb shot, and subsequent elevation of soil Pb concentrations on or near the soil surface. The high loadings of Pb pose a risk to environmental health, especially if there is potential for movement of Pb from the sites, however little is known of the fate of the Pb at CTS ranges.
1. Introduction

The effect Pb shot accumulation on agricultural land is illustrated by elevated plant Pb concentrations measured in plants growing at CTS ranges (Manninen and Tanskanen, 1993; Mellor and McCartney, 1994) and growing in soil collected from a CTS range (Rooney et al., 1999). There have been cases of cattle poisoned by exposure to soil-Pb or Pb shot derived from shooting activities in Ireland (Rice et al., 1987), Germany (Braun et al., 1997) and New Zealand (The Dominion, 1978; G.B. Daivs, personal communication, 22 August 1997). Spent Pb shot has also caused poisoning of mourning doves (upland game birds) feeding in fields used for shooting in the US (Castrale, 1989), and elevated tissue Pb concentrations in small mammals at a CTS site in the US (Stansley and Roscoe, 1996).

The high loadings of Pb present at clay target shooting sites pose a risk to environmental health and warrant further investigation, as little is known of the fate of Pb at such sites. The objectives of this experimental study were:

- To improve the understanding of the behaviour of Pb in soils;
- To quantify the rate of transformation of metallic Pb shot into ‘soil’ Pb compounds under New Zealand conditions;
- To use a fractionation technique to identify the forms in which transformed Pb exists;
- To establish the potential for leaching of Pb in relation to soil properties;
- To provide information for the development of possible management or remedial strategies for contaminated sites.
1. Introduction

1.2 Clay Target Shooting

Clay target shooting is an outdoor recreational and competitive sport which involves participants firing shotguns containing cartridges of spherical pellets of Pb to break moving targets launched into the air. It is different to the sport of target shooting, which involves the use of rifles and pistols to shoot at stationary, bulls-eye type targets. Clay target shooting was developed from live-bird shooting that was popular in late 18th century England and subsequently in North America, where scarcity of live pigeons and protests about the shooting of live birds prompted the creation artificial targets made from kiln-fired clay. Modern clay targets are made from a mixture of lime and pitch (Baer et al., 1995), and the modern-day trap is a spring-loaded throwing arm which can throw targets for distances of up to 135 m. In the past, each ammunition cartridge contained a maximum of 1¼ ounces (32 g) of spherical Pb pellets, or shot. This weight has now been reduced to 1 ounce (28 g).

Clay target shooting involves many variations of the sport in the way that targets are presented to the shooters, such as changes in the height and speed of the target, the direction of flight, and the location of stations where shooters stand. The more common disciplines are Trap, Skeet and Sporting Clays.

Trap shooting, also referred to as ‘down the line’ shooting (DTL), involves targets launched from a single traphouse within a horizontal spread of approximately 90° (Lobb et al., 1997). A shooter successively shoots at the launched targets from different positions in five lanes positioned in an arc of about 40° behind the traphouse (Plate 1.2). Generally a minimum of 25 targets are launched in a shooter’s round. A second shot is usually fired at a target that is not broken with the first shot. The targets used commonly measure 11 cm in diameter and weigh about 100 g, and the size of Pb shot is usually ‘No. 7.5’ (2.4 mm diameter). The Pb shot appears to be deposited directly in front of the trap for a distance of some 250 m (Rooney et al., 1999).
1. Introduction

Skeet shooting, also referred to as ‘across the line’ shooting, involves shooting two clay targets launched from two separate traps in towers located about 40 m apart. The targets are released alternately or simultaneously along intersecting flight paths and shooters stand in a series of 8 shooting stations (Figure 1.1). A smaller shot size (‘No. 8’ to ‘No. 9’; 2.3 to 2.0 mm diameter) is used for skeet shooting so that there is a more dense pattern of shot dispersal in flight. There is some evidence that the Pb shot may be deposited mainly in two areas approximately 80 m beyond the skeet towers in line with the intersecting trajectories of the targets (Rooney et al., 1999).

Figure 1.1. Diagrammatic layout of a skeet shooting field.
1. Introduction

Sporting Clays is a relatively new discipline which simulates actual field hunting by combining different target flight speeds and angles and different target sizes. The targets might be crossing, climbing, incoming, outgoing, streaking high overhead, flying low, or any combination of the above. The area of Pb shot deposition from Sporting Clays is less well-defined and a predictable pattern of deposition is unlikely due to the use of mobile traps and target flight variations.
1.3 Thesis Structure

The thesis structure is summarised in Figure 1.2.

Chapter 2 presents a review of literature pertinent to Pb in soil and the current research published on Pb shot contamination of soil.

Chapter 3 details general analytical methods used throughout the experiments.

Chapter 4 describes a survey of Pb contamination at selected Canterbury clay target clubs.

Chapter 5 is concerned with the transformation rate of Pb shot in contact with soil.

Chapter 6 determines the potential for leaching of Pb from contaminated soils at CTS ranges.

Chapter 7 assesses the use of amendments for the mitigation of the effects of Pb at shooting ranges, firstly in a review of literature pertaining to the topic of phosphate amendment of Pb-contaminated soil, followed by experimental work.

Chapter 8 contains a discussion of the implications for CTS ranges and range management of the information gained from the experimental work. Issues requiring future research are identified.
Chapter 2

T

hesis summary, general discussion, conclusions, and recommendations

Chapter 8

Effect of Pb shot deposition on the distribution of elevated soil Pb concentrations at CTS ranges

Chapter 4

Potential for Pb mobility

Chapter 6

Management strategies to reduce Pb mobility

Chapter 7

Thesis summary, general discussion, conclusions, and recommendations

Chapter 8

Nature and rate of transfer of Pb from pellets to soil

Chapter 5

Effects of elevated soil Pb concentrations

Figure 1.2 Overall thesis structure (Fate of Lead in Soils Contaminated with Lead Shot)
2.1 Release of Lead into the Environment

The present amount of Pb in the environment is a result of release by natural processes and a long history of anthropogenic use of Pb. Lead is released naturally into the environment by way of weathering rocks, ash from bush fires, wind-borne soil, volcanic activity, and sea-spray (Markus and McBratney, 2000), however natural sources supply approximately only 1% of the present-day atmospheric Pb burden (Royal Society of New Zealand, 1986). Anthropogenic use of the metal for more than 5000 yrs (Table 2.1) has caused substantial change to the natural global biogeochemical cycle of Pb, and has lead to widespread pollution of the atmosphere, soils, water bodies and sediments. The sources of anthropogenic Pb most commonly recognised to have contributed to this pollution are primary metal production (mining and smelting), industrial sites where Pb is processed or products containing Pb are synthesised, automobile exhaust emissions, Pb pigments in house-paints, and horticultural pesticides.

Table 2.1. Examples of anthropogenic uses of Pb

<table>
<thead>
<tr>
<th>Ancient uses</th>
<th>Subsequent and/or present uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water pipes and ducting</td>
<td>Ammunitions</td>
</tr>
<tr>
<td>Lining cooking vessels</td>
<td>Paint pigments</td>
</tr>
<tr>
<td>Weather-proofing buildings</td>
<td>Pesticides, bird repellents</td>
</tr>
<tr>
<td>Medicinal and cosmetic uses</td>
<td>Colouring pottery and glassware</td>
</tr>
<tr>
<td>Shot for sling-shots used in ancient warfare</td>
<td>Telephone and power cable sheathing</td>
</tr>
<tr>
<td>Writing slates and pencils</td>
<td>Pb-based bearings</td>
</tr>
<tr>
<td>Sinkers and anchors</td>
<td>Petrol additive</td>
</tr>
<tr>
<td>Coinage</td>
<td>Pb-acid batteries</td>
</tr>
<tr>
<td>Wine additives</td>
<td></td>
</tr>
</tbody>
</table>

(Sources: Burns, 1948; Adriano, 1986; Markus and McBratney, 2000).
The current global rate of production of Pb is approximately $5 \times 10^7$ t year$^{-1}$ (Markus and McBratney, 2000). Calculations and estimates of maximum anthropogenic Pb emissions have been reducing since the 1980's, for example, $3.76 \times 10^5$ t year$^{-1}$ in 1983 (Nriagu and Pacyna, 1988) and $2.09 \times 10^5$ t year$^{-1}$ in 1989 (Pacyna et al, 1995 in Markus and McBratney, 2000). Approximately 70% of the 1989 value is derived from the use of leaded petrol, and therefore Pb emissions will continue to reduce as further countries decrease the use of leaded petrol.

2.1.1 Background soil lead concentrations

Much has been published on the background concentrations of Pb in soil. A range of values are given for the background concentration of Pb in surface soils, as they are influenced by local, regional and global anthropogenic contributions as well as naturally occurring sources of Pb from parent materials.

The range of mean Pb concentrations in rocks is approximately 3-24 mg kg$^{-1}$ for igneous rocks and 6 to 30 mg kg$^{-1}$ for sedimentary rocks (Markus and McBratney, 2000). Similar ionic radii leads to Pb substituting isomorphically for potassium (K), barium (Ba) and calcium (Ca) in minerals, so that Pb is commonly found in feldspars, micas, phosphate minerals and plumbogummite minerals (Nriagu, 1978; McLaughlin et al., 1996).

Pristine soils probably no longer exist with respect to Pb, therefore the lowest background Pb concentrations are now found in ‘remote’ soils – soils some distance from anthropogenic sources of Pb and therefore under only slight influence from such inputs. Lead concentrations quoted for remote soils are generally in the range 10-30 mg kg$^{-1}$ (Davies, 1990). The widespread low-level Pb pollution from anthropogenic activities has resulted in ‘normal’ background soil Pb concentrations in the range 10-100 mg kg$^{-1}$ (Davies, 1990; McLaughlin et al., 1996; Breckenridge and Crockett, 1998; Markus and McBratney, 2000). Naturally elevated soil Pb concentrations up to 45,000 mg kg$^{-1}$ can exist in areas containing Pb-bearing ore deposits (Zimdahl and Arvik, 1973; Royal Society of New Zealand, 1986).

In New Zealand, rural soils may be considered to be ‘remote’ soils, with background concentrations of Pb only slightly elevated by anthropogenic sources. Nriagu (1978) lists the mean soil Pb concentration in New Zealand as 16 mg kg$^{-1}$. Background soil Pb concentrations of approximately 20 mg kg$^{-1}$ have been measured in the Te Aroha area unaffected by ore deposits (Ward et al., 1977a). Rooney et al. (1999) determined background Pb concentration in the Leeston area to be <10 mg kg$^{-1}$. 
2. Literature Review

2.1.2 Elevation of soil lead concentrations

Soil is a major sink for Pb released into the environment. Approximately 60-70% of annual global atmospheric Pb emissions are estimated to be deposited onto soil (Nriagu and Pacyna, 1988; Nriagu, 1989; McGrath, 1997 in Markus and McBratney, 2000). Historic or current inputs of Pb to soil have occurred from a variety of sources including mining and smelting, the use of petrol containing Pb additives, industrial activities, paint additives, and the application of biosolids, fertilisers and agrochemicals. There is a large amount of literature covering Pb pollution from various individual sources which will not be covered in this review. Typical soil Pb concentrations that result from pollution are summarised in Figure 2.1. The divisions are somewhat arbitrary, but the abundance of literature covering instances of soil Pb contamination indicates the concentrations quoted in Figure 2.1 are common.

![Figure 2.1](image-url)  
Figure 2.1. Typical concentrations of Pb in soil contaminated according to land use (adapted from Markus and McBratney, 2000).

Reductions in the use of leaded petrol have caused some reduction in atmospheric Pb deposition onto soil in recent decades. However, calculations by Nicholson et al. (1998) show that atmospheric deposition continues to be a significant source of Pb input into agricultural land in England and Wales (Table 2.2). Hird et al. (1996, in Nicholson et al., 1998) found that the average rate of atmospheric deposition for Pb at 29 rural sites in England and Wales was 33 g ha⁻¹ yr⁻¹. Alloway (1999) obtained a mean atmospheric deposition rate of 42.2 g Pb ha⁻¹ yr⁻¹ for 34 remote sites in England and Wales. A further site downwind from a large lead-zinc smelter recorded Pb deposition greater than those at the remote locations by a factor of 35. Literature compiled from European and North American studies by Bergkvist et al. (1989) showed that deposition rates over 100 g Pb ha⁻¹ yr⁻¹ have commonly been recorded. Gray et al. (2001) recorded a mean atmospheric Pb deposition rate of 19.7 g ha⁻¹ during a 12 month monitoring period at 7 rural New Zealand sites.
Table 2.2. Annual Pb input (t) from various sources to agricultural land in England and Wales (from Nicholson et al., 1998).

<table>
<thead>
<tr>
<th>Source</th>
<th>Annual Pb Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric deposition</td>
<td>365</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>95</td>
</tr>
<tr>
<td>Animal manures</td>
<td>52</td>
</tr>
<tr>
<td>Fertilisers and lime</td>
<td>13</td>
</tr>
<tr>
<td>Irrigation water</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Industrial by-product wastes</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Agrochemicals</td>
<td>0</td>
</tr>
</tbody>
</table>

2.1.3 Guidelines for soil protection and risk assessment

Regulatory limits and guidelines for Pb in soil are ubiquitous. The Dutch soil protection guidelines, first drawn up in 1983, are well recognised. These have been refined a number of times, and now take into account the amount of clay and organic matter in soils. The current values that relate to soil Pb contamination are: a reference/target value of 85 mg Pb kg⁻¹ soil (for soil with 25% clay and 10% organic matter), 290 mg kg⁻¹ for ecotoxicity intervention, and 300 mg kg⁻¹ for intervention where risk is posed to human health (Smit 1998, in McLaughlin et al., 2000). Further refining and the consideration of soil type and land use of agricultural soils has lead to the desirable limit for Pb in agricultural soil being 150-200 mg kg⁻¹ (Smit 1998, in McLaughlin et al., 2000).

The New Zealand Ministry for the Environment adopted the guidelines for the assessment and management of contaminated sites developed by the Australian and New Zealand Environment and Conservation Council and the National Health and Medical Research Council (ANZECC/NHMRC, 1992). These guidelines are largely derived from the Dutch regulations (Moen 1988, in McLaughlin et al., 2000), and are based on threshold levels for phytotoxicity and unacceptable residue levels. The guideline level established by ANZECC for Pb in soil is 300 mg Pb kg⁻¹ soil. This defines the concentration of soil Pb at which further investigation of a contaminated site is recommended. Any further action such as remediation, or restrictions on use or access is to be determined after considering site-specific data including land use, and soil and contaminant characteristics.
2.2 Contamination of Soil by Lead Shot

The risks of Pb shot deposition in wetland environments (waterfowl Pb toxicosis, elevated sediment Pb concentrations) have been recognised for some decades. It has also become apparent that the deposition of Pb shot at shooting ranges in dryland environments routinely leads to substantial soil Pb contamination. Elevated soil Pb concentrations have been reported in every study of shooting ranges that has analysed soil for Pb (Table 2.3). Jørgensen and Willems (1987b) and Rooney et al. (1999) have shown that a relatively small proportion of the Pb shot at shooting ranges has oxidised and become associated with the soil solid phase. This indicates that the substantially elevated soil Pb concentrations, commonly >10,000 mg Pb kg\(^{-1}\), reported at shooting ranges (Table 2.4) are only the tip of the iceberg. Murray et al. (1997) and Rooney et al. (1999) have demonstrated that there is a definable area where elevated Pb concentrations occur as a result of Pb shot deposition at CTS ranges.

Mellor and McCartney (1994) calculated that approximately 6000 t of lead shot was deposited on the soil surface by CTS activities in the United Kingdom (UK). Based on information for Canterbury CTS ranges (Lobb et al., 1997), a conservative estimate of the proportion of UK CTS ranges situated on agricultural land would be 50%. Even at this level, input of lead shot far outweighs all other sources of Pb quantified by Nicholson et al. (1998; Table 2.2). This is also likely to be the case in New Zealand, where annual deposition rates of Pb shot at individual Canterbury CTS ranges were estimated to be between 0.2 and 9.8 t yr\(^{-1}\) (Lobb et al., 1997).

New Pb pellets deposited onto the soil commonly contain approximately 97% metallic Pb, 2% antimony (Sb) and <2% arsenic (As), and sometimes contain <0.5% nickel (Ni) (Jørgensen and Willems, 1987b; Tanskanen et al., 1991). Lead shot with a mottled appearance, caused by light grey, white, and brown coatings, is invariably reported at shooting ranges (Jørgensen and Willems, 1987b; Lin et al., 1995; Uren et al., 1995; Murray et al., 1997). These coatings effectively form a ‘weathering crust’ around the pellets, and have been referred to as transformation products or crust material. Lead in soil samples collected from shooting ranges is found as metallic Pb in the pellets, as Pb minerals in the crust covering the pellets, and as extractable Pb associated with the soil solid phase. There are essentially two stages in the transformation of Pb shot into soil-Pb compounds:

(i) the initial weathering of the Pb shot to form transformation products; and
(ii) the interaction of the transformation products with the soil solution and soil colloids.
Table 2.3. Summary of the concentration of Pb (mg kg\(^{-1}\)) and density of Pb shot (kg shot m\(^{-2}\)) at shooting ranges as reported by various authors.

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Maximum total soil Pb †</th>
<th>Maximum EDTA-extractable soil Pb †</th>
<th>Maximum Pb shot density</th>
<th>Depth of soil analysed (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jørgensen and Willems (1987b)</td>
<td>–</td>
<td>1,000</td>
<td>0.4</td>
<td>0 - 50</td>
</tr>
<tr>
<td>Castrale (1989)</td>
<td>–</td>
<td>–</td>
<td>≈ 2.3 *</td>
<td>–</td>
</tr>
<tr>
<td>Fahrenhorst and Renger (1990)</td>
<td>≈ 1,000</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tanskanen et al. (1991)</td>
<td>10,500</td>
<td>–</td>
<td>22.35</td>
<td>0 - 70</td>
</tr>
<tr>
<td>Stansley et al. (1992)</td>
<td>–</td>
<td>–</td>
<td>≈ 10.4 \times 10^3 *</td>
<td>0 - 75</td>
</tr>
<tr>
<td>Engström 1993, in Lin (1996)</td>
<td>24,500</td>
<td>–</td>
<td>–</td>
<td>0 ≤ 100</td>
</tr>
<tr>
<td>Manninen and Tanskanen (1993)</td>
<td>54,000</td>
<td>52,000</td>
<td>–</td>
<td>0 - 40</td>
</tr>
<tr>
<td>Mellor and McCartney (1994)</td>
<td>10,620</td>
<td>–</td>
<td>≈ 534 *</td>
<td>0 - 150</td>
</tr>
<tr>
<td>Lin et al. (1995)</td>
<td>3,400</td>
<td>475</td>
<td>–</td>
<td>0 - 60</td>
</tr>
<tr>
<td>Merrington and Alloway (1995)</td>
<td>7,390</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Siepel (1995)</td>
<td>–</td>
<td>–</td>
<td>1.01</td>
<td>0 - 50</td>
</tr>
<tr>
<td>Uren et al. (1995)</td>
<td>31,200</td>
<td>–</td>
<td>2.3 \times 10^4</td>
<td>0 - 50</td>
</tr>
<tr>
<td>Stansley and Roscoe (1996)</td>
<td>75,000</td>
<td>–</td>
<td>≈ 10.4 \times 10^3 *</td>
<td>0 - 75</td>
</tr>
<tr>
<td>Merrington and Alloway (1997)</td>
<td>8,100</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Murray et al. (1997)</td>
<td>987</td>
<td>–</td>
<td>–</td>
<td>50 - 150</td>
</tr>
<tr>
<td>Rooney et al. (1999)</td>
<td>–</td>
<td>8,300</td>
<td>–</td>
<td>0 - 75</td>
</tr>
<tr>
<td>Bruell et al. (1999)</td>
<td>420</td>
<td>–</td>
<td>–</td>
<td>0 - 900</td>
</tr>
<tr>
<td>Chen et al. (2001a)</td>
<td>15,368</td>
<td>83 pellets 100 g soil(^{-1})</td>
<td></td>
<td>0 - 10</td>
</tr>
</tbody>
</table>

† Lead shot removed
* Estimated from data provided, on the basis of 1 pellet = 28 g
2. Literature Review

2.2.1 Initial transformations of lead shot

Various authors have analysed the mineralogy of crust material on Pb shot by x-ray diffraction (XRD). Results consistently show a predominance of Pb$_3$(CO$_3$)$_2$(OH)$_2$ (hydrocerussite) and minor amounts (<10%) of PbCO$_3$ (cerussite), PbSO$_4$ (anglesite), PbO (massicot) and PbO$_2$ (plattnerite) (Jørgensen and Willems, 1987b; Fahrenhorst and Renger, 1990; Tanskanen et al., 1991; Lin et al., 1995; Lin, 1996; Murray et al., 1997). Fahrenhorst and Renger (1990) also found pyromorphite (Pb$_5$(PO$_4$)$_3$X$^-$, where X$^-$ may be OH$^-$, chloride (Cl$^-$), fluoride (F$^-$) or nitrate (NO$_3^-$) ions) in crust material.

Pellet crust morphology has only been studied to any great extent by Lin (1996). Electron microprobe analysis (EMPA) identified two concentric layers of crust material: a light grey-coloured, discontinuous inner layer of between 10 and 30 µm width, and a darker grey coloured, continuous outer layer of between 50 and 150 µm width. The Pb concentration of the corroded pellets was in the order, pellet core (≈ 97% Pb) > inner layer (88-92% Pb) > outer layer (77-84% Pb), indicating that the crust material consisted of secondary Pb minerals with lower Pb stoichiometry. When Lin compared this data to the stoichiometry of known Pb minerals (Table 2.4), the Pb content of the two layers suggested the presence of PbO and PbO$_2$ in the inner layer, and Pb$_3$(CO$_3$)$_2$(OH)$_2$ in the outer layer. X-ray diffraction analysis of the overall crust provided a semi-quantitative estimation of mineralogy: 75-80% Pb$_3$(CO$_3$)$_2$(OH)$_2$, ≈10% PbSO$_4$, 5-10% PbO, 5% PbCO$_3$ and <5% PbO$_2$. This provided further evidence that Pb$_3$(CO$_3$)$_2$(OH)$_2$ was the dominant mineral in the outer layer of the crust, which represents about 80% of the total crust volume. Considering the Pb content of PbO.PbCO$_3$ and PbCO$_3$ (Table 2.4), it is possible these minerals could also have contributed to the lower Pb content of the outer layer. Jørgensen and Willems (1987b) observed a similar reduction in the Pb content of crust material. The authors measured 68-73% Pb in the crust material of pellets from four sites, which compares well with the content of a number of possible Pb minerals (Table 2.4).
Table 2.4. Content of Pb in important Pb minerals by stoichiometry (from, Jørgensen and Willems, 1987b; Lin et al., 1995).

<table>
<thead>
<tr>
<th>Pb mineral</th>
<th>Molecular formula</th>
<th>% Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plattnerite</td>
<td>PbO₂</td>
<td>92</td>
</tr>
<tr>
<td>Massicot</td>
<td>PbO</td>
<td>86</td>
</tr>
<tr>
<td>Anglesite</td>
<td>PbSO₄</td>
<td>68.3</td>
</tr>
<tr>
<td>Lead oxide carbonate</td>
<td>PbO·PbCO₃</td>
<td>84.5</td>
</tr>
<tr>
<td>Hydrocerussite</td>
<td>Pb₃(CO₃)₂(OH)₂</td>
<td>80.1</td>
</tr>
<tr>
<td>Cerussite</td>
<td>PbCO₃</td>
<td>77.5</td>
</tr>
</tbody>
</table>

Uren et al. (1995) reported much thinner coatings of transformation products (up to 20 µm thick) on Pb pellets, and scanning electron microprobe (SEM) analysis of pellets showed the presence of the soil-derived elements aluminium (Al), calcium (Ca), iron (Fe), potassium (K), silicon (Si) and titanium (Ti). Presumably these elements were associated with the crust materials, which suggests formation of various mixed-mineral precipitates or elemental substitution. SEM analysis by Merrington and Alloway (1995) revealed surface corrosion and exfoliation of pellets, with small particles of <2 µm commonly found adjacent to the pellet. This could suggest differential dissolution of the crust material, leaving small particles of less immediately-soluble mineral, or illustrate the tendency for the crust material to disintegrate after slight disturbance, as noted by Rooney et al. (1999).

Lin (1996) concluded that the EMPA data suggest that Pb-oxides form on the pellet surface and are then replaced by Pb-carbonates. Replacement appears to first take place along Pb oxide fractures, which are filled with the darker grey Pb₃(CO₃)₂(OH)₂ material. Park and MacDiamid (1970, in Lin, 1996) hypothesised that when the temperature of a mineral is raised, a point is reached at which the atomic structure of a mineral is disordered but loosely tied together, allowing ions to diffuse through the crystal with ease. Lin (1996) lends this hypothesis to the rise in temperature of Pb pellets when they are fired from the shotgun, and that the loosely tied atomic structure would allow carbon dioxide to diffuse through fractures and form Pb-carbonates.
A few authors have found a small amount of PbSO₄ in some samples of pellet crust material, particularly in pellet samples from sites with low soil pH (Jørgensen and Willems, 1987b; Lin et al., 1995; Lin, 1996). Lin (1996) showed that the PbSO₄ was most likely present only in the inner rim of crust material and then only in some of the crust samples, suggesting that PbSO₄ becomes completely replaced by Pb-carbonates. The solubility of PbSO₄ is not affected by pH, and it is theoretically more stable than Pb₃(CO₃)₂(OH)₂ and PbCO₃ at low pH, but there is generally insufficient sulphur present in soils for PbSO₄ to be present in much larger proportions. Competition (for ion association with Pb²⁺) from the large proportion of carbonate ligands produced by the soil organic carbon pool results in the overriding precipitation of Pb₃(CO₃)₂(OH)₂ (Lin, 1996).

It appears that PbCO₃ is more likely to be present in the crust material at higher pH. Jørgensen and Willems (1987b) observed that while Pb₃(CO₃)₂(OH)₂ always dominated crust mineralogy, PbCO₃ was present in the greatest amount at the site with the highest soil pH(CaCl₂) (7.4). Less PbCO₃ was present at the two sites with soil pH(CaCl₂) of 5.5, and no PbCO₃ was present at the site with soil pH(CaCl₂) of 3.5. Lin et al. (1995) studied the crust material found on pellets at five shooting ranges. Less than approximately 5% of the crust material was PbCO₃ at the three sites where soil pH(KCl) < 4.5, but the proportion of PbCO₃ increased 3- to 4-fold at the two sites where soil pH(KCl) was 6.8-7.0. These two high-pH sites were rifle backstop berms that contained corroding lead bullets, instead of the lead pellets at the 3 low-pH shooting ranges, but effectively the two types of ammunition are exposed to the same type of soil conditions. Therefore corrosion would be expected to occur by similar processes. Interestingly, crust composition was not greatly affected by organic matter content at near-neutral pH. The two high-pH sites (pH(KCl) 6.8 and 7.0) differed greatly in organic matter content (12.5 and 2.4% respectively) but the proportions of Pb minerals measured (semi-quantitatively) varied little (75-80% Pb₃(CO₃)₂(OH)₂; 15-20% PbCO₃; 5% PbSO₄).
2.2.2 Secondary transformations of lead shot

The vast majority of the Pb at shooting ranges is present as metallic Pb shot (Jørgensen and Willems, 1987b; Rooney et al., 1999). Rooney et al. (1999) found that only 11% of the total Pb burden at a site was associated with the fine earth fraction. Jørgensen and Willems (1987b) reported the distribution of Pb between pellet, crust and soil at four shooting range sites (Figure 2.2). There is a clear difference between the cultivated and uncultivated sites. Approximately three times more Pb is associated with the crust and soil fractions at the two cultivated sites. This difference seems to be of greater influence than pH, soil type or organic matter content. The crust material is relatively brittle and the action of ploughing would easily dislodge fragments of crust material from the Pb shot. This could lead to more rapid dissolution of the fragments, and encourage further corrosion of a pellet where the crust has been removed. At most of the sites studied by Jørgensen and Willems (1987b) the distribution of Pb is in the order metallic Pb > EDTA-extractable soil Pb > crust Pb, however one site (Parup-C) presents an anomaly in that there is a build-up of crust material but less Pb has transferred into the soil (Figure 2.2). Formation of crust material at the Parup-C site may be advanced by the CO₂ produced by increased mineralisation caused by the ploughing of the highly organic soil, but subsequent dissolution of the crust may be prevented by the high soil pH.

It is evident that pellet decomposition is controlled by a complex combination of environmental factors including soil pH, organic matter content, available ligands and leaching rate. The rate of Pb shot decomposition was estimated by Jørgensen and Willems (1987b) from analytical data obtained from studying the reactivity of the crust material. The authors estimated that in some Danish soils, half of the Pb shot would be transformed into soil-Pb compounds in 40 to 70 years, and that complete transformation would occur in 100 to 300 years. Lin (1996) estimated that complete transformation of Pb shot to soil Pb compounds would occur in approximately 200 years.
In summary, the existing literature indicates that:

(i) pH is an important factor in crust formation and dissolution;
(ii) \( \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 \) is the dominant mineral formed, regardless of soil pH;
(iii) The amount (thickness) of crust material is affected by \( \text{pCO}_2 \), regardless of soil pH;
(iv) At high soil pH, pH is more important in the formation of \( \text{PbCO}_3 \) than \( \text{pCO}_2 \);
(v) The presence of \( \text{PbSO}_4 \) is determined by the S:C ratio.
2.2.3 The effects of lead shot contamination

Elevated soil Pb concentrations where Pb shot is deposited on the soil suggest a proportionately greater risk of Pb leaching. Evidence of downward migration of Pb at a shooting range was reported by Murray et al. (1997). Soil Pb concentrations of over 200 mg kg\(^{-1}\) were measured at 90-100 cm depth and the spatial distribution of Pb in subsurface soil horizons corresponded to the spatial distribution of elevated Pb concentrations in surface soil, indicating that Pb was migrating downward through the profile. This case indicates that there is potential for leaching of Pb at shooting ranges under certain environmental conditions.

Where a shot-fall zone is within an area used for agricultural production, elevated soil Pb concentrations could potentially impact on crops and grazing animals. Lead toxicity could adversely affect animal health, crop growth and soil health, and the safety of food produced from the area could be diminished. The area of land affected by Pb shot at CTS ranges is relatively small, but the potential effects of the high Pb concentrations present are substantial. The contamination greatly diminishes the future use and productive value of the affected land.

Most of the Pb in the fine earth fraction of the soil is in EDTA-extractable form (Manninen and Tanskanen, 1993; Mellor and McCartney, 1994; Rooney et al., 1999), which is considered to indicate potential bioavailability. Several authors have considered that soil Pb concentrations >500 mg kg\(^{-1}\) are toxic for plants (Kabata-Pendias and Pendias, 1992). Manninen and Tanskanen (1993) found elevated Pb levels in plants, mushrooms and berries growing at a shooting range, but concluded that the shooting range Pb was unlikely to enter the food chain via plants. Where agricultural production takes place in shot-fall zones, such as in Canterbury, this may be of greater concern. Rooney et al. (1999) demonstrated that Pb uptake by various plant species grown in Pb-contaminated soil from a Canterbury shot-fall area could lead to plant Pb concentrations in excess of the allowable limit.
All reported cases of Pb poisoning in cattle following ingestion of Pb shot have resulted in fatalities. In some cases, poisoning occurred after cattle consumed silage made from fields within which shot-fall areas existed (Howard and Braum, 1980; Frape and Pringle, 1984; Rice et al., 1987). Poisoning has also occurred where cattle were grazing on pasture that included a shot-fall area (G.B. Davis, personal communication, 22 August 1997; The Dominion, 1978) and in calves grazing an area that contained severely Pb-contaminated soil and grass adjacent to the backstop berm of a rifle range (Braun et al., 1997). However, Bjørn et al. (1982) demonstrated that there was no effect on blood Pb levels of cattle grazing on pasture where Pb shot was deposited. The bioavailability of different forms of Pb may have affected the outcome of Pb ingestion. Lead shot in the digestive system appears to have the least impact on animal health, while ingestion of contaminated soil and pasture containing more bioavailable forms of Pb cause greater effects. The acidity of silage appears to further increase the likelihood of poisoning by promoting the solubilisation of the Pb shot (Frape and Pringle, 1984).

Numerous studies have presented evidence showing that heavy metal contamination can have an adverse effect on soil microbiota. Consequently, this can influence litter decomposition and nutrient cycling processes. Soil heavy metal contamination can impact on soil microflora populations by reducing the growth and diversity of soil microbiota, promoting the development of metal-resistant strains, and inhibiting the synthesis and activities of soil enzymes (Tyler, 1981a). Given these findings, it would be expected that the elevated soil Pb concentrations and consequent bioavailability of Pb at shooting ranges would also affect soil biota. Siepel (1995) investigated the effect of Pb contamination at a CTS range on soil mites (microarthropod invertebrates). Significantly fewer mites were extracted from soil samples with higher masses of metallic Pb, and the species most affected by population reductions were those which most rapidly accumulated Pb through their diet. Further effects of the Pb contamination at shooting ranges on soil biota are unknown. Clay target shooting ranges appear to provide a good opportunity to study the effect of Pb contamination on soil biota in the field.
2. Literature Review

2.3 FORMS OF SOIL LEAD

2.3.1 Lead in the soil solution

Soluble Pb in the soil solution is central to the focus of soil heavy metal chemistry due to its major role in soil chemical processes, particularly those affecting metal bioavailability and mobility. While a dynamic equilibrium can be assumed between solution and (mineral and organic) solid phase compartments (Davies, 1990), only a very small proportion of the total soil Pb is present in dissolved forms. Tyler and Olsson (2001) reported that approximately 0.002-0.006% of the total soil Pb was present in solution (<0.2 µm) in an uncontaminated soil. The proportion of total soil Pb present in the soil solution may be much greater in some contaminated soils than those with background Pb concentration (Gregson and Alloway, 1984; Jopony and Young, 1994). Jopony and Young (1994) found that the relationship between total soil Pb concentration, free Pb$^{2+}$ concentration and solution pH could be described by a pH-dependent Freundlich adsorption equation over a Pb concentration range of 4 log units in the pH range 3.5-7.5.

The standard filter size used to isolate soluble components from particulate matter is 0.45µm. There is some variation in filter size selected for this process by authors, but given the variation in solution Pb concentration with pH and the influence of various other soil components (Gregson and Alloway, 1984; Tyler and Olsson, 2001), the use of the 0.45µm filter for isolating soil solution appears acceptable (Davies, 1990).

Dissolved Pb may exist in the soil solution as free Pb$^{2+}$, inorganic ion-pairs and organic complexes. Total soil Pb content, solution pH, and the concentrations and nature of various inorganic and organic ligands are important in controlling soluble Pb. The free Pb$^{2+}$ species becomes dominant at low solution pH, when solid phases such as organo-Pb complexes and Pb precipitates are less stable, and hydrolysis of the Pb$^{2+}$ ion is not favoured (Figure 2.3). As solution pH increases, aqueous Pb$^{2+}$ hydrolysates resulting in a possible suite of soluble hydroxy-Pb complexes (Figure 2.3; Table 2.5), however at pH <8 only Pb$^{2+}$ and PbOH$^+$ contribute significantly to total Pb in solution (Lindsay, 1979). Approximately between pH 8 and 10, PbOH$^+$ becomes the dominant hydroxy species in solution, and only above pH 10 does Pb(OH)$_2$ formation become important (Figure 2.3; Hahne and Kroontje, 1973). Organic matter solubility is promoted as pH increases, significantly raising the concentration of soluble organic ligands which can elevate total soluble Pb concentrations through the formation of soluble metal-organic complexes (Sauvé et al., 1998).
2. Literature Review

Figure 2.3. Speciation diagram for dissolved Pb hydroxy species in terms of pH; [Pb(II)\textsubscript{tot}] = 0.01 M (modified by Adriano, 1986, from Hahne and Kroontje, 1973).

Table 2.5. Equilibrium constants for reactions of Pb\textsuperscript{2+} in the soil solution, calculated from ion activities (true for all ionic strengths) and 25\textdegree C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium reaction</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>(\text{Pb}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{PbOH}^+ + \text{H}^+)</td>
<td>-7.71</td>
</tr>
<tr>
<td></td>
<td>(\text{Pb}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Pb(OH)}_2^0 + 2\text{H}^+)</td>
<td>-17.12</td>
</tr>
<tr>
<td></td>
<td>(\text{Pb}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Pb(OH)}_3^- + 3\text{H}^+)</td>
<td>-28.06</td>
</tr>
<tr>
<td></td>
<td>(3\text{Pb}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Pb}_3\text{(OH)}_4^{2+} + 4\text{H}^+)</td>
<td>-23.89</td>
</tr>
<tr>
<td></td>
<td>(4\text{Pb}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Pb}_4\text{(OH)}_4^{4+} + 4\text{H}^+)</td>
<td>-20.89</td>
</tr>
<tr>
<td></td>
<td>(6\text{Pb}^{2+} + 8\text{H}_2\text{O} \leftrightarrow \text{Pb}_6\text{(OH)}_8^{4+} + 8\text{H}^+)</td>
<td>-43.58</td>
</tr>
<tr>
<td>Other complexes</td>
<td>(\text{Pb}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{PbSO}_4)</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>(\text{Pb}^{2+} + \text{NO}_3^- \leftrightarrow \text{PbNO}_3^+)</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>(\text{Pb}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{PbCO}_3^0)</td>
<td>6.27</td>
</tr>
<tr>
<td></td>
<td>(\text{Pb}^{2+} + \text{HCO}_3^- \leftrightarrow \text{PbHCO}_3^+)</td>
<td>3.45</td>
</tr>
<tr>
<td></td>
<td>(\text{Pb}^{2+} + 2\text{CO}_3^{2-} + \leftrightarrow \text{Pb(CO}_3)_2^{2-})</td>
<td>9.49</td>
</tr>
</tbody>
</table>

\(\text{a Sauvé et al.}(1998)\)

b Lindsay (1979)
Using the GEOCHEM-PC model (Parker *et al.*, 1995), Alloway (1990) predicted that the main chemical species of Pb in acid soil solutions under oxidising conditions are likely to be Pb$^{2+}$, organic complexes, PbSO$_4$ and PbHCO$_3^+$. Predictions generated by GEOCHEM-PC software for Pb species in alkaline soil solutions under oxidising conditions are PbCO$_3$, PbHCO$_3^+$, Pb(CO$_3$)$_2^{2-}$ and PbOH$^+$ (Alloway, 1990).

From data obtained by batch equilibrium studies using whole soils, Santillan-Medrano and Jurinak (1975) observed that Pb solubility depended on pH and that Pb(OH)$_2$ appeared to regulate Pb$^{2+}$ activity at solution pH approximately <6.6. Sauvé *et al.* (1998) confirmed this, showing that estimated Pb$^{2+}$ activity reduced linearly with increasing pH to pH 6. Sauvé *et al.* (1998) also showed that dissolved organic matter appeared to cause a significant increase in Pb solubility at higher pH. The high proportion (>90%) of the total dissolved Pb present as organo-Pb complexes at pH >6 demonstrates the importance of the formation of soluble organo-Pb complexes on Pb solubility at higher pH. This is supported by Verloo and Cottenie (1972) who illustrated the effect of pH on the speciation of Pb in solution in the presence of purified humic acids (Figure 2.4). Overall, the presence of soil organic ligands can increase heavy metal mobility by forming soluble organo-Pb complexes or decrease heavy metal mobility by forming insoluble organo-Pb complexes. The effect depends on the concentration, ratio and nature of all the reactive components (Gorbatov, 1988).

![Figure 2.4. Distribution of Pb in the presence of excess humic acids; from Verloo and Cottenie (1972).](image-url)
2.3.2 Lead associated with the soil solid phase

Free Pb\(^{2+}\) and hydrolysed Pb species are efficiently removed from soil solution via solid phase associations with clay minerals, metal oxides and hydrous oxides such as those of Fe and manganese (Mn), and formation of insoluble organo-Pb complexes in soil (Davies, 1990; Fergusson, 1990). Three main processes control the partitioning of metal species between the solution and solid phase:

(i) Removal from solution by sorption onto soil colloids;
(ii) Release from soil colloids to solution by desorption; and,
(iii) Precipitation and dissolution as an independent phase in the soil matrix.

Possible reaction mechanisms which affect solid/solution dynamics are summarised in Figure 2.5. Solution Pb concentrations are generally predominantly controlled by adsorption mechanisms and much less by surface precipitation (Gorbatov, 1988; Kabata-Pendias and Pendias, 1992; Strawn and Sparks, 2000).

The soil medium provides a variety of reactive sites on soil organic matter, hydrous oxides and clay minerals, that can strongly sorb large amounts of Pb from solution by various mechanisms (Figure 2.5). Experimental desorption studies show that little Pb which is sorbed onto the soil is able to be desorbed. Different time scales exist for Pb sorption and desorption due to the strong fixation of Pb by various soil colloids. In most soils, and certainly at low solution Pb concentrations, sorption/desorption equilibria control the behaviour of Pb (Kabata-Pendias and Pendias, 1992; Strawn and Sparks, 2000). Sorption and desorption of Pb in soils is discussed in detail in the following section.

The precipitation and dissolution of Pb minerals as independent phases in the soil matrix is most likely to occur at high solution pH (Singh and Sekhon, 1977; Harter, 1979; Basta and Tabatabai, 1992b) or high solution Pb concentration (Basta and Tabatabai, 1992b; Kabata-Pendias and Pendias, 1992; McBride, 1994; Strawn and Sparks, 2000). Figure 2.6 gives an indication of the effect of pH on the dominant Pb minerals in water. In oxidising conditions carbonate and hydroxide precipitates are most likely to form, and sulphide precipitates are most likely in reducing conditions. Precipitation of Pb is more likely to occur in calcareous soils, where considerable amounts of CaCO\(_3\) encourage Pb-carbonate associations (Santillan-Medrano and Jurinak, 1975; Nriagu, 1978). In soils where phosphate concentrations are well maintained by fertiliser, Pb-phosphate precipitates may be favoured over Pb-oxides.
Figure 2.5. Possible reaction mechanisms which can affect the Pb²⁺ concentration in the soil solution (adapted from McLaren and Cameron, 1996).
and -carbonates (Santillan-Medrano and Jurinak, 1975; McBride, 1994). Assessment of the relative importance of precipitation reactions in removing Pb from the solution is hampered by the difficulty in making a distinction between metal adsorption and metal precipitation from experimental data (Basta and Tabatabai, 1992b).

![Figure 2.6. Stability relations among Pb compounds in water at 25°C (from Brookins, 1988). Dissolved species activities: \([\text{Pb}^{2+}(\text{aq})] = 10^{-6} \text{ M}; [\text{Inorganic C(aq)}] = 10^{-3} \text{ M}; [\text{S(aq)}] = 10^{-3} \text{ M}.\)
Sequential fractionation techniques that partition metals into chemically similar forms have been used to gain further information on metal associations with the solid phase. The individual extractions are not entirely specific, so such techniques are limited to providing semi-quantitative evidence of metal partitioning and an indication of the chemical reactivity of fractions (Chlopecka et al., 1996; Ma and Rao, 1997). Direct comparison of most fractionation studies is difficult, as there is no standardised technique. Many fractionation parameters differ between schemes: fractions targeted, type and concentration of reactants, soil-solution ratios, extraction time, and reaction pH and temperature. The fractionation scheme designed by Tessier (1979) (original or modified) is one of the most widely used schemes; it identifies five nominal fractions: exchangeable, carbonate, oxide, organic, and residual.

Sequential extraction procedures for Pb show that the proportions associated with the various soil components varies with soil type and composition, and source of contamination (Fergusson, 1990), however, the exchangeable Pb fraction is generally <5% (for example, Miller and McFee, 1983; Garcia-Miragaya, 1984; Jardao and Nickless, 1989; Ramos et al., 1994; Taylor et al., 1995; Chlopecka et al., 1996). The majority of soil Pb is commonly associated with the oxide (Ramos et al., 1994; Chlopecka et al., 1996) and/or organic (Miller and McFee, 1983; Jardao and Nickless, 1989; Chlopecka, 1996) fractions. Lead can also exhibit a substantial association with the carbonate fraction in some soils (Ramos et al., 1994; Chlopecka et al., 1996), particularly those onto which biosolids have been applied (for example, Sposito et al., 1982b; Taylor et al., 1995) or calcareous soils (Chlopecka, 1996). Chlopecka (1996) compared metal partitioning in some calcareous and gley soils containing background or elevated metal concentrations. At background concentrations, greater proportions of Pb were associated with the carbonate fraction in calcareous soils compared to gley soils, but the oxide and organic extractions still yielded the majority of the total soil Pb. In soils with elevated metal concentrations, a much greater proportion of the soil Pb was associated with the organic fraction in contaminated soils, and Pb in the residual (immobile) fraction became a minor component. This suggests greater potential for Pb mobility in contaminated soils. In addition, decreasing soil pH resulted in a substantial increase in the mean proportion of Pb extracted in the exchangeable fractions of the soils studied.
2. Literature Review

2.4 Sorption and Desorption of Lead by Soils

Sorption is a combined term encompassing the reactions of metals with soil colloids by non-specific (outer sphere, electrostatic) ion exchange, specific (inner sphere) adsorption and chelation, and surface co-precipitation mechanisms. Desorption processes control the amount and rate of release of metals. Many authors have reported that in comparison with other heavy metals, Pb has a high sorption affinity with soils (Basta and Tabatabai, 1992c; Schulte, 1994), and the soil components: organic matter (Bunzl et al., 1976; Strawn and Sparks, 2000), pure clays (Bittell and Miller, 1974; Farrah et al., 1980), and Fe and Mn oxides (McKenzie, 1980; Sauvé et al., 2000b).

Studies examining the relationships between Pb sorption and soil parameters have attempted to establish the best predictors of sorption capacity. Most commonly, authors have found that Pb sorption correlates well with pH (for example, Korte et al., 1976; Harter, 1979; Gerritse and van Driel, 1984; Basta and Tabatabai, 1992a) and that cation exchange capacity (CEC) has corresponding or secondary importance (Hassett, 1976; Soldatini et al., 1976; Zimdahl and Skogerboe, 1977). Other parameters connected to pH or CEC also correlate with Pb sorption, such as organic matter (Soldatini et al., 1976; Zimdahl and Skogerboe, 1977; Gerritse and van Driel, 1984), Fe/Mn oxides (Korte et al., 1976; Zimdahl and Skogerboe, 1977), clay (Soldatini et al., 1976; Zimdahl and Skogerboe, 1977; Schulte, 1994), surface area (Korte et al., 1976; Schulte, 1994), and base saturation (Harter, 1979; Basta and Tabatabai, 1992a). These studies illustrate the interrelationship between sorption capacity and the pH-dependent surface charge of reactive soil colloids.

The principle of hard and soft acids and bases (HSAB principle) was originated by Pearson from the Lewis definition of acids and bases (Sullivan, 1977). This principle is: hard acids tend to associate with hard bases and soft acids with soft bases. The high binding affinity of Pb in soils has been explained using the HSAB principle. Under Pearson’s classification Pb is a ‘borderline’ acid which behaves as a relatively ‘hard’ or ‘soft’ species depending on the solution chemistry (Alloway, 1990; Basta and Tabatabai, 1992c). Soil exchange materials are classified as relatively soft bases (Sullivan, 1977; Basta and Tabatabai, 1992c). Lead will behave as a soft acid relative to the dominant exchange cations (hard acids) in solution and will therefore be more likely to bind with exchange sites and ligands (Basta and Tabatabai, 1992c). However, such conclusions made about cation exchange selectivity based on HASB
theory can only be considered an approximation (Sullivan, 1977). Perhaps the binding affinity of Pb for soil components is better explained by the ease of hydrolysis of the free Pb\(^{2+}\) ion as discussed by a number of authors (Abd-Elfattah and Wada, 1981; Alloway, 1990; Basta and Tabatabai, 1992c), particularly at circum-neutral to alkaline pH. Specific surface adsorption, in which no water molecule is interposed between a surface hydroxyl group and the metal ion or complex, creates strong soil-metal associations. Metals which readily form hydroxy complexes are specifically adsorbed to the greatest extent (Alloway, 1990).

The sorption of Pb onto soil is characterised by two stages (Soldatini et al., 1976; Sparks, 2000):

(i) an initial period of rapid removal of Pb from solution, followed by

(ii) a much slower rate of removal.

Traditionally this two-stage process has been described in terms of concentration, where rapid sorption occurs at low initial solution Pb concentrations and slower sorption takes place at higher Pb concentrations (Sparks, 2000). This phenomena was attributed to rapid adsorption of Pb onto specific sites followed by slower sorption onto non-specific sites of lower reactivity, interparticle diffusion/sorption into micropores and surface precipitation of Pb onto clay mineral and hydrous Al surfaces. More recent literature presents an alternate view – that the two-stage process occurs regardless of solution Pb concentration, and that the rapid initial sorption may include non-specific adsorption, which can occur on a similar time scale (\(\mu s - h\)) as specific sorption reactions (Sparks, 2000). In addition, surface precipitation via metal-hydroxide formation can occur on relatively rapid time-scales and therefore could also be a mechanism for rapid removal of metal from solution (McBride, 1994; Sparks, 2000). This increases the difficulty of making experimental distinction between adsorption and precipitation. Reasons given by Strawn and Sparks (2000) for the slow sorption phase include interparticle diffusion into porous minerals and soil organic matter, surface precipitation which can sometimes be slower than sorption, and adsorption to sites with relatively large activation energies \(E_a\). However, Sparks (2000) observed that surface-precipitation of Pb species doesn’t seem to occur as for other heavy metals, apparently due to the large ionic radius of Pb\(^{2+}\) (Sparks, 2000). Therefore consideration of the adsorption mechanism alone appears to be sufficient for describing the sorption of soil Pb.
Desorption processes are important in controlling the amount and rate of release of Pb into the soil. According to the theory of specific adsorption, adsorption may or may not require a significant activation energy, $E_a$, but desorption always requires an activation energy, $E_d$, since desorption necessitates that the energy of adsorption, $\Delta H$, be overcome (Adamson 1976 in McBride, 1989). Therefore metal desorption will tend to be slower than adsorption. The ability of Pb to desorb from whole soils and soil components varies. Within the time scales of experiments, it appears that Pb sorption onto clays and Fe oxides is largely reversible, and desorption from organic matter and whole soils is slow and not completely reversible. In natural soil systems the contact time between Pb and sorbents is most likely much longer, which may have implications for reversibility of sorption reactions. Naturally, desorption of Pb also increases with decreasing pH, but this does not represent desorption behaviour in terms of a reversible reaction in which the desorption conditions are the same as those for sorption.

2.4.1 The role of soil components in sorption and desorption

The colloids considered to be the most important in contributing to metal sorption can be grouped into organic materials, hydrated metal oxides and clay minerals. Investigations of Pb sorption onto these groups of colloids are reviewed below.

**Organic materials**

Soil organic matter, both soluble and insoluble, forms complexes with metals by exchange and adsorption reactions. Soil organic compounds, predominantly humic substances, play a primary role in Pb sorption due to the existence of negative charge over a wide pH range. This is the main reason why a high correlation is often reported between Pb sorption and soil CEC. The common accumulation of Pb in topsoil also indicates the significant role of solid-phase soil organic matter. The largely pH-dependent charge is generated by the dissociation of protons from carboxylic (R–COOH; $K_d \sim 3-5$), phenolic (R–C$_6$H$_4$–OH; $K_d \sim 7$) and alcoholic (R–OH) functional groups on humic surfaces. Sorption reactions between Pb and organic matter take place by ion exchange, adsorption by functional groups or complexation into ring-structured chelates, and precipitation of organo-Pb complexes from solution. In acidic media, the adsorptive capacity of humic acids for metals tends to be greater than those of clays (Hatton and Pickering, 1980).
The efficient specific adsorption of Pb by soils was explained above using the Lewis HSAB theory. The theory can be continued to organic materials. When the comparative softness of soil component functional groups are considered, the hydroxyl functional groups on mineral surfaces are classified as hard bases, but the functional groups on soil humus are considered to be soft bases (Strawn and Sparks, 2000). Lead, acting as a borderline soft acid, would be expected to preferentially bind with organic matter.

The effect of organic matter on the two-stage sorption kinetics of Pb in soil is illustrated well by Strawn and Sparks (2000), who observed that a soil treated to remove organic matter displayed rapid sorption only, and the rate of Pb sorption reduced as soil organic matter increased. The results strongly suggested that the slow sorption stage for Pb is a result of sorption onto organic matter. The authors attributed this to slow diffusion into interior binding sites within the organic molecules. The role of organic materials in sorption kinetics of Pb is supported by Bunzl et al. (1976), who observed a slow rate of Pb adsorption and desorption for peat, relative to other metal cations.

The importance of organic matter for Pb sorption was clearly demonstrated by Strawn (2000), where removal of the 2% organic matter in the soil studied resulted in a 40% reduction in Pb sorbed. Strawn and Sparks (2000) observed apparent hysteresis in the desorption of Pb from organic matter, and suggest that organic matter plays an important role in slow Pb desorption reactions.

Metal oxides
Hydrous oxides of Fe, Mn (for example McKenzie, 1980) and Al (for example Strawn et al., 1998), are important sorbents for various metals including Pb. The mechanism of Pb sorption identified in the literature is invariably specific adsorption of hydroxy-Pb species by highly reactive surface (oxygen and hydroxyl) functional groups, as bidendate edge-sharing complexes (Strawn et al., 1998; Scheinost et al., 2001). The functional groups exhibit pH-dependent variable charge generated by amphoteric dissociation. The strong affinity of heavy metals for hydroxyl groups allows the strong specific adsorption of heavy metals onto metal oxides below their respective pHs for zero charge (point of zero charge; PZC; Hildebrand and Blum, 1975). Sorption of Pb can also occur by occlusion during formation of oxides. Isomorphic substitution of Fe$^{3+}$ and Mn$^{2+}$ ions in the crystal lattice structure of oxides by Pb$^{2+}$ is a mechanism which appears not to be supported by the relatively large ionic radii of Pb (Padmanabham, 1983; Ainsworth et al., 1994).
Scheinost et al. (2001) studied the kinetics of Pb sorption onto ferrihydrite. Initial rapid sorption was identified as specific adsorption, and the slow sorption that followed was attributed to diffusion of Pb into the interior of the Fe oxide aggregates. The authors suggested that the relatively large ionic radii of Pb$^{2+}$ may limit diffusion into small pores in the aggregates.

Sauvé et al. (2000b) compared the Pb adsorption capacity of pedogenic Fe oxides and (synthetic) ferrihydrite. The pedogenic oxides had lower affinity for Pb, particularly at the lower total Pb loadings (total range approximately 0-40,000 mg kg$^{-1}$). The authors also observed that pedogenic and synthetic Fe oxide materials had higher adsorption affinity for Pb relative to that of organic matter (in the form of leaf compost). This suggests that organic matter may block reactive sites on Fe oxides and reduce the total affinity of soil colloid surfaces for Pb.

McKenzie (1980) observed Pb sorption by Mn oxides that was up to 40 times greater than that by Fe oxides. High specific adsorption onto Mn oxides occurred over a wide pH range. In contrast, Pb sorption by hematite and goethite increased sharply as pH increased. Hematite adsorbed greater amounts of Pb than goethite, even though the surface area of the latter mineral is greater. The author concluded that Mn oxides and hematite are likely to be important sinks for Pb in soils. It has also been suggested to that Pb$^{2+}$ oxidises to the Pb$^{4+}$ ion at Mn oxide surfaces to form PbO$_2$ precipitates (Hem, 1978, in McBride, 1989; Gatte and Laitenen, 1974, in Matocha et al., 2001).

Although the metal oxides invariably have high affinity for Pb, and Pb has been shown to accumulate in the Mn oxide fraction of soils (Taylor and McKenzie, 1966; Norrish, 1975, in McKenzie, 1980), Hooda and Alloway (1998) found no correlation between Pb sorption by soils and Fe or Mn oxide content of the soils. Soldatini et al. (1976) found that organic matter and clay were the dominant soil constituents contributing towards Pb sorption in 12 soils, and the contribution of Mn oxides was only slight. However, high initial lead concentrations used in these experiments (20-830 mg L$^{-1}$) may have induced precipitation reactions.
Ainsworth et al. (1994) studied the sorption and desorption of Pb by ferrihydrite. Despite the high affinity of Pb with specific adsorption sites on ferrihydrite surfaces, Pb remained associated with the surface and was rapidly desorbed with no hysteresis of the adsorption edge after contact time of up to 86 weeks. This was attributed to the exclusion of Pb\(^{2+}\) from incorporation into the oxide lattice structure due to relatively large ionic radius. Padmanabham (1983) showed similar behaviour of Pb with adsorption sites on goethite after contact time of 8-12 days. McKenzie (1980) reported that Pb adsorbed onto hematite was less extractable (by 2.5% acetic acid) than that on goethite. In addition, a high proportion of the Pb adsorbed onto Mn oxides was not extractable. Strawn et al. (1998) reported desorption of Pb from Al\(_2\)O\(_3\) is completely reversible within approximately 3 days. Phillips (1999) reported that in soils aged with Pb under waterlogged conditions, Pb extractability (by 1 M MgCl\(_2\), pH 7) reduced with contact time of 0-15 days. A subsequent increase in Pb extractability was attributed to the dissolution of Fe and Mn oxides in the reduced conditions.

Layer silicate clays

Layer silicate clays such as kaolinite (1:1) and illite and montmorillonite (2:1) provide sorption sites via external hydroxyl functional groups and interlayer ion exchange sites. Clays may play a lesser role in Pb sorption than organic matter (Hildebrand and Blum, 1975), but Pb also has high affinity for clay minerals. As pH increases, clay edge sites become more negatively charged and sorption of cations increases. Bittell and Miller (1974) found that Pb\(^{2+}\) may compete with common divalent ions in the soil for sorption sites on various clay minerals, and that Pb\(^{2+}\) adsorption was favoured over Ca\(^{2+}\).

Results of various studies of Pb sorption onto pure and natural clays (Farrah and Pickering, 1977; Farrah et al., 1980; Yong et al., 1990) have indicated that Pb retention is due to cation exchange at approximately pH <4, and specific adsorption of hydroxy-Pb species at pH >5. Strawn and Sparks (1999) studied adsorption mechanisms of Pb on montmorillonite using X-ray absorption fine structure spectroscopy (XAFS). The authors reported Pb exchange on basal planes at low ionic strength and pH, and specific adsorption at edge sites at higher ionic strength and pH. Low ionic strength and high pH, and high ionic strength and low pH appeared to result in Pb forming both outer- and inner-sphere adsorption complexes.
Interpretation of metal-sorption behaviour of simple clay minerals is complicated by variation in adsorption with solution pH, nature of the clay, electrolyte solution composition and the nature and concentration of ligands in the system (Farrah et al., 1980). Individual clay minerals have different surface areas and reactivities. The surface area of clays increases in the order: kaolinite, chlorite < illite < vermiculite, montmorillonite (Kabata-Pendias and Pendias, 1992), and studies of Pb adsorption onto clays have shown a similar order for relative amounts of pH-dependent charge (Farrah and Pickering, 1977; Yong et al., 1990; Li and Li, 2000).

Although these components have been discussed individually, in the soil environment interactions between organic, oxide and clay colloids result in various component combinations. This somewhat complicates any simple explanation of Pb fixation and soil component behaviour. Metal oxides occur in cracks and as coatings on other sorbents, and as concretions; likewise, organic material can coat oxides and clays (Hatton and Pickering, 1980; Slavek and Pickering, 1981; Kabata-Pendias and Pendias, 1992; Sauvé et al., 2000b). These component interactions can influence solid-solution distributions by blocking sorption sites, by encouraging surface reactions, or by reducing complex formation due to lower equilibrium ligand concentrations. Ternary (surface-metal-ligand) complexes can occur, where the inorganic or organic ligand is capable of complexing the metal ion while allowing simultaneous coordination of the metal to the surface (McBride, 1989).
2.4.2 Effect of pH on lead sorption

A strong increase in Pb sorption occurs with increasing pH within the pH range of soils (Harter, 1983; Adriano, 1986; Basta and Tabatabai, 1992b; Basta et al., 1993). Sorption of Pb is affected by soil pH through the solubility control of Pb-hydroxides, -carbonates and -phosphates, and the influence of pH on Pb hydrolysis, organic matter solubility and surface charge of metal oxides, organic matter and clays (McBride, 1994; Sauvé and McBride, 1998; Sauvé et al., 1998).

The mechanisms proposed to explain the strongly pH-dependent adsorption of heavy metals in soils include (Bunzl et al., 1976; Harter, 1983; Basta and Tabatabai, 1992b):

(i) Metal precipitation – both adsorption and precipitation involve binding to metal-oxides and -hydroxides, and it may be difficult to make a distinction between them from experimental data; and abnormally high solute concentrations are often used;
(ii) Degree of metal hydrolysis, followed by preferential adsorption of the metal hydrolysis species;
(iii) Competition of metal cations with H⁺ for exchange sites.

Basta and Tabatabai (1992b) concluded that increasing adsorption proportional to pH, particularly at high soil Pb concentrations, was related to exchange reactions and soil components with pH-dependent charge. Appel and Ma (2002) demonstrated that increasing soil pH increased the amount of negative surface charge in selected soils, and sorption of Pb was generally closely related to these factors. Various authors have observed that Pb sorption by soils is affected less by pH than that of Zn, Cd and Ni (Gerritse and van Driel, 1984; Basta and Tabatabai, 1992b; Appel and Ma, 2002). Appel and Ma (2002) also found that Pb had a greater tendency than Cd to undergo both inner- and outer-sphere adsorption over a wide pH range, including at pH< PZC.

McKenzie (1980) reported that an increase in pH of 2 pH units, from 3.5 to 5.5, resulted in an increase in adsorption of Pb onto hematite and goethite from a low level up to 100% of the Pb added. A similar effect of pH was reported by Ainsworth et al. (1994) for Pb sorption by amorphous ferrihydrite. McKenzie (1980) showed that sorption onto Mn oxide was significantly less influenced by pH increase. Matocha et al. (2001) reported strong sorption of Pb on birnessite (MnO₁.7) over the pH range 1.5-7.5, characterised by substantial sorption at and below the PZC for the mineral. In contrast, Pb sorption by manganite (MnOOH) was highly pH-dependent.
2.5 Summary

Due to widespread Pb pollution, and the potentially serious impacts of the toxic metal on environmental and human health, a large amount of work has been carried out on many aspects of soil Pb chemistry. In contrast, the research currently available on the contamination of soil at shooting ranges by Pb shot is scarce. The available literature predominantly consists of surveys of the spatial distribution of Pb in soil at shooting ranges and studies of corrosion crust mineralogy. Given the extremely high loadings of Pb common at shooting ranges, there is an urgent need for research on the interactions between Pb shot and soil, and the fate of Pb solubilised from the Pb shot. The existing literature on soil Pb chemistry at natural background concentrations and elevated concentrations will aid the interpretation of data gained from such research.
3.1 **SOIL CHARACTERISATION**

3.1.1 **Soil preparation**

Unless stated, all soil was air-dried at approximately 25°C and sieved before analysis. Once dry, any lead shot visible in the sample was removed by hand before the soil was gently disaggregated and passed through a 1mm sieve to remove all remaining lead shot. The amount of lead shot removed from the soil during sieving was recorded, and calculated as a percentage weight of the original dry soil sample. Samples prepared in this way are referred to as the ‘fine earth fraction’ of the soil.

3.1.2 **Soil particle size analysis**

Twenty grams of soil was weighed out into a large beaker. To remove the organic matter a small amount of water and 5 mL of H₂O₂ was added, and the beaker was heated at approximately 70°C. Further H₂O₂ was added every hour until frothing ceased, indicating that all organic matter had been removed. The sample was transferred using de-ionised water into a 100 mL beaker and dispersed using an ultra sound bath at 35 kHz. The suspension was passed through a 63 µm sieve. The ultra sound treatment and sieving was repeated until the suspension was clear. The >63 µm fraction (sand) was oven dried at 100°C and weighed. The <63 µm fraction was transferred to a 500 mL measuring cylinder containing 25 mL calgon, and the cylinder made up to the mark with de-ionised water. The pipette method was used for silt and clay assessment; ISSS particle size divisions were used.

3.1.3 **Soil pH**

Ten grams of the fine earth fraction was mixed with 20 mL of deionised water, stirred intermittently for 30 minutes, then left to stand overnight. The pH of the supernatant was measured using a combined glass/calomel electrode.
3. Methods and Materials

3.1.4 Cation exchange capacity

Soil cation exchange capacity (CEC) was determined by the leaching method (Blakemore et al. 1987). Leachate NH₄-N was measured by Flow Injection Analysis (FIA).

3.1.5 Total carbon

Total soil carbon concentrations in the fine earth fraction were measured using a Leco CNS-2000 elemental analyser.

3.1.6 Oxalate extractable iron

The amount of amorphous iron (Fe) oxide material was assessed using an acidic ammonium oxalate extraction (Blakemore et al. 1987). The acid oxalate reagent was made up with 16.5 g L⁻¹ ammonium oxalate and 10.8 g L⁻¹ oxalic acid. Two grams of air-dry soil was reacted in the dark with 50 mL acid oxalate reagent in 100 mL polypropylene centrifuge tubes on an end-over-end shaker for 4 h. Samples were centrifuged at 2000 rpm for 10 minutes then filtered (Whatman No. 42). Samples were diluted (1:10) using 0.15 M CsCl, and the concentration of Fe was determined by AAS.
3.2 **SOIL ANALYSES**

#### 3.2.1 Total fine earth lead

Half a gram of the fine earth fraction (three replicates) was combined with 10 mL concentrated nitric acid and digested in a microwave digester using pressurised teflon vessels, equivalent to USEPA Method 3051. Samples were then cooled and filtered (Whatman No. 52) into 50 mL volumetric flasks, which were then made up to the mark with deionised water. Lead concentrations were determined by flame or graphite furnace AAS.

To obtain an indication of the accuracy of the total Pb analysis, three National Institute of Standards and Technology (NIST) standard reference soil materials were analysed using the USEPA Method 3051 microwave digestion technique described above. The results are shown in Table 3.1. The concentrations determined using the USEPA Method 3051 microwave method are generally within the ranges of published values although the mean values of the contaminated reference samples (2710 and 2711) are approximately 10% lower than the published median values. It should be noted that the published values were determined using a non-microwave digestion method (USEPA 3050) and thus the two methods are not directly comparable. Nevertheless, the relatively close agreement of the two sets of data provides confidence in the accuracy of the microwave digestion method used.

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Pb concentration (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Published values</td>
</tr>
<tr>
<td></td>
<td>Range</td>
</tr>
<tr>
<td>San Joaquin soil 2709</td>
<td>12 – 18</td>
</tr>
<tr>
<td>Montana soil 2710</td>
<td>4300 – 7000</td>
</tr>
<tr>
<td>Montana soil 2711</td>
<td>930 – 1500</td>
</tr>
</tbody>
</table>
3.2.2 EDTA-extractable fine earth lead

Lead was extracted from the fine earth fraction by shaking 10 g samples (three replicates) for 2 h with 50 mL 0.04M Na₂EDTA in 50 mL polypropylene centrifuge tubes, centrifuging for 10 min at 10,000 rpm, and filtering the supernatant solution through a Whatman No. 54 filter paper. Lead in the extracts was determined using flame or graphite furnace AAS.

3.2.3 Fractionation of fine earth lead

A modification of the sequential extraction (fractionation) technique of Tessier (1979) was employed to assess solid-phase Pb partitioning. The procedure is summarised in Table 3.2 and described below. The fractions determined are nominal; in particular the sodium acetate solution is likely to extract Pb present in carbonate precipitates and some specifically adsorbed Pb, perhaps from readily desorbable metal oxide sorption sites.

<table>
<thead>
<tr>
<th>Nominal fraction extracted</th>
<th>Extractant solution</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>1 M Mg(NO₃)₂, pH 7.0</td>
<td>Shaken 1 h, 20°C</td>
</tr>
<tr>
<td>Carbonate</td>
<td>1 M NaOAc, pH 5.0</td>
<td>Shaken 5 h, 20°C</td>
</tr>
<tr>
<td>Fe and Mn oxides</td>
<td>0.04 M NH₂OH.HCl in 25% (v/v) acetic acid</td>
<td>6 h, 96°C</td>
</tr>
<tr>
<td>Organic</td>
<td>0.02 M HNO₃ and 30% H₂O₂, pH 2.0 3.2 M NH₄Oac in 20% HNO₃</td>
<td>5 h, ca. 85°C Shaken 0.5 h, 20°C</td>
</tr>
<tr>
<td>Residual</td>
<td>Microwave digestion 70% HNO₃</td>
<td>Equivalent to USEPA Method 3051</td>
</tr>
</tbody>
</table>

Table 3.2. Summary of fine earth Pb fractionation procedure.
1. Exchangeable Pb: 1 g of fine earth and 8 mL of 1 M Mg(NO₃)₂, pH 7.0 were shaken in a 50 mL polypropylene centrifuge tube for 1 h on an end-over-end shaker. The samples were centrifuged at 10,000 rpm for 30 min and the supernatant filtered through No. 42 filter. The residue was washed by shaking thoroughly with 8 mL of deionised water. The samples were centrifuged again at 10,000 rpm for 30 min and the supernatant was filtered into the same 25 mL flask. The filter paper was washed with a small amount of deionised water and then the flask was made up to the mark with deionised water. The Pb concentration in the resulting 25 mL solution was determined.

2. Carbonate Pb: The residue from step 1 was shaken for 5 h with 8 mL of 1 M sodium acetate adjusted to pH 5.0 with acetic acid. Samples were centrifuged at 10,000 rpm for 30 min and the supernatant filtered through Whatman No. 42 filter paper into a 25 mL volumetric flask. The residue was washed by shaking thoroughly with 8 mL of deionised water. The samples were centrifuged again at 10,000 rpm for 30 min and the supernatant was filtered into the same 25 mL flask. The filter paper was washed with a small amount of deionised water and then the flask was made up to the mark with deionised water. The Pb concentration in the resulting 25 mL solution was determined.

3. Pb bound to Fe and Mn oxides: 20 mL of 0.04 M NH₂OH.HCl in 25% (v/v) acetic acid was added to the residue from step 2. Samples were placed in a water bath at 96°C for 6 h and agitated occasionally. Samples were then centrifuged at 10,000 rpm for 30 min and the supernatant filtered through Whatman No. 42 filter paper into a 50 mL volumetric flask. The residue was washed by shaking thoroughly with 8 mL of deionised water. The samples were centrifuged again at 10,000 rpm for 30 min and the supernatant was filtered into the same 50 mL flask. The filter paper was washed with a small amount of deionised water and then the flask was made up to the mark with deionised water. The Pb concentration in the resulting 50 mL solution was determined.
4. **Pb bound to organic matter:** 3 mL of 0.02 M HNO$_3$ and 5 mL of 30% H$_2$O$_2$ adjusted to pH 2.0 with HNO$_3$ was added to the residue from step 3. Samples were placed in a water bath at 85°C for 2 h and agitated occasionally. A further 3 mL of 30% H$_2$O$_2$ (pH 2.0 with HNO$_3$) was added and samples heated at 85°C for further 3 h with occasional agitation. Once cool, 5 mL of 3.2 M NH$_4$OAc in 20% (v/v) HNO$_3$ was added and then samples were diluted to 20 mL with deionised water and shaken for 30 min. Samples were then centrifuged at 10,000 rpm for 30 min and the supernatant filtered through Whatman No. 42 filter paper into a 50 mL volumetric flask. The residue was washed by shaking thoroughly with 8 mL of deionised water. The samples were centrifuged again at 10,000 rpm for 30 min and the supernatant was filtered into the same 50 mL flask. The filter paper was washed with a small amount of deionised water and then the flask was made up to the mark with deionised water. The Pb concentration in the resulting 50 mL solution was determined. The residue was dried in the centrifuge tube in an oven at 80°C.

5. **Residual Pb:** The weight of the dry residue from step 4 was recorded and the residue was finely ground. Half a gram of the ground residue was combined with 10 mL concentrated nitric acid and digested in a microwave digester using pressurised vessels, equivalent to USEPA Method 3051. Samples were then cooled and filtered (Whatman No. 52) into 25 mL volumetric flasks, which were then made up to the mark with deionised water. The Pb concentration in the resulting 25 mL solution was determined.

### 3.2.4 Atomic adsorption spectrophotometry (AAS)

Flame AAS was carried out mainly on a GBC Avanta spectrophotometer; some analysis was carried out on a Shimadzu AA-6200. Background correction was used for all measurements. Pb was measured at a wavelength of 217 nm with background correction using an air-acetylene flame. The limit of detection was 0.2 mg Pb L$^{-1}$.

Low levels of Pb ($< 0.2$ mg Pb L$^{-1}$) were analysed using a GBC 909 AA spectrophotometer equipped with a graphite furnace. Lead was measured at a wavelength of 217 nm, with background correction. The limit of detection was 2 µg Pb L$^{-1}$.
3.3 **SOIL SOLUTION AND LEACHATE ANALYSES**

3.3.1 **pH**
Solution pH was measured in unfiltered samples using a combined glass/colomel electrode.

3.3.2 **Soluble lead**
Solution Pb was measured in filtered (0.45 µm) samples by flame or graphite furnace AAS.

3.3.3 **Soluble carbon**
Soluble organic and inorganic carbon was determined in filtered (< 0.45 µm) samples using a Shimadzu Total Organic Carbon Analyser.

3.3.4 **Major cations**
Concentrations of Ca, Mg, Na and K in solution were measured in filtered (< 0.45 µm) samples using flame AAS with the addition of a Strontium (Sr)/Caesium (Cs) modifier (5000 mg L⁻¹ Sr and 1000 mg L⁻¹ Cs). A nitrous oxide-acetylene flame was used for Ca and Mg measurements, and an air-acetylene flame was used for Na and K measurements.

3.3.5 **Major anions**
Concentrations of NO₃⁻·N, PO₄³⁻·P, SO₄²⁻·S, and Cl⁻ in solution were measured on filtered (< 0.45 µm) samples using ion exchange chromatography (IEC).
3.3.6 Aqueous phase speciation modelling

The speciation of soil solution and leachates was estimated using GEOCHEM-PC v 2.0 speciation modelling software (Parker et al., 1995). This software was developed from the GEOCHEM program developed by Sposito and Mattigod (1980 in Sposito et al., 1982a), which bases the method of calculation on chemical thermodynamics. The software, including the database of critical data for metals and ligands, is contained on the CD-ROM accompanying this thesis (see back cover).

Input into the program was soil solution (Chapter 5) or leachate solution (Chapter 6) composition data in terms of total Pb concentration, pH, major cation and anion concentrations, and dissolved organic carbon concentration. The organic acids constituting the soluble organic fraction and their relative proportions of the total soluble organic concentration were estimated using the mixture model of Sposito et al. (1982a) (Table 3.3). The concentration of free Pb\(^{2+}\) and of the ion-pairs with inorganic and organic solution constituents were calculated. The program was run as an open system with respect to CO\(_2\), with P\(_{CO2} = 10^{-2.5}\) atm.

The main assumption of this model is that reactions are at equilibrium, which is generally not the case in the systems discussed in this thesis. In addition, the thermodynamic constants used in the model are developed from pure compounds, and the corresponding compounds present in the systems studied are unlikely to have the same purity or particle size. However, use of the GEOCHEM-PC model allows a valuable indication of the behaviour of Pb in the systems studied.

Table 3.3. Organic acids and their reference concentrations in the mixture model (from Sposito et al., 1982a); pC\(_T\) = -log total molar concentration of inorganic carbon species.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Concentration (pC(_T))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arginine</td>
<td>4.49</td>
</tr>
<tr>
<td>Benzensulfonic</td>
<td>4.27</td>
</tr>
<tr>
<td>Citric</td>
<td>4.14</td>
</tr>
<tr>
<td>Lysine</td>
<td>4.36</td>
</tr>
<tr>
<td>Maleic</td>
<td>3.97</td>
</tr>
<tr>
<td>Ornithine</td>
<td>4.36</td>
</tr>
<tr>
<td>Phthalic</td>
<td>3.97</td>
</tr>
<tr>
<td>Salicylic</td>
<td>4.27</td>
</tr>
<tr>
<td>Valine</td>
<td>4.36</td>
</tr>
</tbody>
</table>
3.4 **STATISTICAL ANALYSIS**

Statistical analysis was performed where appropriate using the statistical computer program Minitab 13.0.
Chapter Four

Soil Lead Contamination at Canterbury Clay Target Shooting Ranges

4.1 INTRODUCTION

In New Zealand it has been common practice to establish shooting ranges on or adjacent to farm-land. Recreational shooting creates intense concentrations of Pb in the small areas of shooting ranges. The impact of Pb shot on the environment is a potential hazard, and the continuing use of contaminated land for grazing and food production is not sound practice.

Following a study by Rooney et al. (1999) of Ellesmere Clay Target Club (CTC), a further 18 sites in Canterbury were identified by the Canterbury Regional Council (CRC) which are, or have been used for recreational CTS (Lobb et al., 1997; Figure 4.1). This total comprises 14 active sites and 4 inactive sites, spread throughout the region (Table 4.1). The inactive sites identified no longer support shooting activities due to amalgamation of clubs and/or relocation of shooting activities. Additional inactive sites were documented by the CRC but their locations have not been identified or included in any investigation. At Ashburton, a site upstream (west) of the current Ashburton CTC site has also been used, and a number of sites in the Waimate region became inactive after the formation of the Waimate CTC in 1963.

Table 4.1 provides selected data from the survey of Canterbury CTCs carried out by the CRC (Lobb et al., 1997). The majority of sites have been used for 20 to 60 years and an estimated total of 849 tonnes of Pb shot has been deposited at 16 sites, based on conservative estimates of Pb shot use at each individual site. Most of the clubs have relatively modest facilities and membership numbers (Lobb et al., 1997). This is reflected in an estimated Pb shot deposition at most individual sites of <2 t y\(^{-1}\). Notable exceptions are the clubs of Canterbury (9.9 t y\(^{-1}\)), Timaru (2.8 t y\(^{-1}\)) and Waihora (2.5 t y\(^{-1}\)), and the former Christchurch and Belfast clubs (both 2.9 t y\(^{-1}\)). The Canterbury and Timaru clubs have the most extensive facilities of active clubs in the region, and regularly hold regional and national championship events. The Canterbury CTC has also been the venue for major international events.
Figure 4.1. Location of clay target clubs in Canterbury (modified from Lobb et al., 1997).
Table 4.1. Details of clay target shooting ranges in Canterbury (from data of Lobb et al., 1997).

<table>
<thead>
<tr>
<th>Name of Club</th>
<th>Year of establishment</th>
<th>Years of Pb shot deposition *</th>
<th>Estimated Pb shot deposition † (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methven</td>
<td>1927</td>
<td>70</td>
<td>51</td>
</tr>
<tr>
<td>Ellesmere</td>
<td>1930</td>
<td>67</td>
<td>85</td>
</tr>
<tr>
<td>Mead-Tc Pirita</td>
<td>1939</td>
<td>58</td>
<td>85</td>
</tr>
<tr>
<td>Ex North Canterbury ‡</td>
<td>1946</td>
<td>40</td>
<td>13</td>
</tr>
<tr>
<td>Waihora</td>
<td>1946</td>
<td>51</td>
<td>127</td>
</tr>
<tr>
<td>Christchurch ‡</td>
<td>1952</td>
<td>38</td>
<td>109</td>
</tr>
<tr>
<td>Geraldine</td>
<td>1952</td>
<td>45</td>
<td>62</td>
</tr>
<tr>
<td>Amberley</td>
<td>1954</td>
<td>43</td>
<td>37</td>
</tr>
<tr>
<td>Belfast ‡</td>
<td>1954</td>
<td>30</td>
<td>86</td>
</tr>
<tr>
<td>Waimate</td>
<td>1963</td>
<td>34</td>
<td>21</td>
</tr>
<tr>
<td>Ashburton</td>
<td>1972</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>Timaru</td>
<td>1972</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>Banks Peninsula</td>
<td>1973</td>
<td>24</td>
<td>5</td>
</tr>
<tr>
<td>Darfield</td>
<td>1982</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Fairlie-Mackenzie</td>
<td>1988</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>Canterbury</td>
<td>1990</td>
<td>7</td>
<td>69</td>
</tr>
<tr>
<td>North Canterbury</td>
<td>1997</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>Ex Fairlie-Mackenzie ‡</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* As at time of survey by Lobb et al. (1997)
† conservatively based on average shooters and shots per shooter data
‡ Inactive site - club has relocated
– Not recorded
References are made to shooting matches being held in paddocks circa 1860 to 1875, but in most cases it is not clear if permanent shooting sites had been established. The Press carries reports of shooting matches held in paddocks behind the Carlton Hotel, Bealey Avenue (News of the Day, 1874; News of the Day, 1875), hotels in Papanui Rd (News of the Day, 1864; News of the Day, 1872b) and Leithfield (News of the Day, 1870), and further matches held at Ilam (News of the Day, 1872a; News of the Day, 1873), Woodend (News of the Day, 1876), and Teddington (News of the Day, 1901). By 1905 the Christchurch Gun Club had arranged for all club shooting matches to be held at the old racecourse at New Brighton (News of the Day, 1905b). The present-day siting of many shooting clubs on agricultural land appears to be a continuation of early practice.

The objective of this study was to assess the magnitude and spatial distribution of Pb contamination at various CTS ranges in Canterbury, and to assess the suitability of sites for further study.
4.2 METHODS AND MATERIALS

4.2.1 Study sites

Four clay target clubs situated on the Canterbury plains were selected for assessment of the extent of Pb contamination, on the basis of soil characteristics and local characteristics of ground- or surface-water. The suitability of the sites for further experimental investigation was kept in mind, especially from the point of view of future access to the sites for sampling.

*Ashburton CTC*

The Ashburton CTC is situated off Alford Forest Road, close to the Ashburton River (Figure 4.1)*. The soil is a Waimakariri stony sandy loam (Immature Pallic soil, NZ; Typic Ustifluvent, USA) of approximately 350 mm depth underlain by stony sand. Groundwater occurs at a depth of <10 m below ground surface with no confining layer identified (Lobb et al., 1997).

The shooting range facilities consist of 3 trap and 2 skeet fields (overlapping). The site has been used by the club since 1972, resulting in an estimated accumulation of 15 tonnes of Pb shot (conservatively based on average shooters and shots per shooter data) at the site (Lobb et al., 1997). The shot-fall area is grazed pasture and has been ploughed during the period of use by the club.

*Canterbury CTC*

The Canterbury CTC is located at McLeans Island†, on recent deposits of the Waimakariri River (Figure 4.1). The soil is a combination of Waimakariri very stony sand and shallow loamy sand (Recent soil, NZ; Typic Ustifluvent, USA) of approximately 50-150 mm depth underlain by very stony sand. Groundwater occurs at a depth of <10 m below ground surface in an unconfined aquifer (Little, 1997; Lobb et al., 1997).

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* Map reference K37:0807-0105; Legal description: Lot1 DP 53125 c/t 38C/455
† Map reference M35:6459-4838; Legal description: Lot 1 DP 56068
4. Canterbury shooting ranges

The shooting facilities are the most extensive in Canterbury, consisting of 10 trap, 6 skeet and 2 ball ranges (overlapping) and a separate sporting range. The site has been used by the club since 1990 (12 years), resulting in an estimated accumulation of 69 tonnes of Pb shot (conservatively based on average shooters and shots per shooter data) at the site (Lobb et al., 1997). The shot-fall area, which is grazed periodically by sheep, is covered by moss and lichen, and sparse pasture and tussock plants.

Timaru CTC

The Timaru CTC is adjacent to the Richard Pearce Airport, on the Levels Plains (Figure 4.1)*. The soil is a Templeton silt loam (Immature Pallic soil, NZ; Dystric Haplustept, USA) of approximately 350 mm depth underlain by very stony sand. Groundwater occurs at a depth of 10 m below ground surface with no confining layer identified (Lobb et al., 1997).

The shooting facilities are the second largest in Canterbury, comprising of 6 trap ranges, 3 skeet fields and 1 ball range (overlapping). The site has been used by the club since 1972, resulting in an estimated accumulation of 70 tonnes of Pb shot (conservatively based on average shooters and shots per shooter data) at the site (Lobb et al., 1997). The shot-fall area is within a paddock used for cropping. At the time of sampling the crop was barley, but potatoes have been grown on this land in the past. The paddock has been ploughed. The traps are located 50 m from the fence of the cropping field, so that only the target-fall area is within the club’s designated grounds. The pasture in the target-fall area is periodically grazed by sheep.

Waibora CTC

The Waibora CTC site is located on Duck Pond Road at Motukarara (Figure 4.1)*. The Halswell Canal, a tributary to Lake Ellesmere, borders the site. The soil is a Motukarara loamy sand (slightly saline phase; Gley Soil, NZ; Psammaquent, USA), which consists of accumulated organic matter (30-40 mm) over gleyed estuarine sands. The mean water level of the nearest off-site well is approximately 0.3 m below ground level and the range area is waterlogged during part of the year. A deeper confined aquifer (>50 m below ground level) is unlikely to be in hydraulic connection with surface sediments (Lobb et al., 1997).

* Map reference J38:6863-5418; Legal description: Part of RES 5010
The shooting facilities consist of 2 trap, 1 skeet and 1 ball range (overlapping), and a sporting field in the shot-fall area of the fixed traps. The club began shooting at the site in 1946 but the same land was also used for recreational shooting activity previous to formation of the club (O. Osbourne, personal communication, 1999). An estimated 127 tonnes of Pb shot (conservatively based on average shooters and shots per shooter data) has accumulated at the site (Lobb et al., 1997). Vegetation in the shot-fall area is a mix of gorse, pasture and reeds, which has been grazed by sheep in the past. Beyond the club boundary fence the pasture in used for grazing.

4.2.2 Sampling design

The sampling design was based on the results of an earlier, intensive study of the spatial distribution of Pb at a Canterbury CTS range (Rooney et al., 1999). Sampling was carried out during the period January-February 1997. Soil samples were collected in the shot-fall area along transects perpendicular and parallel to the line of trap houses at each site designed to intersect the area of maximum Pb contamination, identified by Rooney et al. (1999) to occur at 120-140 m from the trap houses. Soil samples were collected at 20 m intervals along most transects (some transects at the Timaru CTC were sampled at 10 m intervals, as described below). At each sampling location ten soil cores (25 mm diameter, 1-75 mm depth) were collected from an area of approximately 1 m², and combined to form a composite sample.

At each site, a perpendicular transect (A) was marked out between the two most frequently used traps (for example, Figure 4.2), which was expected to be the most contaminated area. At the sites with more extensive shooting facilities (Canterbury CTC and Timaru CTC) a second perpendicular transect (B) was marked out (Figures 4.3 and 4.4). At the Timaru site the shot-fall area was within land owned by another party and was not sampled, therefore soil samples were collected along the perpendicular transects at 10 m intervals, until the boundary fence was reached (Figure 4.4). At the Waihora CTC site a second (B) and third (C) perpendicular transect was marked out on either side of the canal bordering the shooting range (Figure 4.5).

* Map reference M36:7541-1914; Legal description: Part of Sec 4 BLK IV Res 959
Figure 4.2. Site plan of Ashburton CTC showing position of sampling transects, soil profile sampling site, shooting facilities and boundary fences.
Figure 4.3. Site plan of Canterbury CTC (McLeans Island) showing position of sampling transects, soil profile sampling site, shooting facilities and boundary fences.
Figure 4.4. Site plan of Timaru CTC showing position of sampling transects, soil profile sampling site, shooting facilities and boundary fences.
Figure 4.5. Site plan of Waihora CTC showing position of sampling transects, soil profile sampling site, shooting facilities and boundary fences.
On the basis of data obtained from the perpendicular transect(s) further soil samples were collected at each site along a transect parallel to the traps at a distance of 100 to 140 m from the traps, where the highest concentration of soil Pb had been measured (Figures 4.2-4.5). At the Timaru site the parallel transect was marked out 50 m from the traps, next to the boundary fence.

At each site a single location with approximately the highest concentration of soil Pb was also identified, at which the soil profile was sampled in 50 mm increments to a total depth of 0.5 m. At the Waihora site the soil profile was sampled to the greater depth of 1 m using 100 mm increments beyond 0.5 m depth. The location of the soil profile samples are shown in Figures 4.2-4.5.

4.2.3 Sample preparation and analysis

After air-drying the soil samples, all visible Pb shot was removed by hand and the remaining soil was gently crushed to pass through a 2 mm stainless steel sieve. The lead shot removed from the soil was weighed and calculated as a percentage weight of the original soil sample. Soil pH and carbon content were determined (Table 4.2).

<table>
<thead>
<tr>
<th>Club</th>
<th>Soil pH</th>
<th>Soil carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ashburton</td>
<td>6.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Canterbury</td>
<td>7.2</td>
<td>2.7</td>
</tr>
<tr>
<td>Timaru</td>
<td>6.8</td>
<td>8.9</td>
</tr>
<tr>
<td>Waihora</td>
<td>6.9</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Lead was extracted from the soil by EDTA and total digestion methods (Chapter 3.2). Lead concentrations in extracts were determined by flame AAS. A representative sample from each site was analysed to establish the soil pH and the amount of carbon in each soil (Chapter 3.1.5).
All soil analyses were replicated twice. In addition, analyses of just over 5% of the soil samples taken were replicated either 4 (EDTA-extractable Pb) or 6 (total Pb) times in order to establish precision of the Pb analyses. Coefficients of variation were relatively high for both types of analysis, with values for EDTA-extractable Pb (range 13.4-97.3%, mean 36.9%) substantially higher than for total Pb (range 1.4-115.5%, mean 20.6%). This variation is undoubtedly associated with the problem of weighing subsamples of sieved soil that contain particulate Pb shot of less than 2 mm diameter. Even small differences in the amount of particulate Pb between subsamples could result in large differences in Pb content. Theoretically, it might be expected that the smaller the weighed subsample, the larger the potential variation between subsamples. However, in this study, as noted above, greater variation was observed for the EDTA-extractable Pb analyses (10 g subsamples) than for the total Pb analyses (0.5 g subsamples). This possibly suggests some unconscious bias in weighing the smaller subsamples, for example, selecting predominantly only the finest soil material for weighing.

In spite of the relatively poor precision of both EDTA-extractable and total Pb analyses, there was very good agreement between the two sets of values, particularly when three obvious outliers were ignored (Figure 4.6). Rooney et al. (1999) and Mannenin and Tanskanen (1993) have also observed that a very high proportion of the total Pb in soil can be extracted using EDTA. Since the two sets of data are so similar, only the results of the total Pb analyses are discussed in the following section, as the precision of the total Pb data is higher.

In the following section the soil Pb concentrations are discussed using two soil fractions:

(i) Pb which has dissolved from the Pb shot and is associated with the <2 mm soil fraction (referred to as the fine earth fraction); and

(ii) the overall Pb concentration, that is, sieved Pb shot >2 mm + soil Pb <2 mm.
Figure 4.6. Comparison of EDTA-Pb and total Pb concentrations in the fine earth fraction (mg kg⁻¹) for each sample (after the removal of three outliers) showing regression of the data and a 1:1 plot for reference.
4. Canterbury shooting ranges

4.3 RESULTS AND DISCUSSION

4.3.1 Spatial distribution of lead (fine earth fraction)

All the sites were contaminated with Pb to some extent and contained Pb in the fine earth (<2 mm) fraction in excess of the ANZECC/NHMRC (1992) Environmental Soil Quality Guideline of 300 mg Pb kg⁻¹ soil (Figures 4.7-4.10). Soil Pb concentrations at the Ashburton, McLeans Island and Waihora sites rose from near-background levels at the traps to a maximum which occurred 100 to 140 m from the traps and then began to reduce towards background levels at greater distance, as shown in Figure 4.11. This is consistent with the pattern of distribution of Pb concentrations reported in an earlier, more intensive study of one Canterbury CTS range (Rooney et al., 1999; Figure 4.12).

The background concentration of Pb in soil at these sites is considered to be <30 mg kg⁻¹. The control values for Pb content in the soil at the four study sites was expected to be found in the first sample on the perpendicular transect(s) (0 m), where no Pb shot is deposited. This was the case at Ashburton, McLeans Island and Timaru, where <30 mg Pb kg⁻¹ soil was measured at 0 m (Figures 4.7-4.9). However, at Waihora the Pb concentration at 0 m on transect A was 139 mg kg⁻¹ – substantially higher than general background concentration (Figure 4.10). This is confirmed by the measurements at 0 m on transects B and C, which are <30 mg kg⁻¹. Similarly, Murray et al. (1997) observed elevated soil Pb concentrations in two areas of a Detroit CTS range: (i) the shot-fall zone; and, (ii) the area where shooters stand to shoot. The authors noted that the elevated soil Pb concentrations in the shooters’ area appeared to be related to the release of Pb-styphnate gas and particulate matter produced by the shotshell primer. An absence of Pb pellets and elevated soil Sb concentrations in the area supported this theory. At least 5 mg of Pb is present in the primer contained in each cartridge (Laender Ministers for the Environment, 1998).

At the McLeans Island site the very low fine earth Pb concentrations (<10 mg kg⁻¹) measured at the ends of the parallel transect and after 200 m on transect A suggest that the background Pb level for this Recent soil is likely to be <10 mg kg⁻¹. Taking this into consideration, there may be some mild elevation of soil Pb concentrations in the shooters’ area however the data is inconclusive at this stage. Further sampling in the future (that is, 5-10 years) should help to clarify this possibility.
Figure 4.7. Total fine earth Pb concentrations at the Ashburton CTC and the estimated position of a line of iso-concentration representing the ANZECC guideline of 300 mg Pb kg\(^{-1}\) soil.
Figure 4.8. Total fine earth Pb concentrations at the Canterbury CTC (McLeans Island) and the estimated position of a line of iso-concentration representing the ANZECC guideline of 300 mg Pb kg⁻¹ soil.
Figure 4.9. Total fine earth Pb concentration at the Timaru CTC and the estimated position of a line of iso-concentration representing the ANZECC guideline of 300 mg Pb kg⁻¹ soil.
Figure 4.10. Total fine earth Pb concentrations at the Waihora CTC and the estimated position of a line of iso-concentration representing the ANZECC guideline of 300 mg Pb kg\(^{-1}\) soil.
Figure 4.11. Total fine earth Pb concentrations (mg kg\(^{-1}\)) at each CTC on a transect perpendicular to the line of traps in front of the most frequently used trap.
Figure 4.12. Spatial distribution of EDTA-extractable fine earth Pb at Ellesmere Clay Target Club showing lines of iso-concentration; dashed line represents ANZECC guideline limit of 300 mg Pb kg$^{-1}$ (reproduced from Rooney et al., 1999).
At all sites the maximum soil Pb concentration measured was substantially elevated above background concentration. At Ashburton a maximum of 1632 mg kg\(^{-1}\) was measured on the parallel transect (at 120 m), directly in front of the most frequently used trap (Figure 4.7). At McLeans Island, Timaru and Waihora the maximum fine earth Pb concentration for each site was found on the perpendicular transect – 719 mg kg\(^{-1}\) at McLeans Island, 576 mg kg\(^{-1}\) at Timaru and 55958 mg kg\(^{-1}\) at Waihora. The concentrations of Pb in the fine earth fraction measured at Timaru on the parallel transect 50 m from the traps (300-500 mg kg\(^{-1}\)) are similar to the fine earth Pb concentrations at the same distance at the Ellesmere CTC (Rooney et al., 1999; Figure 4.12). From this comparison, it is estimated that the maximum fine earth Pb concentrations in the shot-fall area at Timaru would be in the range 6000 to 8000 mg kg\(^{-1}\).

The magnitude of maximum concentrations of Pb in the fine earth fraction can be related to the duration of use of sites for shooting activities, and therefore the time over which oxidation of the deposited Pb shot has occurred. The highest maximum fine earth Pb concentration was measured at the Waihora site, which has the longest history of use. The McLeans Island site, after just 7 years of deposition and subsequent oxidation of Pb shot, has the lowest maximum fine earth Pb concentration.

The data suggest that the shot-fall area extends beyond the boundary fences at most of the sites, indicating that it is difficult to contain the shot-fall area within the boundaries of a small site. The areas of the Ashburton, Timaru and Waihora sites range between 3 and 8 hectares. Fine earth Pb concentrations remain well above background level at boundary fences located in the shot-fall area (Figures 4.7, 4.9 and 4.10). The spatial distribution of fine earth soil Pb concentrations reported by Rooney et al. (1999), as shown in Figure 4.12, indicates that the three overlapping trap shooting ranges, at the common distance of approximately 40 m apart, have led to an area of elevated soil Pb concentrations of approximately 6 ha, and the shot-fall area extends approximately 220 m from the traps. The full influence of the single skeet field was difficult to determine, however the lateral distance of elevated Pb concentrations was estimated to be approximately 290 m. The three sites in this study are of insufficient area to contain the area of shot-fall and elevated fine earth Pb concentrations. In contrast, the Canterbury CTC site at McLeans Island is much larger at 72 ha, creating a well-contained shooting area within the site boundaries.
4. Canterbury shooting ranges

4.3.2 Lead removed by 2 mm sieve

The majority of Pb in samples from the sites (68-99%) was removed by sieving through a 2 mm sieve during sample preparation. The maximum concentration of Pb shot >2 mm at each of the four sites ranged from 1.15 to 19.80% (Table 4.3). This indicates that there is a large volume of Pb at all four sites that remains as intact Pb shot that is not yet associated with the fine earth fraction. As this Pb shot oxidises, it is foreseeable that the concentration of Pb in the fine earth fraction will increase substantially. The maximum overall concentration of Pb (fine earth Pb + sieved Pb shot) present at each site appears to be related to the frequency and intensity of shooting at each site. The McLeans Island site is used intensively, and this is reflected in the data, which show that in 7 years, the McLeans Island site has accumulated a Pb loading approximately half that of the Waihora site (Table 4.3), at which Pb shot has accumulated Pb for at least 50 years.

Table 4.3. Maximum concentration of Pb shot removed from samples at each site.

<table>
<thead>
<tr>
<th>Site</th>
<th>Sieved (&gt;2 mm) Pb shot</th>
<th>Total fine earth Pb</th>
<th>Overall Pb concentration (Fine earth Pb + sieved Pb shot)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% of air dry soil</td>
<td>Equivalent soil Pb concentration (mg kg(^{-1}))</td>
<td>(mg kg(^{-1}))</td>
</tr>
<tr>
<td>Ashburton</td>
<td>1.49</td>
<td>14,918</td>
<td>453</td>
</tr>
<tr>
<td>McLeans Island</td>
<td>10.14</td>
<td>101,392</td>
<td>300</td>
</tr>
<tr>
<td>Timaru</td>
<td>1.15</td>
<td>11,526</td>
<td>457</td>
</tr>
<tr>
<td>Waihora</td>
<td>19.80</td>
<td>198,029</td>
<td>12,356</td>
</tr>
</tbody>
</table>

At McLeans Island, the continued oxidation of the rapidly accumulating Pb shot is likely to produce a rapid rise in potentially soluble Pb and fine earth Pb concentrations. This is of particular concern at the McLeans Island site where there is a high rate of Pb shot deposition onto a sandy soil with low Pb-sorption capacity (due to few weathering products and low soil carbon; Table 4.2).
4.3.3 Lead in the soil profile

The concentration of lead in the fine earth fraction of the soil profile at all four sites was greatest at or near the surface and reduced substantially as depth increased (Figure 4.13). The depth to which elevated levels of Pb were measured varied between the sites, however, Pb concentrations that may be considered to be within the local background range (10-30 mg kg\(^{-1}\)) were reached at all sites within the sampling depth (Table 4.4).

<table>
<thead>
<tr>
<th>Site</th>
<th>Maximum fine earth Pb concentration (mg kg(^{-1}))</th>
<th>Depth at which ANZECC guideline exceeded (mm)</th>
<th>Depth below which soil contains background Pb concentration * (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ashburton</td>
<td>1,373</td>
<td>0-200</td>
<td>300</td>
</tr>
<tr>
<td>McLeans Island</td>
<td>472</td>
<td>0-50</td>
<td>100</td>
</tr>
<tr>
<td>Timaru</td>
<td>417</td>
<td>0-100</td>
<td>250</td>
</tr>
<tr>
<td>Waihora</td>
<td>19,574</td>
<td>0-150</td>
<td>600</td>
</tr>
</tbody>
</table>

* Assumes a local background Pb concentration of <30 mg kg\(^{-1}\)

The distribution of fine earth Pb in the soil profile at Ashburton, where similar soil Pb concentrations occur throughout the top 200 mm of the profile, differs from the distribution at the McLeans Island and Waihora sites (Figure 4.13). The shot-fall area of the Ashburton CTC has been ploughed periodically, which has caused the mixing of Pb shot into the top 150-200 mm of the profile and increases the fine earth Pb concentration to exist to this depth. A similar pattern of distribution was observed at another CTC range where the shot-fall area had been ploughed (Rooney et al., 1999).

Elevated concentrations of soil Pb were detected at the greatest depth in the Waihora soil profile (Table 4.4). This movement down the profile may be related to the persistent waterlogging that occurs at the site, the substantially elevated fine earth Pb concentration, the high organic matter content of the soil, or a combination of these factors. This leads to the premise that there is further potential for Pb to move down the soil profile if there is insufficient Pb retention capacity.
Figure 4.13. Total fine earth Pb concentrations (mg kg⁻¹) in the soil profile in the area of approximate maximum shot-fall at each of the four sites.
Lead is strongly bound to organic matter and clay in a soil, therefore a sandy and/or recent soil will be less conducive to Pb retention as there are relatively few reactive soil colloids to provide binding sites for Pb. The soil at the McLeans Island range, which has shallow or non-existent topsoil with little organic matter (2.7%), is an example of this. As the Pb concentration of the soil in the shot-fall zone increases due to further Pb shot oxidation, there may be movement of the Pb down the profile. While the fine earth Pb concentrations measured in the McLeans Island soil profile below 100 mm were within the range generally considered to be the background concentration for Pb (10-30 mg kg⁻¹), the lowest Pb concentrations from the transect samples (Figure 4.3) suggest that <10 mg kg⁻¹ is a more suitable background concentration for this Recent soil. If this is taken into account, the Pb concentrations detected in the soil profile can be considered to be elevated throughout most of the profile (0-500 mm), which suggests some Pb movement is already occurring.

While the data suggest movement of Pb at the study sites, the greater loadings of fine earth Pb that will occur in the future as oxidation progresses may cause further problems if there is downward migration of the Pb. Such mobilisation and migration of Pb downward through the unsaturated zone of the soil profile is documented in a recent American study of Pb at an outdoor shooting range (Murray et al., 1997). This downward movement of Pb was noted as a potential threat to groundwater present at the American study site at a depth of <1 m. The groundwater levels at the four sites in this study are all within 10 m of the ground surface (Lobb et al., 1997) and can be considered to be relatively shallow. The high intensity of shooting and rapidly increasing Pb loading on the recent soil at the McLeans Island site indicates a high risk of downward movement into the groundwater in the future as more oxidation occurs. Although the Waihora site is waterlogged during part of the year, the near-surface groundwater is unlikely to be in hydraulic connection with the confined groundwater at >50 m below ground surface. However, the adjacent Halswell Canal may act as a receptor for contaminated near-surface water via horizontal sub-surface flow.
4. Canterbury shooting ranges

4.3.4 General discussion

An investigation of many of the other Canterbury clay target shooting club sites listed in Table 4.1 by McLaren and Clucas (1998) confirmed that all of the sites are contaminated with lead to a greater or lesser extent, generally well in excess of the ANZECC/NHMRC (1992) soil quality guideline of 300 mg Pb kg\(^{-1}\) soil. Although the total area of land affected is relatively small, the loading of Pb at the sites is substantial, and similar to or greater than Pb concentrations resulting from more common sources of Pb contamination (Davies, 1990; Wixson and Davies, 1993). Even sites used by clubs with comparatively small membership numbers (Lobb et al., 1997) were shown to have substantially elevated soil Pb concentrations, showing that sites that sustain relatively light use are still significantly affected by Pb shot contamination. Although the rate of Pb shot dissolution is slow (Jørgensen and Willems, 1987b), the large burden of Pb at the sites has resulted in serious elevation of soil Pb concentrations.

Potential exposure pathways that can be considered for these sites include soil drainage to groundwater; dust accumulating on or adjacent to a site; and surface water drainage at the Waihora site, which is bordered by a tributary of Lake Ellesmere. Rooney et al. (1999) found that the uptake of lead by plants grown in soil contaminated by Pb shot was sufficient to create plant Pb concentrations that exceed allowable concentrations for consumption. At three CTC sites in Canterbury the shot fall areas are within land used for cropping (Lobb et al., 1997). Acute Pb poisoning of cattle grazing on Pb shot contaminated land has occurred overseas (Rice et al., 1987; Braun et al., 1997) and in New Zealand (G.B. Daivs, personal communication, 22 August 1997\(^*\)). Pasture is grazed in the shot fall areas at 14 Canterbury CTC sites (Lobb et al., 1997; Personal observation) There has been little study of the effects of Pb shot contamination to date, however it is already obvious that the shot fall area of shooting ranges should not be used for grazing or food production for animals or humans.

\(^*\) Appendix A
4. Canterbury shooting ranges

4.4 CONCLUSIONS

Clay target shooting ranges are potential sites for Pb contamination of the soil. This study demonstrates that the onset of Pb shot oxidation is relatively rapid, however the high proportion of Pb present as undecomposed Pb shot indicates that the ongoing dissolution of the pellets is a relatively slow process. Total Pb loadings of up to 20% were measured, indicating that gross levels of contamination are possible at clay target shooting ranges. It is expected that already elevated soil Pb concentrations will increase further as more Pb shot dissolves, and the large burden of lead present at the sites may result in leaching of Pb from the soils and more widespread contamination.

The area affected by shooting activities is not always contained within the boundaries of the site where shooting occurs, and existing site dimensions appear arbitrary in most cases. At the very least, consideration is required of the extent of the shot-fall area so that the contaminated area can be defined. It is be desirable that the boundaries of a site are situated to reflect the actual size of the shot-fall area.
Chapter Five

Oxidation Rate of Lead Shot

5.1 INTRODUCTION

The rate of Pb shot oxidation and transformation from elemental Pb into soil Pb compounds is known to be relatively slow, as evidenced by the large proportion of elemental Pb at CTS ranges (Jørgensen and Willems, 1987b; Rooney et al., 1999). Past studies of Pb shot oxidation have not been able to determine the rate of transformation due to the inability to calculate the residence time of Pb shot in the soil at CTS ranges. Using an estimated average residence time and experimental data on the reactivity of crust material, Jørgensen and Willems (1987b) estimated that complete transformation of Pb shot in some Danish soils would occur in 100 to 300 years. Lin (1996) estimated that complete transformation of Pb shot to soil Pb compounds would occur in approximately 200 years. The commonly small proportion of the total Pb burden associated with the soil matrix supports these estimates. The rate of complete transformation estimated in literature may be slow, but the results of Chapter Four showed that the Canterbury CTC at McLeans Island has developed elevated soil Pb concentrations in excess of 300 mg kg⁻¹ after only 7 years. Thus, the onset of transformation appears rapid.

Metallic Pb (Pb⁰) is thermodynamically unstable in aerobic environments and therefore Pb pellets corrode. Lead-oxides appear to form, but are some of the least stable Pb minerals in soil environments. Therefore transformation into or replacement by more stable Pb-carbonate, -sulphate and -phosphate minerals would be favoured. The literature indicates that the crust material on Pb shot is dominated by Pb₃(CO₃)₂(OH)₂ with some incidence of PbCO₃, PbSO₄, PbO and PbO₂.
5. Lead shot oxidation

The stability of the crust minerals appears to be strongly influenced by soil pH. Lead shot crust material has been reported to be dominated by Pb$_3$(CO$_3$)$_2$(OH)$_2$ over a wide soil pH range, from $>7$ (Jørgensen and Willems, 1987b; Lin et al., 1995; Lin, 1996) to values as low as pH 2.9 (Lin, 1996). Jørgensen and Willems (1987b) reported that powdered crust material dissolves rapidly under laboratory conditions at pH $\leq$5, and that only a minute amount of PbSO$_4$ remained at pH 2. This indicates that the solubility of Pb$_3$(CO$_3$)$_2$(OH)$_2$ is substantially lowered in the soil environment. Lin (1996) attributed this dominance of Pb$_3$(CO$_3$)$_2$(OH)$_2$ to the greater pCO$_2$ which exists in soil environments compared to surface environments due to plant respiration and organic carbon mineralisation. This has the effect of decreasing Pb-carbonate solubility, that is, lowering the pH at which solubilisation occurs. At equilibrium, the solution Pb concentration is determined by the least soluble Pb compound(s). This is often quoted to be Pb$_3$(PO$_4$)$_3$OH, but in soils containing corroded Pb shot the solubility-limiting phase is likely to be Pb$_3$(CO$_3$)$_2$(OH)$_2$, the dominant crust mineral (Lin, 1996).

The main objective of this study was to investigate the effects of pH, moisture content, temperature and soil type, and their interactions, on the oxidation and transformation rate of Pb shot under controlled conditions.
5.2 METHODS AND MATERIALS

5.2.1 Experimental design

An incubation experiment was designed to assess the rate of oxidation of Pb shot and transfer of Pb$^{2+}$ to the soil. Two uncontaminated soils were incubated under a range of soil pH, moisture and temperature conditions after the addition of Pb shot. The main components of the experiment are summarised in Table 5.1 and presented diagrammatically in Figure 5.1. Component A consisted of 3 soil pH levels and two soil moisture conditions in factorial combinations; destructive analysis took place every 6 months. Further separate treatments of a 4th pH level, a higher Pb shot loading, and 2 further soil temperatures were each sampled every 12 months. The experiment was continued for a total of 24 months.

Table 5.1. Summary of variables in the four components of the incubation experiment for each of the two soils.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal soil pH</td>
<td>4.5, 5.5, 6.5, 8</td>
<td>4.5, 5.5, 6.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Pb shot loading</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>20%</td>
</tr>
<tr>
<td>Soil moisture content</td>
<td>Field capacity (FC)</td>
<td>70% of FC</td>
<td>FC</td>
<td>FC</td>
</tr>
<tr>
<td>Soil temperature</td>
<td>25°C</td>
<td>25°C</td>
<td>10°C and 30°C</td>
<td>25°C</td>
</tr>
<tr>
<td>Sampling interval</td>
<td>6 months</td>
<td>6 months</td>
<td>12 months</td>
<td>12 months</td>
</tr>
<tr>
<td></td>
<td>(12 months for pH8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.1. Experimental design for incubation experiment: soil treatments and sampling interval for each of the two soils. M₁ represents field capacity soil moisture content; M₂ represents 70% of field capacity soil moisture content.
5.2.2 Experimental procedure and analysis

Soil collection and characterisation

Two uncontaminated soils were selected on the basis of differing texture and potential sorption capacity. Topsoil (0-100 mm) was collected from the former Templeton Centre, Kirks Road (Waimakariri sandy loam; Immature Pallic soil, NZ; Typic Ustifluvent, USA) and the grounds of the Lincoln Township sewage treatment plant (Temuka silt loam; Gley soil, NZ; Mollic Humaquent, USA). Three soil cores (100 mm diameter and depth) were also collected at each site for determination of moisture content at field capacity.

The bulk soil samples were sieved (<4 mm), homogenised, air-dried, and stored in bags. Subsamples of the bulk soils were used for determination of soil physical and chemical properties (Table 5.2), using the methods detailed in Chapter 3.1.

To determine field capacity of the two soils, a cellulose acetate/acetone mixture was applied to the base of the 100 mm diameter cores and allowed to harden before being removed in order to open any pores blocked due to smearing during core collection (Cameron et al., 1992). A polyester mesh cover was secured to the base of the cores to prevent soil loss. The cores were then saturated and placed on a tension table set at 0.1 bar. Once equilibrium was reached the cores were weighed, oven-dried, and weighed again to record the gravimetric water content.

Table 5.2. Selected physical and chemical characteristics of the two uncontaminated soils.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Waimakariri</th>
<th>Temuka</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>CEC (cmolc kg⁻¹)</td>
<td>11</td>
<td>31</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>2.5</td>
<td>6.7</td>
</tr>
<tr>
<td>Oxalate extractable Fe (%)</td>
<td>0.48</td>
<td>0.63</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>61</td>
<td>14</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>49</td>
<td>81</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>
5. Lead shot oxidation

Adjustment of soil pH

Preliminary equilibration curves were prepared using 100 g subsamples of the two soils collected. Lime and HCl was added at various amounts and the moisture content was adjusted to 75% of field capacity. Soil pH was measured after incubation at 25°C for 2 weeks (moisture content maintained). Data is presented in Appendix B.

Following the preliminary study the two bulk soils were each divided into four portions, and lime and HCl was added at amounts required to adjust soil pH to approximately 4.5, 5.5, 6.5 and 8. The soil portions were adjusted to 75% of field capacity and incubated at 25°C for 4 weeks, after which they were air-dried, sieved to <2 mm and stored in readiness for assembly of the experiment. Subsamples of the adjusted soils were taken for final soil pH determination.

Pb shot addition

To prepare individual soil samples for incubation, 200 g subsamples were weighed into 400 mL polyethylene (PET) jars. Sufficient replicate samples were prepared to allow samples to be removed from incubation for (destructive) analysis throughout the 24-month duration of the experiment. Lead shot was added to these subsamples at loadings of either 5% (a common maximum loading of Pb measured at Canterbury clay target shooting sites) or 20% (the utmost maximum loading of Pb measured at a Canterbury clay target shooting site). Bulk Pb shot (No. 8 size; 2.3 mm diameter) was separated into subsamples of 10.00 ± 0.05 g (5%) and 40.00 ± 0.05 g (20%) using a seed-counter. The number of pellets was checked manually, and the final weight and number of pellets was recorded. For each treatment there were 3 replicate jars (Pb shot added) and 1 control jar (no Pb shot). Jars of soil containing Pb shot were mixed. Screw-on lids, in which large holes had previously been bored, were attached to all (treated and control) jars.

De-ionised water was added to all jars to moisten soil samples to approximate either field capacity or 70% of field capacity as required. All samples were then placed in incubators, at either 10°C, 25°C or 30°C as the experimental design dictated. Soil moisture content was checked 2 to 3 times a week throughout the 24-month experiment by weighing, and the weight loss in individual samples was made up by spraying with deionised water. Samples were removed for (destructive) analysis every 6 to 12 months.
5.2.3 Analysis

Soil solution

At each sampling period, the soil solution was removed from the moist soil (Pb shot included) by centrifugation for analysis and then the soil was air-dried. The soil solution was removed by the method described by Elkhatib et al. (1987). The centrifuge apparatus consisted of (a) a soil-containing cup made of PVC with many small holes bored through the base and (b) a solution collection cup, made by cutting off the top half of a 250 mL polypropylene centrifuge bottle (Figure 5.2). The PVC cup was designed to partly fit into the collection cup.

![Figure 5.2. Centrifugal apparatus for removal of soil solution from moist soil.](image-url)
5. Lead shot oxidation

Whatman No. 42 filter paper of the appropriate diameter was used to line the bottom of the PVC cup to prevent the transfer of fine soil particles to the extracted soil solution. About 100 g of soil (dry-weight equivalent) was packed into the PVC cup and covered with parafilm to prevent soil loss and reduce evaporative loss. The apparatus was centrifuged for 30 min at a relative centrifugal force (RCF) of 1800×g. After centrifugation the collection cup was removed and soil solution was poured into a measuring cylinder for volume measurement.

Solution pH was determined immediately after centrifugation then the solution was filtered using a 0.45 µm cellulose acetate disposable filter. The solution was then analysed for Pb, soluble carbon, and major cations and anions. If these analyses were not carried out immediately the solution was frozen until further analysis was performed.

The data from soil solution analysis were used to predict the speciation of Pb in the solutions using GEOCHEM-PC v 2.0 speciation modelling software (Parker et al., 1995) as described in Chapter 3.3.6.

Soil

After removal of the soil solution, the soil was air-dried. All visible Pb shot was removed by hand, then the soil was gently crushed and sieved to <1 mm to recover the remaining Pb pellets. Thus, all Pb pellets were eliminated from subsequent soil analysis. The recovered Pb shot was counted to ensure complete pellet recovery, and then weighed.

Fine earth soil Pb concentrations were assessed by total microwave digestion (Chapter 3.2.1) and 0.04 M EDTA-extraction (Chapter 3.2.2).

Sequential fractionation of fine earth Pb was carried out using the modified Tessier method described in Chapter 3.2.3. For each treatment block of 3 treated jars, the sample with the median soil pH was selected as representative of the treatment, and used for fractionation analysis.
5. Lead shot oxidation

Lead shot crust material

Oxidised crust material on the Pb pellets in samples incubated for 24 months was removed for mineralogical identification by XRD. The Pb shot recovered from the three replicate samples in each treatment was pooled so that sufficient crust material could be obtained for XRD. Removal of the crust material was carried out by ultra-sound treatment. Each sample of pellets (approximately 30 g) was mixed with 50 mL of de-ionised water in a small beaker and exposed to 35 kHz of ultra-sound energy for 3 minutes. The suspended material was decanted, and the process repeated until the suspension was clear after ultra-sound treatment. The suspended material was freeze-dried, weighed and gently ground to a fine powder by hand with acetone. Random orientation samples were prepared for XRD by vertical loading into a sample holder. X-ray diffraction was carried out on a Phillips PW 1729 X-ray generator using Cu Kα₁ radiation (wavelength 1.5405 Å). Prepared samples were continuously scanned in the range 10-80° 2θ at 0.02° 2θ min⁻¹.

Following XRD analysis, crust samples were digested in concentrated HNO₃ (using the total soil Pb method, Chapter 3. 3.2.1) to assess the Pb content of the crust material and the diluted solutions were analysed for Pb concentration by flame AAS.
5.3 RESULTS AND DISCUSSION

5.3.1 Development of crust material

The development of crust material on the Pb shot was clearly seen over the duration of the experiment in the form of a mottled surface appearance, caused by light grey, white, and brown coatings (Plate 5.1). The visual crust development with time is reflected in solution- and soil-Pb results discussed in the following sections.

To explain the development of crust material, Lin (1996) cited the hypothesis of Park and MacDiamid*, applying it to the rise in temperature of Pb pellets when they are fired from the shotgun (Chapter 2.2.1). While Lin’s linkage of minute fractures observed in the Pb shot and the hypothesis of Park and MacDiamid is plausible, the Pb shot used in this experiment had not been fired. Although the Pb shot used for this experiment was not investigated for structural fractures, the development of crust material on unused Pb shot suggests that an alternative oxidation mechanism was responsible.

The stability of some Pb minerals in water is shown in Figure 5.3 to give an indication of the relative stability of Pb minerals in soils. The topsoil of the majority of Canterbury soils would be considered to be aerobic and redox values for aerobic soil environments are generally between 0.4 and 0.6 (McLaren and Cameron, 1996).

* When the temperature of a mineral is raised, a point is reached at which the atomic structure of a mineral is disordered but loosely tied together, allowing ions to diffuse through the crystal with ease.
Plate 5.1. Development of crust material on Pb shot incubated in Waimakariri soil for up to 24 months at field capacity moisture content and 25°C; soil pH = 5.2 ± 0.2; 6 × magnification.
5. Lead shot oxidation

Figure 5.3. Stability relations among Pb compounds in water at 25°C (from Brookins, 1988). Dissolved species activities (similar to soil solution data gained from the results of this chapter): [Pb$^{2+}$] = 10$^{-6}$ M; [Inorganic C] = 10$^{-3}$ M; [S] = 10$^{-3}$ M.
Corrosion of metals is caused by a flow of energy from metal to soil, or between electrolytic cells of differing potential on the same metal surface, where the soil solution acts as the electrolyte (Chandler and Bayliss, 1985). Where a metal surface is in contact with a soil particle, the point of contact leads to a reduced oxygen concentration on the metal surface. This gives rise to differential aeration of the surface, resulting in anodic and cathodic areas, referred to as electrolytic or corrosion cells. The area with reduced oxygen concentration becomes the anodic area at which localised corrosion occurs. The reactivity of Pb is markedly increased by the presence of small proportions of other metals, notably Sb (Burns, 1948). New Pb pellets commonly contain approximately 1-7% Sb and <2% As, and sometimes contain <0.5% Ni (Jørgensen and Willems, 1987b; Tanskanen et al., 1991; Winchester Ammunition, 2002). Where large cathodic areas surround a highly localised anodic area the current density will be very large at the anodic site, and attack on the metal will be rapid. Such a differential may be present where a soil particle is in contact with the surface of a Pb pellet, thereby causing the rapid corrosion observed in Plate 5.1.

Winchester Ammunition (2002)

The corrosion of Pb shot surfaces can be described using the half equations:

**Oxidation:** \( \text{Pb}^{(c)} - 2e \rightarrow \text{Pb}^{2+} \quad \log K = 4.33^* \)  

**Reduction:** \( \frac{1}{2}\text{O}_2(g) + 2\text{H}^+ + 2e \rightarrow \text{H}_2\text{O} \quad \log K = 41.55^† \)

\[ \text{Pb}^{(c)} + \frac{1}{2}\text{O}_2(g) + 2\text{H}^+ \rightarrow \text{Pb}^{2+} + \text{H}_2\text{O} \quad \log K = 44.88 \]

Commonly, the corroding surface reacts with oxygen and immediately forms an oxide coating (passivation film) which tends to protect the surface from the corrosive environment: \( \text{Pb}^{2+} + \text{H}_2\text{O} \rightarrow \text{PbO} + 2\text{H}^+ \quad \log K \sim 12.8^‡ \)

In some situations these films are either not formed or are not particularly effective in stopping reactions between the environment and the metal, allowing further formation of metal salts. The latter appears to be the case for Pb shot corrosion in soil.

---

* Lindsay (1979)
† Stumm and Morgan (1996)
‡ Lindsay (1979)
The minor amounts of PbO and PbO₂ identified in the crust material of Pb shot (Jørgensen and Willems, 1987b; Fahrenhorst and Renger, 1990; Tanskanen et al., 1991; Lin et al., 1995; Lin, 1996; Murray et al., 1997) suggests that these minerals are the likely primary corrosion products. Experimentation by Lin (1996) consisting of five months exposure to air of pellets after crust material had been removed, resulted in a discontinuous, thin film of PbO and some Pb₃(CO₃)₂(OH)₂ crystals. Atmospheric CO₂ is likely to have contributed to the formation of the minor amount of Pb-carbonate material. Figure 5.3 indicates that Pb-oxides are not stable at pHs common in soils. The formation of Pb-carbonate transformation products from PbO can be described by (Luo and Hong, 1997):

\[
PbO(s) + HCO_3^- \rightarrow PbCO_3(s) + OH^- \quad (5.5)
\]

\[
3PbO(s) + 2H_2O + 2HCO_3^- \rightarrow Pb_3(CO_3)_2(OH)_2(s) + 2OH^- \quad (5.6)
\]

Thus, the dissolved CO₂ in soil solutions appears to enhance the rate of such transformation reactions.

Burns (1948) found that in the presence of CO₂(g) and dilute organic acids, the corrosion product on lead cable sheathing was Pb₃(CO₃)₂(OH)₂. The author states that when Pb metal is in contact with acetic acid vapour, Pb-carbonate is precipitated at an appreciable, although very small, distance from the metal surface and retards, but does not eliminate, the corrosion. In soil environments, soil organic acids would constantly supply the H⁺ ions required for the corrosion reaction. Oxygen in the atmosphere and soil air would depolarise the cathodic area which would lead to continuing transfer of current and corrosion.

Unlike atmospheric corrosion observed by Burns (1948), corrosion of Pb shot in contact with soil would appear to result in the precipitation of corrosion products at the metal surface. Electron microprobe images of cross sections of corroded pellets obtained by Lin (1996) show the corrosion products immediately adjacent to the pellet core. The pellet crust material consisted of two concentric rims (Chapter 2.2.1), suggesting replacement of PbO by Pb-carbonates. PbSO₄ can also be replaced by Pb-carbonates according to the reaction (Park and MacDiarmid, 1970, in Lin, 1996):

\[
PbSO_4 + H_2O + CO_2 \rightarrow PbCO_3 + SO_4^{2-} + 2H^+ \quad (5.7)
\]
Factors relevant to the rate of Pb shot corrosion in soil are discussed briefly below.

**Moisture content**

Water is the basis of the essential electrolyte required for electrochemical corrosion reactions, and thus soil conductivity is directly affected by soil moisture content and ionic strength. The amount of metal that will be removed by corrosion is directly proportional to the amount of current flow. The corrosiveness of water itself depends on the amount of dissolved oxygen, and other factors including organic acid content. Cycles of wet and dry conditions can result in the concentration of corrosive species and mechanical action which tends to break down protective corrosion films and coatings on metal surfaces (Evans, 1981).

**Oxygen**

Oxygen is one of the most influential factors on corrosion in the soil environment (Burns, 1948). It acts as a depolariser of cathodic areas, so that difference in electrical potential and therefore current is maintained between anode and cathode. The corrosion rate of metals in acids increases at a rate approximately proportional to the oxygen content of the water (Evans, 1981). The gaseous oxygen concentration decreases with increasing depth of soil, thus the topsoil, where Pb shot are deposited, is potentially the most corrosive area of the soil profile. Even so, a Pb cannonball found buried at 2.5 m depth for up to 160 years exhibited a corrosion crust visually similar to those observed on Pb shot (NZ Press Association, 1998).

**Soil pH**

More acidic soils represent a greater corrosion risk to Pb due to the role of H⁺ ions in the Pb corrosion reaction (Equation 5.3). Corrosion severity generally increases with the partial pressure of CO₂, due to the formation of carbonic acid and the resulting depression of solution pH.

**Temperature**

There is a dearth of information on the effect of temperature on metal corrosion, apart from very high temperatures (for example >1000°C) which are considered irrelevant to this experiment. This lack of chemical information can be ascribed to the competing influences of temperature on the corrosion process. Although higher temperatures increase the reaction rate, the chemical nature of corrosion products formed and thus the passivity of the film is also temperature dependent (Fairbrother and Reniers, 2002).
5. Lead shot oxidation

**Soil resistivity**

Resistivity is inversely proportional to, and is used as a broad indicator of, soil corrosivity. Soil resistivity generally decreases with increasing water content and the concentration of ionic species. Sandy soils tend to have high resistivity and therefore low corrosivity; Soils with low resistivity and high corrosivity include clay, saline, and organic soils (CorrosionSource, 2002). Uhlig (1971) states that soils high in organic acids may have a Pb corrosion rate 4-6 times greater than the average for soils.

**Soil texture**

Corrosion cell activity is largely dependent on soil texture as it determines the size of the point of contact between soil particle and metal surface (anode; Burns, 1948). This, in turn, impacts upon the relative size and therefore polarisation of the anode and cathode. The finer the soil texture, the less differential aeration, and the relatively smaller the cathodic area becomes, so that a polarised state is more likely to be maintained, despite the depolarising action of the oxygen present in soil air (Burns, 1948).

In general, aerobic soils with high moisture content, high dissolved salts (electrical conductivity) and high acidity will be most corrosive. The last two factors discussed (soil resistivity and soil texture) appear to contradict each other in terms of the effect of soil texture on the corrosion rate. Soil resistivity concentrates on the relationship between soil chemistry and texture, but soil texture also has a purely physical action. This demonstrates the complex nature of environmental determinants on metal corrosion rate.
5.3.2 Analytical precision

The graphed data presented in the following sections represents Pb concentrations from three replicate samples given the same treatment. Significant variation between replicates is apparent for both solution and soil data, with standard deviations being relatively large in some cases. However, trends in the data are clear.

Significant variation between soil analysis replicates (within each replicate sample) was most likely associated with subsampling soil containing particulate crust material of <1 mm diameter. It has been noted that even small differences in the amount of particulate Pb between subsamples can result in large differences in Pb content. Precision was improved by analysing further replicates so that high data points could be removed as outliers (containing particulate Pb). Thus, coefficients of variation were below 20% (EDTA-extractable Pb: range 0.4-19.9%, mean 9.5%; total Pb: range 1.0-19.4%, mean 8.7%).

It is suspected that the accuracy of soil Pb concentrations for some samples incubated for 12 or 18 months was compromised by changes in methodology used in sieving of dried soil + Pb shot samples. Greater amounts of particulate crust material appear to have been removed and entered the soil sample. Soil Pb concentrations were unexpectedly high for most total and EDTA-extractable soil Pb analyses of the 12 month samples, and some of the 18 month samples. Soil fractionation data also indicated a disproportionate Pb carbonate fraction in the samples. This is confirmed by Appendix C, which clearly shows 12 month Pb shot with no crust material and a more angular appearance (cf. 6 months). Thus, soil Pb concentrations measured are most likely to overestimate the true concentration for the 12 month samples. The overestimation appeared to occur most commonly for the middle two pH treatments. These treatments generally developed the greatest amounts of crust material and thus partial crust removal from these samples would easily erroneously raise soil Pb data.
5.3.3 Effect of soil pH

Effect of pH on crust development

Nominal soil pH values of 4.5, 5.5, 6.5 and 8.0 were chosen for the experiment. Initial values attained for soil pH in the two soils were approximately 4.8, 5.2, 6 and 7.5. In both soils, crust material developed on Pb shot at all soil pH values (Plate 5.2). The amount of crust material was noticeably greater in the two higher pH treatments compared with the lowest pH treatment; variation between the two lowest pH treatments was more difficult to determine by eye. It is unclear to what extent the observed differences are due to the effects of pH on corrosion rate or the dissolution of the resulting corrosion products.
Plate 5.2. Effect of pH on Pb shot corrosion crusts after 24 months incubation in Temuka soil at field capacity moisture content and 25°C (6 × magnification).
Effect of pH on soil solution and solid phase Pb

Figure 5.4 shows that the concentration of Pb in solution increased over the 24-month period in both soils and solution pH had a strong effect on Pb solubility. Solution Pb concentrations in the uncontaminated soils were <40 µg L\(^{-1}\). Maximum mean solution Pb concentrations for the two soil types reached 8-10 mg L\(^{-1}\) at the lowest solution pH (ca. 4.4) and <1 mg L\(^{-1}\) at the highest solution pH (ca. 7.0). Solution pH values were approximately 0.5 pH units lower than soil pH measured using the method in Chapter 3.1.3. In most treatments solution Pb concentrations appeared to be stabilising by the end of the experiment. There was little difference in solution Pb concentrations between the two soils, suggesting that soil properties other than pH have little effect on the rate of crust dissolution.

![Figure 5.4. Effect of solution pH on soil solution Pb concentrations (mg L\(^{-1}\)) in Waimakariri and Temuka soil incubated with Pb shot at field capacity moisture content and 25°C. Error bars indicate standard deviation.](image-url)
In both soils, the solution pH of control samples decreased during the 24-month incubation period, but Pb-treated samples generally had greater solution pHs than corresponding control samples (Figure 5.5). This trend was observed in all treatments. A similar pH-elevation effect was observed by Chen et al. (2002) in a field study at a contaminated shooting range.

There are three factors most likely to contribute to this effect:

(i) The Pb corrosion reaction consumes H⁺ ions (Equation 5.3);
(ii) The formation of Pb-carbonate transformation products from the probable primary corrosion product (PbO) produces OH⁻ ions (Equations 5.5 and 5.6);
(iii) The dissolution of Pb-carbonates is an acid-consuming process:

\[
PbCO_3 + 2H^+ \rightarrow Pb^{2+} + CO_2(g) + H_2O \quad \log K = 4.65^* \quad (5.8) \\
Pb_3(CO_3)_2(OH)_2 + 6H^+ \rightarrow 3Pb^{2+} + 4H_2O + 2CO_2 \quad \log K = 17.51^* \quad (5.9)
\]

Fine earth Pb concentrations rose rapidly within 6 months (Figure 5.6). High adsorption affinity of the soils for Pb resulted in relatively rapid sorption of soil solution Pb onto the soil solid phase. Fine earth Pb enrichment factors of 81-353 (Waimakariri soil) and 105-219 (Temuka soil) were measured for the three lower pH treatments after 6 months incubation with Pb shot. For the highest pH treatment, enrichment factors of over 300 were measured in both soils after 12 months incubation. It can be noted from Figure 5.6 that some of the data for 12 and 18 months, particularly for the middle two pH treatments, show anomalously high soil Pb concentrations. This is due to a greater-than-average amount of crust material contained in these samples, as discussed in Section 5.3.2. After taking this into account, the temporal trends indicate that soil Pb concentrations became steady after 12 months incubation for the three highest pH treatments. For the lowest pH treatment, soil Pb concentrations appear to become steady for the Waimakariri soil after 18 months; those for the Temuka soil appear to be increasing throughout the 24 month incubation period. This may be a consequence of the greater sorption capacity of the Temuka soil.

* From Lindsay, 1979
Figure 5.5. Solution pH data for both soils with Pb shot and controls incubated at field capacity moisture content and 25°C. Error bars indicate range.
Comparison of the sequential fractionation data for the initial uncontaminated soil and incubated (contaminated) soil shows a substantial shift in the distribution of Pb between fractions (Figure 5.7). Negligible Pb was associated with the carbonate fraction in the untreated soils. Soil Pb was largely present in oxide, organic or residual fractions. In samples incubated with Pb shot for 24 months approximately half the soil Pb was in potentially labile exchangeable and carbonate fractions, and half in oxide and organic fractions. It was noted in Chapter 3.2.3 that the carbonate fraction may include some weakly specifically adsorbed Pb. However, for the system Pb shot system discussed in this thesis, Pb carbonate corrosion products that have precipitated directly onto the soil solid phase are likely to dominate the nominal carbonate fraction. The high proportion of Pb in the carbonate fraction indicates there is a substantial pool of soil solid phase Pb with potential for solubilisation under favourable conditions. This could be capable of maintaining solution Pb concentrations over a long period.

The proportion of Pb in the exchangeable fraction reduced with increasing soil pH, following the relation between Pb sorption affinity and pH, and Pb-carbonate solubility. For the Waimakariri soil, Pb was contained predominantly in the carbonate and oxide fractions. For the Temuka soil, the effect of greater soil organic matter was evident, as Pb in the oxide fraction was reduced in favour of the organic fraction.

Figure 5.6. Effect of pH on fine earth Pb concentrations (mg kg$^{-1}$) in Waimakariri and Temuka soil incubated with Pb shot at field capacity moisture content and 25°C. Error bars indicate standard deviation.
5. Lead shot oxidation

Figure 5.7. Effect of pH on the proportion (%) of fine earth Pb in nominal fractions of Waimakariri and Temuka soil incubated with Pb shot at field capacity moisture content and 25°C.
5. Lead shot oxidation

The substantial shift in the distribution of Pb between fractions in uncontaminated and contaminated soil suggests a similar shift in the mechanism of Pb solubility control: adsorption in the uncontaminated soil and precipitation-dissolution in contaminated soil. Figure 5.8 illustrates the solubility of the Pb minerals most commonly reported to be present in Pb shot corrosion crust material. Concentrations of total soluble Pb (PbTot) in solutions extracted from soil samples incubated with Pb shot were in the order of 10^-6-10^-4 mol L^-1. It would appear that these Pb concentrations are most likely to be controlled by PbCO_3 solubility, which is dependent on pH. At constant pCO_2, a high pH will result in a low equilibrium solution Pb concentration. As pH decreases, the increasing solubility of PbCO_3 allows a greater equilibrium solution Pb concentration.

![Figure 5.8](image-url)

Figure 5.8. The solubility of important Pb minerals at 25°C in terms of pH, PCO_2(g) and Pb^{2+} activity, using [SO_4^{2-}] = 10^{-3} M (the approximate soil solution concentration measured in the experiment) and assumed PCO_2(g) of 0.03 atm. Equilibrium constants from Lindsay (1979); see Appendix E.
Figures 5.9 and 5.10 show the activity of Pb\(^{2+}\) plotted versus solution pH for the Waimakariri and Temuka soils respectively, as compared to the solubility of PbCO\(_3\). Soil solution data (concentrations of Pb, major anions and cations, organic and inorganic carbon, and pH) were input into the speciation model GEOCHEM-PC in order to estimate Pb\(^{2+}\) activity and the pCO\(_2\). For each case (0, 6, 12, 18 and 24 months), hypothetical values for pCO\(_2\) were calculated by GEOCHEM-PC from inputs of pH and inorganic carbon concentration. Re-equilibration of CO\(_2\)\(_{(aq)}\) in soil solution samples with the atmosphere may have occurred before or during determination of inorganic carbon concentrations, resulting in underestimation of pCO\(_2\) values using the model. Estimated pCO\(_2\) values gained for each pH-treatment set (0-24 months) generally ranged between 1.8 and 3.5, and the range of values has been used to plot an area of PbCO\(_3\) stability. It can be seen from Figures 5.9 and 5.10 that such variation in pCO\(_2\) has relatively little influence on PbCO\(_3\) solubility, particularly compared to the effect of pH.

Figures 5.9 and 5.10 show that as the solution pH increases the plotted groups of data move closer to the area of PbCO\(_3\) stability. Therefore the likelihood of solution Pb concentration being limited by PbCO\(_3\) solubility increases with pH. The stability plots indicate that at the highest pH, maximum allowable Pb solubility appears to be reached after 12 months incubation. This concurs with the trend illustrated in Figure 5.4 where solution Pb concentrations at the highest pH treatment became steady most rapidly. As treatment solution pH lowers, Figure 5.4 suggests that most of the systems are also approaching equilibrium, therefore it would be expected that plotted data points in Figures 5.9 and 5.10 would be nearer the line of PbCO\(_3\) stability. Possible reasons for the anomaly may be associated with the estimations involved in producing the graphs, as discussed above. In addition, free Pb\(^{2+}\) may be underestimated by GEOCHEM-PC for the lower pH treatments.

It would appear that the pH-dependent dissolution of the corrosion products is the first of two mechanisms determining soil and solution Pb concentrations in the reaction between Pb shot and soil (Pb shot corrosion $\rightarrow$ crust dissolution $\leftrightarrow$ solution Pb $\leftrightarrow$ soil sorption of Pb).
Figure 5.9. Waimakariri soil solution data plotted with the solubility of PbCO₃ (shaded area); Pb²⁺ activity (mol L⁻¹) and PCO₂(g) range calculated using the GEOCHEM-PC model; Equilibrium constants from Lindsay (1979).
Figure 5.10. Temuka soil solution data plotted with the solubility of PbCO$_3$ (shaded area); Pb$^{2+}$ activity (mol L$^{-1}$) and PCO$_2$(g) range calculated using the GEOCHEM-PC model; Equilibrium constants from Lindsay (1979).
The second mechanism in the Pb shot-soil system is the sorption of Pb from solution by soil colloids. Because of the high affinity of Pb for soil, Pb will be readily removed from solution, which is itself in equilibrium with soluble corrosion products. The amount of Pb sorption is strongly influenced by solution Pb concentration and pH. The influence of equilibrium solution metal concentration on metal sorption, where metal sorbed increases proportionally to metal in solution at constant pH, is well known. A strong relationship between soil solution pH and Pb sorption has been demonstrated, with metal sorption increasing in proportion to pH (Harter, 1983; Adriano, 1986; Basta and Tabatabai, 1992b). This relationship is shown diagrammatically by Figure 5.11.

The effect of pH on Pb sorption by the incubated soils can be illustrated by calculating the distribution coefficient, \( K_d \) (Table 5.3). A high \( K_d \) value corresponds to strong binding and precipitation of Pb to the soil or weak complexation of Pb in solution. Although Pb sorption is favoured at high pH it is not immediately evident in Figure 5.6 due to the low supply of Pb to the solution caused by the increased stability of carbonate crust material at the highest pH (Figure 5.4), as discussed above.

\[
K_d = \frac{\text{metal sorbed (mg/kg)}}{\text{metal in solution (mg/L)}}
\]

Figure 5.11. Diagrammatic representation of the effect of soil pH on soil Pb sorption.
5. Lead shot oxidation

<table>
<thead>
<tr>
<th>Waimakariri</th>
<th>Mean Solution pH</th>
<th>Mean K\textsubscript{d}</th>
<th>Temuka</th>
<th>Mean Solution pH</th>
<th>Mean K\textsubscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>263</td>
<td>4.5</td>
<td></td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>341</td>
<td>4.7</td>
<td></td>
<td>1344</td>
<td></td>
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<tr>
<td>5.4</td>
<td>1525</td>
<td>5.3</td>
<td></td>
<td>1439</td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>6145</td>
<td>6.9</td>
<td></td>
<td>6842</td>
<td></td>
</tr>
</tbody>
</table>

Therefore, at the highest pH treatment a greater amount of sorption is limited by the equilibrium between solution and sorbed Pb at a Pb\textsuperscript{2+} concentration enforced by the PbCO\textsubscript{3} solubility (Figure 5.11). At the lowest pH treatment the soil Pb concentration continues to increase with time due to the higher solution Pb concentration allowed by high PbCO\textsubscript{3} solubility. The plotted solubility diagrams (Figures 5.9 and 5.10) suggest that solution Pb concentration, if controlled purely by PbCO\textsubscript{3}, has the potential to be higher still.

Soil Pb sorption capacity has the potential to limit the equilibrium solution Pb concentration below that determined by the pH-dependent dissolution of PbCO\textsubscript{3}. This is most likely to occur at relatively low soil pH, as illustrated by Figure 5.12. Higher Pb sorption capacity will result in lower Pb\textsuperscript{2+} activity. It is possible that greater soil pH could actually increase the equilibrium solution Pb concentration, but further pH increase will eventually result in control by PbCO\textsubscript{3}.

It has been suggested that the rate of Pb shot degradation may be slowed by surface coverage of Pb shot by transformation products (Uren \textit{et al.}, 1995), as would be expected from a passivating film on a corroding surface (Evans, 1981). The current results suggest that only once equilibrium is reached between crust minerals, soil solution Pb and sorbed Pb, crust material will begin to build up in an appreciable amount (for example, the two highest pH treatments in Plate 5.2). It seems likely that in this state, the corrosion rate of Pb shot slows dramatically. Thus, a relatively thick layer of crust material may be required for passivation, rather than a thin film as discussed by Evans (1981). The large proportion of Pb present as intact Pb shot (Plate 5.2) confirms that there is a control on the corrosion process.
5. Lead shot oxidation

Figure 5.12. Diagrammatic representation of the relative importance of corrosion compound solubility and soil Pb sorption capacity on equilibrium solution concentration control.

Effect of pH on crust crystallography

X-ray diffraction patterns of corrosion crust material removed from the Pb shot (Figure 5.13) indicate that the minerals present in or associated with the corrosion crusts included Pb₃(CO₃)₂(OH)₂, PbCO₃, PbSO₄, thorikosite (Pb₃(SbO₃)(OH)Cl₂), and calcite (CaCO₃), and quartz and feldspar from the soil material. The dominance of Pb₃(CO₃)₂(OH)₂ in the corrosion crust at all four soil pHs follows the trend reported in other studies (see Chapter 2.2.1). Jørgensen and Willems (1987b) reported that greater amounts of PbCO₃ occurred in the crust of Pb shot recovered from soil samples with pH 7.4, than those with pH 5.5. High pH dictates that less dissolution of all carbonate and oxide crust minerals takes place (Figure 5.8), and accounts for this greater presence of PbCO₃. In Figure 5.13, the majority of PbCO₃ diffraction peaks are obscured by adjacent Pb₃(CO₃)₂(OH)₂ peaks, but at the highest soil pH the PbCO₃ peak at approximately 37°20 is great enough to be distinguished against the adjacent Pb₃(CO₃)₂(OH)₂ peak, which suggests greater abundance of PbCO₃.
It is puzzling that the stability diagrams indicate control of Pb$^{2+}$ solubility by PbCO$_3$, yet the dominant mineral reported in the corrosion crust is invariably Pb$_3$(CO$_3$)$_2$(OH)$_2$, which has greater solubility in soil (Figure 5.8). In pure water PbCO$_3$ is slightly soluble and Pb$_3$(CO$_3$)$_2$(OH)$_2$ is insoluble (Weast, 1974). However, in soils the presence of CO$_2$(aq) and electrolytes alters the solubility relationship so that Pb$_3$(CO$_3$)$_2$(OH)$_2$ is more soluble than PbCO$_3$ (Figure 5.8). It is unclear why the more soluble Pb$_3$(CO$_3$)$_2$(OH)$_2$ dominates the crust material in all reported studies. Jørgensen and Willems (1987b) determined that pellet crust material dissolved rapidly during a pH-static titration, but the procedure did not differentiate between Pb$_3$(CO$_3$)$_2$(OH)$_2$ and PbCO$_3$ due to identical acid requirements for Pb produced (2 moles H$^+$ per mole Pb$^{2+}$). No further explanation of the dominance of Pb$_3$(CO$_3$)$_2$(OH)$_2$ in pellet crust material is available. It is hypothesised Pb$_3$(CO$_3$)$_2$(OH)$_2$ is less soluble than PbCO$_3$ in this Pb shot–soil system.
5.3.4 Effect of moisture content

Effect of moisture content on crust development

In both soils, crust material developed on Pb shot at all soil pH values, as shown by Plate 5.3. The amount of crust material increased in proportion to pH, as was observed for the high moisture content treatment (Plate 5.2). However, the amount of crust material present at corresponding pH was consistently substantially less for the lower moisture treatment. The role of the soil solution as the electrolyte in the electrochemical corrosion of metal surfaces was established in Section 5.3.1. It appears that the reduced amounts of crust material present on the Pb shot incubated with soil at 70% of field capacity was a result of the reduced presence of electrolyte required for corrosion to proceed. This is supported by the generally higher soil pH generated in the high moisture content treatments by the greater amount of corrosion.
Plate 5.3. Effect of moisture content on Pb shot corrosion crusts after 24 months incubation in Waimakariri soil at 25°C (6 × magnification).
5. Lead shot oxidation

Effect of moisture content on soil solution and solid phase Pb

Following the trend observed for the high moisture content treatment, the solution Pb concentrations increased over the 24 month period in both soils incubated at low moisture content. Solution pH again demonstrated a strong effect on Pb solubility (Figure 5.14). Mean solution Pb concentrations were generally considerably less than corresponding pH treatments at higher moisture content. This would be expected for the lower corrosion rates indicated by Plate 5.3. Maximum mean solution Pb concentrations for the two soil types were <3 mg L$^{-1}$ at the lowest solution pH (ca. 4.5). At the highest solution pH, maximum mean Pb concentrations were considerably different for the two soils, with 0.1 mg L$^{-1}$ in the Temuka soil and 2.9 mg L$^{-1}$ in the Waimakariri soil. The high Waimakariri value corresponds with a drop in solution pH of 1 unit during the experimental period. The drop in solution pH was most likely caused by the release of H$^+$ into solution corresponding to the sorption of Pb onto soil solid phases. The solution pH of the middle pH treatment also dropped to a similar level as the lowest pH treatment. Thus, solution pH and Pb concentration became relatively similar in all three treatments after 24 months incubation. The temporal trend in pH reduction was less pronounced in the Temuka soil, most likely due to the greater buffer capacity indicated by comparison of the CEC values (Table 5.2).

Fine earth Pb concentrations rose rapidly within 6 months, but not to the same extent as in the high moisture content study (Figure 5.15). Enrichment factors of 50-189 (Waimakariri soil) and 20-50 (Temuka soil) were measured for the three pH treatments after 6 months incubation with Pb shot. Thus, even when corrosion was limited by low soil moisture, soil Pb concentrations rapidly became elevated above the ANZECC guideline limit of 300 mg kg$^{-1}$. Once again, anomalously high soil Pb concentrations were evident in some of the 12- and 18- month data. After taking this into account, the temporal trends indicate that soil Pb concentrations generally became steady after 12 months incubation. The exception appears to be the lowest pH treatment for the Temuka soil, which mirrors the trend in the same soil at high moisture content, and may be due to the greater sorption capacity of this soil.
Figure 5.14. Effect of moisture content on soil solution Pb concentrations (mg L\(^{-1}\)) in Waimakariri and Temuka soil incubated with Pb shot at 25ºC. Error bars indicate standard deviation.
5. Lead shot oxidation

Figure 5.15. Effect of moisture content on fine earth Pb concentrations (mg kg\(^{-1}\)) in Waimakariri and Temuka soil incubated with Pb shot at 25\(^\circ\)C. Error bars indicate standard deviation.
The effect on Pb sorption of temporal reduction of pH within pH treatments is illustrated by the $K_d$ values shown in Table 5.4. In the Waimakariri soil, solution pHs were lowered to such an extent in the two higher pH treatments that $K_d$ values for all three treatments were of similar magnitude. The $K_d$ value for the highest pH treatment in the Temuka soil indicates that under these conditions the soil had comparatively greater affinity for Pb at low moisture content, however this appears to be due to anomalously low solution Pb concentrations after 24 months incubation (Figure 5.14).

### Table 5.4. Relationship between $K_d$ and solution pH in Waimakariri and Temuka soil incubated with Pb shot after 24 months incubation at 70% of field capacity and 25°C.

<table>
<thead>
<tr>
<th>Waimakariri</th>
<th>Temuka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Solution pH</td>
<td>Mean $K_d$</td>
</tr>
<tr>
<td>4.4</td>
<td>393</td>
</tr>
<tr>
<td>4.3</td>
<td>635</td>
</tr>
<tr>
<td>4.3</td>
<td>398</td>
</tr>
</tbody>
</table>

The shift in the distribution of Pb between fractions once soil became exposed to Pb was similar to that for the high moisture content study (Figure 5.16 and 5.17). Once again, approximately half the soil Pb was in potentially labile exchangeable and carbonate fractions, and half in oxide and organic fractions. The proportion of Pb in the exchangeable fraction generally reduced with increasing soil pH, following the relation between Pb sorption and pH, and Pb-carbonate solubility. The effect of a temporal reduction of pH within pH treatments is clearly shown by a substantial increase in the proportion of Pb in the exchangeable fraction for the highest pH treatment in both soils. As for the high moisture content study, the greater amount of soil organic matter in the Temuka soil resulted in less Pb in the carbonate and oxide fractions, relative to the Waimakariri soil, in favour of Pb in the organic fraction.
Figure 5.16. Effect of moisture content on the proportion (%) of fine earth Pb in nominal fractions of Waimakariri soil incubated with Pb shot at 25°C.
Figure 5.17. Effect of moisture content on the proportion (%) of fine earth Pb in nominal fractions of Temuka soil incubated with Pb shot at 25°C.
Figure 5.18 shows the activity of Pb$^{2+}$ plotted versus solution pH for the Waimakariri and Temuka soils, as compared to the solubility of PbCO$_3$. Values for Pb$^{2+}$ activity and pCO$_2$ were obtained from GEOCHEM-PC outputs as described above (Section 5.3.3). The plots are similar to those generated for high soil moisture content. The stabilising trend indicated in the data for soil solution and fine earth Pb concentrations does not appear to be reflected in the stability diagrams, where data could be expected to be approaching the area of PbCO$_3$ stability. However, as before, the estimations involved in producing the graphs may preclude accurate illustration of the system.
Figure 5.18. Soil solution data for each pH treatment at low moisture content from both soils plotted with the solubility of PbCO₃ (shaded area); Pb²⁺ activity (mol L⁻¹) and pCO₂ range calculated using the GEOCHEM-PC model.
5.3.5 Effect of temperature

Effect of temperature on crust development

In both soils, crust material developed on Pb shot at all soil temperatures, as shown in Plate 5.4. The amount of crust material on Pb shot was substantially less at 10°C than at the two higher temperatures. Little difference can be seen by eye between the crust material developed at 25°C and 30°C. Change in temperature is most likely to impact on the Pb shot-soil system as follows:

(i) Kinetics –
The rate of surface reactions and/or transport of reactants and solutes will be slower at low temperatures. This may have caused reduced presence of crust material at 10°C relative to the higher temperature treatments.

(ii) Solubility of CO₂ –
Contrary to the majority of minerals, a decrease in temperature increases the solubilities of carbonate minerals, as the solubility of CO₂ is a function of temperature (Figure 5.19). Increased Pb-carbonate solubility may have caused the reduced presence of crust material at 10°C.

![Figure 5.19. Henry's Law constant Kₜ for the solubility of CO₂ in water as a function of temperature (°C); Kₜ values from Lloyd and Heathcote (1985); Henry's Law: [CO₂(aq)] = Kₜ × P CO₂.](image)
Plate 5.4. Effect of temperature on crust development on Pb shot in Waimakariri soil after 24 months incubation at field capacity (6× magnification).
5. Lead shot oxidation

**Effect of temperature on soil solution and solid phase Pb**

In general, incubation temperature had a strong effect on soil solution Pb concentrations (Figure 5.20). The plots show that trends in solution Pb concentrations in Waimakariri soil increased relatively proportional to temperature, but were approximately equidistant in Temuka soil. At $10^\circ$C, the solution Pb concentrations in Waimakariri and Temuka soils after 24 months incubation were <5% and 12% respectively of those at $30^\circ$C. For both soils, the generally higher solution pH of the $10^\circ$C treatment relative to the $25^\circ$C and $30^\circ$C treatments would have contributed to this effect to some extent.

![Graph showing effect of temperature on soil solution Pb concentrations](image)

**Figure 5.20.** Effect of temperature on soil solution Pb concentrations (mg L$^{-1}$) in Waimakariri and Temuka soil incubated with Pb shot at field capacity moisture content. Solution pH range is for 0 months + all treated samples. Error bars indicate standard deviation.
5. Lead shot oxidation

Figure 5.21 shows that fine earth Pb concentrations rose rapidly within 12 months, and less Pb sorption occurred onto both soils at 10°C relative to the samples incubated at the higher temperatures. Enrichment factors of 134-436 (Waimakariri soil) and 149-242 (Temuka soil) were measured for the three temperature treatments after 24 months incubation of soil with Pb shot. Once again, some of the soil Pb data obtained from samples incubated for 12 months appear anomalously high. Due to only two data collection periods for the temperature treatments, it is more difficult to interpret temporal trends than for previous treatments.

![Figure 5.21](image)

Figure 5.21. Effect of temperature on total fine earth Pb concentrations (mg kg\(^{-1}\)) in treated samples incubated at field capacity moisture content. Soil pH range is for 0 months + all treated samples. Error bars indicate standard deviation.
5. Lead shot oxidation

Two possible effects of temperature on the Pb shot-soil system – kinetics and CO₂ solubility – were presented above. If the dominant effect of temperature was solubility of CO₂, increased Pb-carbonate solubility at 10°C should have been reflected in higher solution- and soil Pb concentrations. Instead, the relatively low solution Pb concentrations suggest that the dominant effect of temperature is on reaction kinetics, as described by the Arrhenius equation*. The rates of Pb shot corrosion and crust dissolution appear to have been slowed by low temperature (10°C) and raised by higher temperature (30°C).

In both soils, Pb-treated samples generally had higher solution pHs than corresponding control samples (Figure 5.22). The factors most likely to contribute to this effect were presented in Section 5.3.3:

(i) Consumption of H⁺ by corrosion reaction;
(ii) Release of OH⁻ ions during transformation of PbO to Pb-carbonates; and
(iii) Consumption of H⁺ by dissolution of Pb-carbonates.

In addition, the increasing rate of Pb sorption with increasing temperature will have prompted a proportionally greater rate of release of H⁺ ions. At the two higher temperatures this appears to have counteracted the pH increase to some extent.

Temperature variations will affect Pb sorption by soil in terms of the adsorption reaction rate and the equilibrium position (Barrow, 1992). In a review of literature, Barrow (1992) concluded that the sorption rate of most cations is proportional to temperature, and at higher pH the temperature effect on the sorption rate is greater due to temperature effects on variable charge surfaces. Scheinost et al. (2001) found that when Pb was reacted with ferrihydrite a decrease in temperature reduced the amount sorbed and the sorption kinetics. Thus, at low temperature, Pb sorption is expected to be relatively low. The Kᵈ values calculated for both soils in this study, as shown in Table 5.5, were highest for the 10°C treatment. This is most likely to be a pH effect, as the pH range for the 10°C treatment was highest. The Kᵈ values of Waimakariri samples incubated at 25°C and 30°C are suitable for direct comparison as the soil pHs of these samples covered the same range. The effect of temperature on Pb sorption may be apparent in the lower mean Kᵈ of the 25°C samples.

* k = Ae⁻E/RT where k is the rate constant, A is a frequency factor, E is the energy of activation, R is the universal gas constant, and T is absolute temperature (Sparks, 1989).
5. Lead shot oxidation

![Graph showing solution pH data for Waimakariri and Temuka samples incubated with Pb shot and controls incubated at 10-30°C and field capacity moisture content. Error bars indicate range.]

**Table 5.5.** Relationship between Kd and temperature in Waimakariri and Temuka soil after 24 months incubation at field capacity.

<table>
<thead>
<tr>
<th>Soil Temperature</th>
<th>Mean Solution pH</th>
<th>Mean Kd</th>
<th>Soil Temperature</th>
<th>Mean Solution pH</th>
<th>Mean Kd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waimakariri</td>
<td></td>
<td></td>
<td>Temuka</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5.4 ± 0.5</td>
<td>2853</td>
<td>10</td>
<td>5.0 ± 0.2</td>
<td>3628</td>
</tr>
<tr>
<td>25</td>
<td>4.8 ± 0.5</td>
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<td>4.9 ± 0.3</td>
<td>1344</td>
</tr>
<tr>
<td>30</td>
<td>4.8 ± 0.5</td>
<td>423</td>
<td>30</td>
<td>4.8 ± 0.3</td>
<td>650</td>
</tr>
</tbody>
</table>

Figure 5.22. Solution pH data for Waimakariri and Temuka samples incubated with Pb shot and controls incubated at 10-30°C and field capacity moisture content. Error bars indicate range.
Figure 5.23 shows the results from fractionation of the fine earth Pb. After 24 months incubation the proportion of exchangeable Pb increases with temperature and is most likely a result of the reduction in pH as temperature increases. The proportion of Pb in the carbonate fraction was lower in soil incubated at 10°C than at the two higher temperatures, particularly in the Waimakariri soil. It was established above that the solubility of CO$_2$ as a function of temperature does not appear to be the dominant control of the system. However, it is likely to affect carbonate mineral solubility to some extent and may be evident in Figure 5.23. In addition, corrosion cells can develop between Pb shot and soil as well as on Pb shot alone (Section 5.3.1). The reduced rate of corrosion at 10°C is likely to have reduced the direct precipitation of Pb-carbonate corrosion products onto the soil solid phase. At the higher temperatures, lower solubility of CO$_2$ appears to have encouraged precipitation of Pb onto the soil solid phase as carbonates. At 10°C, a greater proportion of the Pb has sorbed onto organic and oxide fractions of the Waimakariri soil, probably due to the reduced stability of Pb-carbonates.

Figure 5.24 shows the activity of Pb$^{2+}$ plotted versus solution pH for the Waimakariri and Temuka soils, as compared to the solubility of PbCO$_3$. The data points of the 10°C plots appear to be further from the range of stability for PbCO$_3$ than at the higher temperatures. Scheinost et al. (2001) found that reducing the reaction temperature created a proportional effect on the sorption kinetics of the reaction between Pb and ferrihydrite. Scheckel and Sparks (2001) observed that Ni sorption by clay minerals was slower at 9°C than at 25°C. Thus, the time taken to attain the equilibrium position of the sorption reaction will be proportional to temperature. As discussed previously, the estimations involved in producing the stability plots in Figure 5.24 may preclude accurate illustration of the system. For Figure 5.24 the solubility of PbCO$_3$ was plotted on all graphs using the equilibrium constant for 25°C, as corresponding constants for 10°C and 30°C were not found in the literature. Calculation of these constants using the van’t Hoff equation$^*$ did not appear to alter PbCO$_3$ solubility to a great extent. However, at 30°C lower PbCO$_3$ solubility could be expected due to reduced pCO$_2$, which would lower the band of PbCO$_3$ solubility for the 30°C plot. Conversely, at 10°C, greater PbCO$_3$ solubility could be expected due to increased pCO$_2$, which would raise the band of PbCO$_3$ solubility for the 10°C plot. When this is considered, as shown by the dashed arrows on the 10°C and 30°C plots, the effect of temperature on the equilibrium position is more apparent.

$^*$ \[ \log K_{T_1} = \log K_{T_0} - \frac{\Delta H_{T_0}}{2.3R} \left( \frac{1}{T_1} - \frac{1}{T_0} \right) \]
Figure 5.23. Effect of temperature on the proportion (%) of fine earth Pb in individual soil fractions in Waimakariri and Temuka soil incubated at field capacity moisture content.
Figure 5.24. Soil solution data for both soils from samples incubated at field capacity moisture content for each temperature treatment, plotted with the solubility of PbCO$_3$ at 25°C (shaded area). Dashed arrows indicate expected effect of temperature on PbCO$_3$ solubility. Pb$^{2+}$ activity (mol L$^{-1}$) and pCO$_2$ range calculated using the GEOCHEM-PC model.
Effect of temperature on crust crystallography

X-ray diffraction patterns of corrosion crust material removed from the Pb shot are shown in Figure 5.25. The general intensity of diffraction peaks reduces with increasing temperature (for example, the Pb$_3$(CO$_3$)$_2$(OH)$_2$ peak at approximately 40° 2θ). Such variation in peak intensity between samples indicates changes in the relative amount of a mineral in the samples. It is most likely that this is related to the different rates of crust dissolution, as controlled by the kinetics of the Pb sorption reaction onto soil discussed above. However, some variation in the ratio of peak intensities between samples is evident (for example, Pb$_3$(CO$_3$)$_2$(OH)$_2$ peaks 1 and 2 as marked in Figure 5.25). This suggests variation in the orientation of minerals with cleavage planes, although no information on cleavage planes in Pb$_3$(CO$_3$)$_2$(OH)$_2$ could be found. Further interpretation of the XRD patterns may clarify these issues.

Figure 5.25. Effect of temperature on X-ray diffraction patterns of corrosion crust material removed from Pb shot after 24 months incubation in Temuka soil at field capacity moisture content.
5.3.6 Effect of lead loading

Effect of lead loading on soil solution and solid phase lead

The concentration of Pb in solution increased over the 24-month period in both soils, but the concentration of Pb in the Temuka soil solution appeared to stabilise considerably after 12 months incubation (Figure 5.26). Maximum mean solution Pb concentrations reached 2.0 and 4.9 mg L\(^{-1}\) in the Waimakariri and Temuka soils respectively.

As with other treatments in previous sections, the solution pH of control samples decreased during the 24-month incubation period, but Pb-treated samples generally had higher solution pHs than corresponding control samples (Figure 5.27). Mean pH values for soil solutions with 20% Pb were almost 1 pH unit higher than the mean pH value for soil solutions with 5% Pb. The difference in pH between control and samples appears to be approximately proportional to the magnitude of the Pb loading. This would most likely be due to the ability of the 20% Pb treatment to sustain the three reactions capable of increasing solution pH (corrosion, Pb-carbonate formation, and PbCO\(_3\) dissolution) at a proportionally greater level than the 5% Pb treatment. The shift in solution pH of the 20% samples means that solution and fine earth Pb concentrations are no longer directly comparable with the second pH treatment containing 5% Pb shot, as there is a difference in pH of 0.8-1.0 pH unit (green plots, Figure 5.26). When the 20% Pb data is instead compared with the 5% Pb data from the 3\(^{rd}\) pH treatment (Section 5.3.3) which have more comparable solution pHs (blue plot, Figure 5.26), the solution Pb generated by incubation of soil with 20% Pb are greater (Waimakariri) or similar (Temuka) in concentration.
5. Lead shot oxidation

Figure 5.26. Effect of Pb loading on soil solution Pb concentrations (mg L⁻¹) in Waimakariri and Temuka soil incubated at field capacity moisture content and 25°C. Error bars indicate standard deviation.

Figure 5.27. Solution pH data for samples from both soils with 20% Pb shot and controls incubated at field capacity moisture content and 25°C. Error bars indicate range.
Fine earth Pb concentrations (Figure 5.28) and enrichment factors (1187 and 876 for the Waimakariri and Temuka soils respectively) measured after 24 months incubation with 20% Pb shot were approximately 4 times that of soil Pb concentrations at 5% Pb addition and corresponding pH. This corresponds to the greater amount of Pb supplied to the soil solution by the 20% Pb loading which is subsequently available for sorption. Calculated $K_d$ values were 3541 for Waimakariri (solution pH = 6.1) and 2577 for Temuka (solution pH = 6.3). These data are approximately what would be expected given the relationship between solution pH and $K_d$ calculated for the 5% Pb treatment (Table 5.3).

![Figure 5.28. Fine earth Pb concentrations (mg L$^{-1}$) during experimental period for 20% treatment. Error bars indicate standard deviation.](image-url)
Soil Pb fractionation data (Figure 5.29) show a greater dominance of Pb in the carbonate fraction in comparison to the second soil pH treatment for the 5% Pb treatment (Figure 5.7). This would be expected, as 4 times the surface area of Pb is present in the soil samples with the greater Pb loading, and thus a greater amount of corrosion products are in direct contact with the soil.

Figure 5.29. The proportion (%) of fine earth Pb in nominal fractions of Waimakariri and Temuka soils incubated with 20% Pb shot at field capacity moisture content and 25°C.
Figure 5.30 shows the activity of Pb$^{2+}$ plotted versus solution pH for the Waimakariri and Temuka soils, as compared to the solubility of PbCO$_3$. The diagrams indicate that solution Pb concentrations became limited by PbCO$_3$ solubility within 12 months of incubation. For the Waimakariri soil this is reflected in the temporal trend in solution Pb concentration (Figure 5.26), but less so for the Temuka soil. Further confirmation of the time taken to achieve a quasi-equilibrium state is more difficult, due to the assumption that, as for the other treatments, the 12-month fine earth Pb concentration data is anomalously high.

![Graphs showing Pb$^{2+}$ activity versus solution pH](image)

Figure 5.30. Soil solution data for both soils plotted separately with the solubility of PbCO$_3$ (shaded area); Pb$^{2+}$ activity (mol L$^{-1}$) and PCO$_2$ range calculated using the GEOCHEM-PC model; Equilibrium constants from Lindsay (1979).
5. Lead shot oxidation

5.3.7 Partitioning of Pb after 24 months incubation

The data indicating the partitioning of Pb after 24 months incubation showed clear trends in the amount of Pb present as elemental Pb in the form of intact Pb pellets. However, the amounts of Pb associated with the corrosion crust and fine earth were variable, probably due to the difficulty in accurately separating brittle corrosion crust material from the fine earth fraction after soil samples were dried.

In all treatments <20%, but generally <10% of the Pb added as Pb shot was transformed into crust-, fine earth- or solution-Pb compounds. Most of the Pb was still present as elemental Pb in the form of intact Pb pellets. As presented in the previous sections, this relatively small proportion of Pb released was sufficient to cause substantially elevated soil Pb concentrations. The concentrations of Pb in solution constituted a very small proportion (typically 10⁻³%) of the total Pb addition to the soils.

The distribution of Pb in treated samples after 24 months incubation at four different pHs is shown in Figure 5.31. The amount of Pb present as intact Pb pellets generally reduced with increasing pH: 95.0>94.4>93.0>91.9 for the Waimakariri samples and 94.6>93.0>82.2<83.4 for the Temuka samples. Although the amount of Pb in either the crust or fine earth varied, the amount of Pb in the combined ‘crust + fine earth’ fractions generally increased with pH. These trends reflect the greater influence of soil Pb sorption at the highest pH in driving the forward reaction (Pb shot corrosion → crust dissolution ↔ solution Pb ↔ soil sorption of Pb).
Figure 5.31. Effect of pH on the partitioning of Pb between pellet, corrosion crust and soil for Waimakariri and Temuka soils incubated at field capacity moisture content and 25°C; Pb in soil solution was approximately 10^4% of total.
The partitioning of Pb in treated Waimakariri samples after 24 months incubation at 10, 25 or 30°C is shown in Figure 5.32. The amount Pb present as intact Pb pellets reduced with increasing temperature: 95.0>94.4>91.9, and the amount of Pb in the combined ‘crust + fine earth’ fractions increased. These trends reflect the influence of temperature on the Pb shot-soil system (Pb shot corrosion ↔ crust dissolution ↔ solution Pb ↔ soil sorption of Pb), particularly increased rates of Pb shot corrosion, corrosion product dissolution, and soil Pb sorption at higher temperature. The lowering of pH with temperature was attributed to the counteractive effect of H+ ions released into solution during soil Pb sorption (Section 7.3.5).

![Figure 5.32. Effect of temperature on the partitioning of Pb between pellet, corrosion crust and soil for Waimakariri soil incubated at field capacity moisture content; Pb in soil solution was approximately 10^-4% of total.](image-url)
The partitioning of Pb in treated samples after 24 months incubation with 5% or 20% Pb shot is shown in Figure 5.33. The combined proportion of Pb in the crust material and fine earth fraction, and thus the amount of Pb removed from the intact Pb shot was consistently greater in the Temuka treatments compared to those in the Waimakariri soil. This most likely reflects the greater sorption capacity of the Temuka soil.

Figure 5.33. Effect of Pb loading on the partitioning of Pb between pellet, corrosion crust and soil for Waimakariri and Temuka soils after incubation for 24 months at field capacity moisture content and 25°C; Pb in soil solution was approximately 10^-4% of total.
5. Lead shot oxidation

5.4 CONCLUSIONS

Lead is readily released from Pb shot into the soil environment due to rapid corrosion of the Pb shot. The corrosion products, dominated by Pb carbonates, rapidly accumulate on the surface of Pb shot and are readily solubilised in the soil environment. A significant pool of potentially soluble corrosion products is contained in the corrosion crust or precipitated onto the soil solid phase. The total soil Pb burden generally becomes partitioned approximately as follows: intact Pb shot (90%), corrosion crust Pb (5%), fine earth Pb (5%), soil solution (0.0001%).

Solubility diagrams strongly indicate that solution Pb concentrations are primarily controlled by PbCO$_3$ solubility. Thus, the mechanism of Pb solubility control is altered from adsorption in uncontaminated soil to precipitation-dissolution in soil containing Pb shot. Soil sorption of Pb removes the metal from the solution until equilibrium is reached between solution- and sorbed-Pb. At lower pH, soil Pb sorption capacity may limit solution Pb concentration below that determined by the solubility of corrosion products. The rate of transformation of metallic Pb shot and release into the soil environment is defined by an initial rapid period of corrosion and dissolution until equilibrium between solution- and solid phase Pb is achieved. Further transformation will be controlled by the removal of Pb from the system, mainly by water percolation through the soil.

Soil pH, moisture content and temperature impact the Pb shot-soil system in a number of ways, particularly the rate of Pb shot corrosion, solubility of corrosion products, solid-solution partitioning, and reaction kinetics.

The results presented here have lead to the identification of the system components which are responsible for controlling Pb concentrations in the aqueous and solid phases of soils contaminated with Pb shot. The information will aid understanding of the conditions under which solubility may be controlled order to minimise the potential movement and bioavailability of the Pb.
6.1 INTRODUCTION

Chapter Four clearly demonstrates that substantially elevated soil Pb concentrations occur at four Canterbury clay target shooting (CTS) ranges. Combined with surveys of the remaining ranges in the region (McLaren and Clucas, 1998; Rooney et al., 1999), the data shows that elevated soil Pb concentrations at CTS ranges are ubiquitous. Chapter Five confirms that Pb is released from Pb shot into the soil solution via progressive dissolution of corrosion crust material. Therefore there is significant potential for movement of Pb at CTS ranges where Pb shot has accumulated, and Pb mobility is not expected to be effectively controlled by soil sorption as suggested by the (U.S.) National Shooting Sports Foundation (1996). Soil profile survey results (Figure 4.13) show evidence of elevated subsoil Pb concentrations to a depth of 0.6 m at the Waihora CTC range, indicating movement of Pb from the surface soil. Such movement of Pb from the topsoil at CTS ranges is undesirable, and migration of the lead though soil caused by water infiltration is of particular concern as contamination of groundwater may occur. Protection of Canterbury’s groundwater resource beneath the region’s generally free-draining soils is of high priority. The majority of the CTS ranges are situated in areas with unconfined aquifers (Lobb et al., 1997), and the Canterbury Clay Target Club at McLeans Island is situated within the recognised recharge zone for the Christchurch city aquifer (Little, 1997).

Lead is generally reported to have low mobility in most soils and sediments relative to other metals due to high retention by soil components (for example Korte et al., 1976; Merrington and Alloway, 1994; Tack et al., 1999). This assumption has pervaded conventional wisdom for some time, most likely due to the predominant use of repacked columns of homogenised soil for experimental studies. It is becoming accepted that metal mobility in field soils can be greatly underestimated by the use of repacked soil in experiments. Camobreco et al. (1996) found that repacked soil columns retained substantially greater amounts of Pb than undisturbed soil columns, when Pb was added as dissolved inorganic salts or soluble organic complexes. Without doubt, the use of undisturbed lysimeters for the study of metal mobility aids the interpretation of data in terms of metal mobility expected in the field.
6. Lead mobility

There is evidence (particularly from studies of sewage sludge applications onto soil) that soil Pb should not be expected to remain in the topsoil, regardless of its low mobility in soil relative to other heavy metals. A study of acid sandy soils that had received runoff water for eight centuries from the lead roofs of village churches has also revealed elevated soil Pb concentrations to a depth of 1-1.3 m (Jørgensen and Willems, 1987b). Peryea and Creger (1994) reported that downwards leaching of Pb had occurred in orchard soils that had received high loading rates of Pb-arsenate. Coarse-textured soils, low soil organic matter and the use of irrigation promoted the deepest movement of Pb.

Mobilisation and migration of Pb downward through the soil profile has been recently documented at a CTS range by Murray et al. (1997). The spatial distribution of Pb in subsurface soil horizons at a contaminated CTS range corresponded to the spatial distribution of Pb in surface soil, indicating that Pb was migrating downward through the profile. Soil Pb concentrations in the clay-rich profile were approximately 1000 mg kg\(^{-1}\) at the surface and >200 mg kg\(^{-1}\) at a depth of 1 m. Bruell et al. (1999) and Basunia and Landsberger (2001) used the USEPA TCLP* and SPLC† methods to establish that Pb in a shooting range soil was capable of leaching. Bäckström et al. (2000) reported elevated Pb concentrations in shallow groundwater at a CTS range situated on a peat bog, confirming that leaching of Pb from organic soils contaminated with Pb shot can occur, despite the high affinity of Pb for organic matter.

Astrup et al. (1999) and Bricka et al. (1998) have investigated Pb movement from raised bullet backstop berms made of soil at rifle firing ranges. Astrup et al. (1999) found that soil Pb concentrations indicated there may have been some movement of Pb within the berm. However, soil Pb concentrations were not elevated in the original soil profile below the berm. The results of an investigation of selected American military small-arms ranges by Bricka et al. (1998) showed that Pb was slowly migrating from backstop berms. Elevated soil Pb concentrations were measured to a depth of up to 2 m in acidic sandy loam or silt loam soils. Soils with higher clay content, or clay layers within the soil profile limited Pb movement to some extent.

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* Toxicity characteristic leaching procedure; USEPA method 1311
† Synthetic precipitation leaching characteristic; USEPA method 1312
6. Lead mobility

Quantification of the amount of Pb movement from contaminated CTS soils would contribute significantly to the information on leaching of Pb from shooting range soils. Therefore, the objectives of this experiment were to:

- assess the potential for leaching of lead from soils contaminated with lead shot by investigating leaching of Pb from undisturbed lysimeter cores;
- quantify output rates of Pb from the contaminated soils;
- determine whether Pb leaching occurs prior to a soil’s sorption capacity being reached.
6.2 METHODS AND MATERIALS

6.2.1 Study soils

Three contaminated clay target shooting ranges were chosen for this study, on the basis of site access and representation of Canterbury soil types. These sites are briefly described below and selected physical and chemical characteristics are listed in Table 6.1.

**Waibora CTC**

The site is located on Duck Pond Road, Motukarara, map reference M36:7541-1914 (Lobb et al., 1997). The soil is a Motukarara loamy sand (slightly saline phase; Gley Soil, NZ; Psammaquent, USA), which consists of accumulated organic matter (30-40 mm) over gleyed estuarine sands. The mean water level of the nearest off-site well is approximately 0.3 m below ground level and the soil is waterlogged during part of the year. A deeper confined aquifer (>50 m below ground level) is unlikely to be in hydraulic connection with surface sediments (Lobb et al., 1997).

**Mead - Te Pirita CTC**

The site is located close to the north bank of the Rakaia River, on Burns Road at Te Pirita, map reference L36:2913-2328 (Lobb et al., 1997). The soil is a Lismore stony silt loam (Brown Soil, NZ; Dystric Haplustept, USA), formed from moderately weathered greywacke alluvium. Groundwater occurs at a depth in the order of 13 m below ground surface with no confining layer identified (Lobb et al., 1997).

**Yaldhurst**

The site, previously used by the Christchurch CTC, is located at 145 Old West Coast Road, Yaldhurst, map reference M35:6879-4387 (Lobb et al., 1997). The soil is a Waimakariri stony sandy loam (Immature Pallic soil, NZ; Typic Ustifluvent, USA), formed from weakly weathered greywacke alluvium. Groundwater occurs at a depth of 10-15 m below ground surface in an unconfined aquifer (Little, 1997; Lobb et al., 1997).
Table 6.1. Selected physical and chemical characteristics of the study soils.

<table>
<thead>
<tr>
<th></th>
<th>Motukarara</th>
<th>Lismore</th>
<th>Waimakariri</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (dried soil, H2O)</td>
<td>7.1</td>
<td>5.7</td>
<td>5.5</td>
</tr>
<tr>
<td>CEC (cmolc kg⁻¹)</td>
<td>47.8</td>
<td>14.3</td>
<td>13.1</td>
</tr>
<tr>
<td>Organic carbon (%)</td>
<td>7.9</td>
<td>4.6</td>
<td>3.5</td>
</tr>
<tr>
<td>Tamm. Oxalate Fe (%)</td>
<td>0.35</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>80</td>
<td>39</td>
<td>49</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>13</td>
<td>29</td>
<td>42</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>6</td>
<td>32</td>
<td>9</td>
</tr>
</tbody>
</table>

6.2.2 Lysimeter preparation

Ten intact soils cores (68 mm diameter, 100 mm deep) were collected at each site – five from an area of the site expected to represent background concentration of soil Pb and five from an area 120-140 m in front of the traps where approximate maximum soil Pb concentrations would be found. The lysimeter casings and method of sampling has been described by Cameron et al. (1992). Briefly, the method involves digging a small trench around the lysimeter casing to expose a small depth of soil monolith below the casing. The casing is then gently pushed down over the exposed depth of soil and repeated until the casing is full.

Two cores from each area of Pb concentration (that is, four per site) were set aside for destructive sampling. The soil bulk density, soil porosity and pore volume of each soil was estimated using these representative cores (Table 6.2). Sequential fractionation of soil Pb in the representative contaminated lysimeters was carried out using the modified Tessier method described in Chapter 3.2.3. Comparison of values obtained for total fine earth Pb concentration by digestion and the sum of the fractions showed good agreement (coefficients of variation <10%), given the presence in the fine earth samples of small corrosion crust particles (Chapter 5.3.2).
6. Lead mobility

Table 6.2. Average bulk density, porosity and pore volume measured in representative lysimeters.

<table>
<thead>
<tr>
<th></th>
<th>Motukarara</th>
<th>Lismore</th>
<th>Waimakariri</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>1.22</td>
<td>1.09</td>
<td>0.90</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>54</td>
<td>59</td>
<td>66</td>
</tr>
<tr>
<td>Pore Volume (mL)</td>
<td>200</td>
<td>215</td>
<td>240</td>
</tr>
</tbody>
</table>

The remaining cores (three from each area; six per site) were prepared for leaching. A cross section of a prepared lysimeter is shown in Figure 6.1. The annular gap between the casing and soil core was sealed with warm liquid petrolatum to prevent edge-flow effects once leaching commenced in the laboratory (Cameron et al., 1992). The lysimeters were brought into the laboratory and a cellulose acetate/acetone mixture was allowed to harden on the base of the cores before being removed in order to open any pores blocked due to smearing during core collection. The bottoms of the cores were covered with acid-washed silica sand and a polyester mesh cover secured to the lysimeter base to prevent soil loss. The cores were stood in a 4% formalin mixture to encourage earthworms to exit from the cores, after which they were wet up to field capacity with de-ionised water and stored at 4°C until required.

![Figure 6.1. Cross-section of the lysimeter core prepared for the leaching experiment.](image)
6.2.3 Experimental procedure and analysis

Six lysimeters for each soil (3 background; 3 contaminated) were leached with 1 pore volume of de-ionised water for up to 10 leaching events every second day, so as to allow for some re-equilibration between leaching events (a total of 10 pore volumes over 20 days). The leachate from each core was collected in fractions of one-tenth of a pore volume. The total volume of the leachate fractions was measured, as was the pH. Leachates were then filtered using disposable 0.45µm cellulose acetate membrane filters then analysed for soluble Pb (flame or graphite furnace AAS), cations (Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, by FAAS), anions (NO$_3^-$, PO$_4^{3-}$, SO$_4^{2-}$, Cl$^-$, by IEC) and soluble organic and inorganic carbon (Shimadzu TOC analyser).

After leaching, the soil cores were removed from their casings and cut into 20 mm depth sections. The soil was air-dried and sieved (Chapter 3.1.1), and total- and EDTA-extractable Pb concentrations in the fine earth fraction were determined.

Speciation of Pb in leachate solutions was estimated using GEOCHEM-PC v 2.0 speciation modelling software (Parker et al., 1995) as described in Chapter 3.3.6. Chemical data from fractions 1, 4 and 7 of leaching events 1, 2, 3, 5, 7 and 9 where applicable were input into the model.

Pb sorption isotherms were determined using uncontaminated soil. Three replicates of 0.25 g of the fine earth fraction were equilibrated with 50 mL of 0.01M KNO$_3$ containing varying amounts of Pb added as Pb(NO$_3$)$_2$ for 24 h in polypropylene tubes. This follows the method of Elkhatib et al. (1991). Samples were centrifuged for 10 min at 10,000 rpm. The pH of every supernatant was measured before filtering (Whatman No. 42 filter paper). The solutions were analysed for Pb by FAAS.
6.3 RESULTS AND DISCUSSION

6.3.1 Motukarara lysimeters

Pb in the soil profiles

Lysimeters collected from an area of the site estimated to have background concentrations of fine earth Pb contained some Pb shot in the top 20 mm (Table 6.3). Figure 6.2a shows that the Pb shot raised fine earth Pb concentrations in the 0-20 mm section of the profile above the true background concentrations of <30 mg kg\(^{-1}\) measured in Chapter 4.3.1. Even so, fine earth Pb concentrations in the ‘background’ lysimeters were substantially less than those of the lysimeters collected from a contaminated area of the site (Table 6.3). Figure 6.2b illustrates the typical gradient of fine earth Pb concentrations found in the contaminated lysimeters. Concentrations in the surface 40 mm peat layer were influenced by the substantial masses of Pb shot, which were predominantly contained in the peat. Concentrations of Pb in the underlying sand (<2 mm) were much less, although still substantially elevated above true background concentrations.

![Graph of fine earth Pb concentrations](image)

Figure 6.2. Fine earth Pb concentrations (mg kg\(^{-1}\)) in representative profiles of the Motukarara soil.
Table 6.3. Amount of Pb contained in the Motukarara lysimeters and Pb removed during leaching.

<table>
<thead>
<tr>
<th>Lysimeter</th>
<th>Mean fine earth Pb concentration (0-100 mm) (mg kg(^{-1}))</th>
<th>Total Pb</th>
<th>Total Pb leached (mg)</th>
<th>Proportion of soil Pb leached (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean fine earth Pb (g)</td>
<td>Pb shot (g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>'Background' 1</td>
<td>20</td>
<td>(8 \times 10^{-3})</td>
<td>9.1</td>
<td>1.2 (\times 10^{-6})</td>
</tr>
<tr>
<td>'Background' 2</td>
<td>10</td>
<td>(7 \times 10^{-3})</td>
<td>0.1</td>
<td>ND</td>
</tr>
<tr>
<td>'Background' 3</td>
<td>62</td>
<td>(30 \times 10^{-3})</td>
<td>0.2</td>
<td>ND</td>
</tr>
<tr>
<td>Contaminated 1</td>
<td>6918</td>
<td>2.16</td>
<td>20.82</td>
<td>1.1</td>
</tr>
<tr>
<td>Contaminated 2</td>
<td>6327</td>
<td>1.88</td>
<td>22.18</td>
<td>2.8</td>
</tr>
<tr>
<td>Contaminated 3</td>
<td>8251</td>
<td>2.47</td>
<td>19.13</td>
<td>1.9</td>
</tr>
</tbody>
</table>

ND Not detectable (< 2 µg L\(^{-1}\))
6. Lead mobility

**Pb Leached from Background lysimeters**

Despite the presence of some Pb shot, Pb concentrations leached from the lysimeters containing ‘background’ fine earth Pb concentrations were generally below the limit of detection (2 µg L⁻¹). Only one of the ‘background’ lysimeters leached Pb which was detectable during part of the duration of the experiment (Figure 6.3).

![Figure 6.3. Pb concentrations (µg L⁻¹) and pH of leachates from ‘background’ Motukarara lysimeter in which Pb was detectable (>2 µg L⁻¹).](image)

**Pb Leached from Contaminated lysimeters**

Concentrations of Pb in leachates from contaminated lysimeters were substantially greater than those in leachates from ‘background’ lysimeters. Leachate Pb concentrations increased from approximately 0.5 mg L⁻¹ during the first few leaching events, reaching maximums of 1.6-3.4 mg L⁻¹. Leachate Pb concentrations gradually reduced during the later stages of the experiment to approximately 0.5 mg L⁻¹ once again. Figure 6.4 shows the characteristic breakthrough curve (BTC) of separate leaching events, particularly in Lysimeters 1 and 2. This was less evident for Lysimeter 3, where leachate Pb concentrations remained fairly constant throughout most leaching events.
Figure 6.4. Pb concentrations (mg L\(^{-1}\)) and pH of leachates from contaminated Motukarara lysimeters.
Fine earth Pb fractionation

Sequential fractionation of the Motukarara fine earth shows that <10% of the total Pb is present in the exchangeable fraction and <5% is present in the residual fraction (Figure 6.5). Most of the Pb is proportioned relatively equally between the organic, oxide and carbonate/specifically adsorbed fractions. This conforms with reported soil Pb fractionation data (Chapter 2.3.2). As discussed in Chapter Five, the exchangeable and carbonate/specifically adsorbed fractions represent potentially soluble Pb, particularly since fine particulate Pb-carbonate corrosion products are likely to contribute significantly to the latter fraction.

![Partitioning of Pb in contaminated Motukarara soil](image)

Figure 6.5. Partitioning of Pb in contaminated Motukarara soil (mean total fine earth Pb (sum of fractions) = 7300 mg kg⁻¹).

Modelling leachate speciation from contaminated lysimeters

The speciation of leachate Pb predicted using the GEOCHEM-PC model is summarised in Figure 6.6. The results of the GEOCHEM-PC calculations support the dominant role of soluble organic matter in the transport of Pb from the surface horizon of the Motukarara soil. The proportion of Pb as Pb-hydroxy species (mainly as PbOH⁺) generally increased as the experiment progressed and corresponds with the increase in leachate pH. The calculations indicated that Pb-Cl species were initially important in this slightly saline soil. However, supply of Cl⁻ to the solution was exhausted rapidly.
Figure 6.6. GEOCHEM-PC model predictions for Pb speciation (as % of total soluble Pb) in selected leachates from Contaminated Motukarara lysimeter 2.
The BTCs show that soluble Pb is rapidly and repeatedly replenished in the soil solution during re-equilibration periods. Chapter Five established that the Pb-carbonate crust material dissolved to maintain solution Pb concentrations. It follows that dissolution of Pb-carbonates associated with the corrosion crust and soil matrix is a probable mechanism for loss of Pb from the contaminated lysimeters. This would account for the continual replenishment of solution Pb concentrations during leaching events and re-equilibration periods between leaching events. Release of soil-Pb from exchange and specific adsorption sites may also have contributed to solution Pb replenishment.

Breakthrough curves of soluble organic carbon (SOC) in leachates (Figure 6.7) correspond closely to the BTCs obtained for soluble Pb (Figure 6.4), in terms of both the relative magnitude of Pb and SOC between BTCs, and within individual BTCs. Sauvé et al. (1998) demonstrated the importance of the formation of soluble organo-Pb complexes on Pb solubility at higher pH. It appears that SOC is facilitating total Pb solubility above the solution Pb$^{2+}$ activity determined by Pb mineral dissolution. Leachate pH was relatively high throughout the experiment (Figure 6.4) which supports the importance of soluble organic-Pb species in the mobility of Pb in this organic matter-rich soil. Tyler (1981b) also observed that Pb concentration maxima corresponded with soluble organic matter maxima in percolates from lysimeters containing intact organic soil. Bäckström et al. (2000) investigated a CTS range on a peat bog. Data indicated that 96-100% of Pb in shallow groundwater samples taken from the range was associated with soluble organic matter.

![Figure 6.7](image-url). Soluble organic carbon concentration (mg L$^{-1}$) in selected leachates from contaminated Motukarara lysimeters.
Only 8-11% of the total Pb (fine earth Pb + Pb shot) in the contaminated lysimeters occurred as fine earth Pb (Table 6.3). It is expected that a similar proportion of Pb is present as Pb shot crust material that has contributed substantially to Pb concentrations leached from the contaminated lysimeters. Figure 6.5 shows that greater than 30% of the fine earth Pb was associated with the two most soluble fractions (exchangeable and carbonate/specifically adsorbed). However, the amount of Pb leached from the lysimeters during the experiment was equivalent to less than 0.2% of the fine earth Pb (Table 6.3). This indicates that the solubility of the Pb was very low, being limited by the pH-dependent equilibrium between Pb in solution and soil-Pb sorption, as discussed in Chapter 5.3.3. It also indicates the large pool of Pb potentially available for leaching, and therefore why little or no decrease of leachate Pb concentrations was observed during the experiment.

Figure 6.8 shows the activity of Pb$^{2+}$ in the first leachate fraction of the leaching events selected for speciation modelling plotted versus leachate pH, compared to the solubility of various Pb minerals. Only the first leachate fraction from each selected leaching event was plotted on the stability graph as it was considered most representative of the equilibrium solution Pb concentration due to the re-equilibration period between leaching events. As in Chapter Five, values for Pb$^{2+}$ activity were obtained from GEOCHEM-PC outputs of selected leachate fractions as described above (Section 6.2.3) and presented in Figure 6.6. An assumed PCO$_2$ of 0.03 atm was input into the GEOCHEM-PC model.
Figure 6.8. Leachate-Pb data for Motukarara lysimeters plotted with the solubility of important Pb minerals. Pb$^{2+}$ activity (mol L$^{-1}$) calculated using the GEOCHEM-PC model. Stability constants from Lindsay (1979). [SO$_4^{2-}$] = 10$^{-5}$ M, [Cl$^{-}$] = 10$^{-3}$ M, assumed PCO$_2$ of 0.03 atm.
The Pb$^{2+}$ activities in leachates from the contaminated lysimeters appear to be greater than can be explained by the solubility of PbCO$_3$ alone, even when a greater PCO$_2$ is considered, which is perhaps more appropriate for this organic matter-rich soil. The use of solubility equilibria in natural soil systems has limitations. In particular, reactions are assumed to be at equilibrium and solubility constants are derived from minerals in a pure state, free from surface contamination or other impurities (Jurinak and Tanji, 1993; Jopony and Young, 1994). It is unlikely that either of these conditions are satisfied in the natural soil system studied. The solubility plot suggests that Pb solubility was controlled by a mixture of Pb minerals. Concentrations of Cl$^-$ in leachates from the Motukarara lysimeters were in the order of 10$^{-3}$ M and were an order of magnitude greater than concentrations in leachates from the other two soils. GEOCHEM-PC predictions of Pb speciation (Figure 6.6) indicated the importance of Pb-Cl complexes in this soil. This suggests that PbCO$_3$Cl$_2$ may also have influenced leachate Pb$^{2+}$ activity. Another Pb-carbonate, PbCO$_3$.PbO, may also be important in controlling Pb$^{2+}$ activity.

The ‘background’ lysimeters contained small amounts of Pb shot (Table 6.3), which appear to have caused some Pb leaching to occur. Although leachate Pb concentrations are substantially lower than in the highly contaminated lysimeters, the activity of Pb$^{2+}$ in the leachates also appears to be controlled by the dissolution of Pb minerals.
6.3.2 Lismore lysimeters

Pb in the soil profiles

Mean fine earth Pb concentrations in the background lysimeters were <10 mg kg\(^{-1}\) (Table 6.4), and Figure 6.9a shows the typical concentrations in the soil profile to 100 mm. Figure 6.9b illustrates the typical gradient of fine earth Pb concentrations found in the lysimeters with elevated fine earth Pb concentrations. The relatively uniform concentrations are a result of ploughing, which has redistributed Pb shot initially deposited on the soil surface into the plough layer.

![Figure 6.9. Fine earth Pb concentrations (mg kg\(^{-1}\)) in representative profiles of the Lismore soil](image)

Pb Leached from Background lysimeters

Lead concentrations in leachates from background lysimeters were below the limit of detection (2 µg L\(^{-1}\)) throughout the experiment.
<table>
<thead>
<tr>
<th>Lysimeter</th>
<th>Mean fine earth Pb concentration (0-100 mm) (mg kg⁻¹)</th>
<th>Total Pb</th>
<th>Total Pb leached (mg)</th>
<th>Proportion of soil Pb leached (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background 1</td>
<td>6.4</td>
<td>2 × 10⁻³</td>
<td>0</td>
<td>ND</td>
</tr>
<tr>
<td>Background 2</td>
<td>2.4</td>
<td>1 × 10⁻³</td>
<td>0</td>
<td>ND</td>
</tr>
<tr>
<td>Background 3</td>
<td>5.9</td>
<td>1 × 10⁻³</td>
<td>0</td>
<td>ND</td>
</tr>
<tr>
<td>Contaminated 1</td>
<td>4745</td>
<td>1.37</td>
<td>12.35</td>
<td>0.34</td>
</tr>
<tr>
<td>Contaminated 2</td>
<td>4722</td>
<td>1.12</td>
<td>14.07</td>
<td>0.54</td>
</tr>
<tr>
<td>Contaminated 3</td>
<td>4384</td>
<td>1.17</td>
<td>13.14</td>
<td>0.70</td>
</tr>
</tbody>
</table>

ND Not detectable (<2 µg L⁻¹)
**Pb Leached from Contaminated lysimeters**

Concentrations of Pb in leachates from contaminated lysimeters were substantially greater than those in leachates from background lysimeters. Overall, leachate Pb concentrations generally remained steady or increased during the duration of the experiment, with typical concentrations ranging between approximately 0.1 and 0.5 mg L$^{-1}$, reaching maximums of 0.37-0.50 mg L$^{-1}$. Figure 6.10 (overleaf) shows the characteristic breakthrough curve of Pb leaching from individual lysimeters. The Pb BTCs show that soluble Pb was rapidly and repeatedly replenished in the soil solution during re-equilibration periods. This occurred to a greater extent than for the contaminated Motukarara lysimeters, where reducing Pb concentrations appeared to be linked to reducing SOC concentrations. The Lismore soil has a much greater amount of clay (32%; Table 6.1) which, given the observations by Strawn and Sparks (2000) and Ainsworth *et al.* (1994) that clay and oxide components readily exchange/desorb Pb, may give rise to the greater ability of the soil to maintain more constant solution Pb concentrations throughout the entire 10 leaching events.

**Fine earth Pb fractionation**

Sequential fractionation of the Lismore fine earth Pb shows that <10% of the total Pb is present in each of the exchangeable and residual fractions (Figure 6.11). Most of the Pb is proportioned relatively equally between the organic, oxide and carbonate/specifically adsorbed fractions.

![Figure 6.11. Partitioning of Pb in contaminated Lismore soil (mean sum of fractions = 4800 mg kg$^{-1}$).](image-url)
Figure 6.10. Pb concentrations (mg L⁻¹) and pH of leachates from contaminated Lismore lysimeters.
Modelling leachate speciation from contaminated lysimeters

The speciation of Pb in leachates predicted using the GEOCHEM-PC model is summarised in Figure 6.12 (page 161). Results of the GEOCHEM-PC calculations indicate that in the first two leaching events over half of the Pb in leachates was bound in soluble organic complexes. Organic-Pb species are predicted to have declined rapidly, being replaced by free Pb$^{2+}$. The small proportion of Pb-hydroxy species (mainly as PbOH$^+$) increased as the experiment progressed and corresponds with the increase in leachate pH.

The BTCs of SOC in leachates are shown in Figure 6.13. The trend in SOC corresponds to the speciation of Pb in leachates predicted by GEOCHEM-PC (Figure 6.12 – overleaf), where organic-Pb species dominated total soluble Pb in the two leaching events. The dominance of free Pb$^{2+}$ in leachates during the latter half of the experiment supports the theory that considerable Pb is readily available via the dissolution of corrosion products (in the corrosion crust and fine earth), and possibly ion exchange and release from specific adsorption sites.

Figure 6.13. Soluble organic carbon concentration (mg L$^{-1}$) in selected leachates from contaminated Lismore lysimeters.
Figure 6.12. GEOCHEM-PC model predictions for Pb speciation (as % of total soluble Pb) in selected leachates from Contaminated Lismore lysimeter 2.
In the contaminated lysimeters only 7-10% of the total Pb (fine earth Pb + Pb shot) at the site occurred as fine earth Pb (Table 6.4). It is expected that a similar proportion of Pb present as Pb shot crust material has also contributed to Pb concentrations leached from the contaminated lysimeters. The fractionation data (Figure 6.11) indicated that almost 40% of the fine earth Pb is associated with the two most soluble fractions (exchangeable and carbonate/specifically adsorbed). However, as for the Motukarara lysimeters, very small proportions (equivalent to <0.1% of the fine earth Pb) leached during the experiment. The constant replenishment of Pb in the leachates between leaching events indicates the presence of a large pool of potentially soluble Pb (consisting mainly of corrosion products associated with the crust and fine earth) that is able to rapidly re-equilibrate solution Pb concentrations during and after leaching events. This suggests that elevated Pb concentrations in water percolating from contaminated topsoil may be expected over a substantial period of time.

Figure 6.14 shows the activity of Pb\(^{2+}\) in the first leachate fraction of the leaching events selected for speciation modelling plotted versus leachate pH and compared to the solubility of various important Pb minerals. No detectable Pb concentrations were obtained in leachates from the background lysimeters. The leachate Pb\(^{2+}\) activities from the contaminated lysimeters appear to be controlled by a mixture of Pb minerals. There is possibly greater control by PbCO\(_3\) (compared to the Motukarara plots), as the Pb\(^{2+}\) activities more closely approximate that determined by the solubility of PbCO\(_3\). The concentrations of Cl\(^-\) in leachates from the Lismore soil are an order of magnitude less than those from the Motukarara lysimeters. This has the effect of increasing the solubility of PbCO\(_3\)Cl\(_2\) to the extent that the mineral is not expected to control leachate Pb\(^{2+}\) activity in this soil. Given that PbO is likely to be the initial mineral formed in the corrosion crust on Pb shot (Equation 5.6) the mixed mineral PbCO\(_3\).PbO may be present in the corrosion crust. This mineral could be responsible for the increase in Pb\(^{2+}\) activity above that controlled by PbCO\(_3\) alone. This mechanism is also proposed for the Pb\(^{2+}\) activity in leachates from the Waimakariri soil (Section 6.3.3).
Figure 6.14. Leachate-Pb data for Lismore lysimeters plotted with the solubility of important Pb minerals. Pb$^{2+}$ activity (mol L$^{-1}$) calculated using the GEOCHEM-PC model. Stability constants from Lindsay (1979). [SO$_4^{2-}$] = 10$^{-5}$ M, [Cl$^{-}$] = 10$^{-4}$ M, assumed PCO$_2$(g) of 0.03 atm.
6. Lead mobility

6.3.3 Waimakariri lysimeters

Pb in the soil profiles

Lysimeters containing background concentrations of soil Pb were collected from an area of the site least likely to be affected by Pb shot deposition, but closest to the adjacent major road in order to account for the contribution of automotive Pb to background soil Pb concentrations. Mean fine earth Pb concentrations in the background lysimeters ranged from 14 to 31 mg kg\(^{-1}\) (Table 6.5), and Figure 6.15a shows the typical concentrations in the soil profile to 100 mm. Automotive Pb appears to have resulted in only slightly elevated background concentrations. Figure 6.15b illustrates the typical gradient of fine earth Pb concentrations found in the lysimeters with elevated Pb concentrations. The relatively uniform concentrations are a result of ploughing, which has redistributed Pb shot initially deposited on the soil surface throughout the plough layer. The area from which the contaminated lysimeters were collected is not expected to have received significant inputs of automotive Pb.

![Figure 6.15](image-url)

Figure 6.15. Fine earth Pb concentrations (mg kg\(^{-1}\)) in representative profiles of the Waimakariri soil.
Table 6.5. Amount of Pb contained in the Waimakariri lysimeters and Pb removed during leaching.

<table>
<thead>
<tr>
<th>Lysimeter</th>
<th>Mean fine earth Pb concentration (0-100 mm) (mg kg(^{-1}))</th>
<th>Total Pb</th>
<th>Total Pb leached (mg)</th>
<th>Proportion of soil Pb leached (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean fine earth Pb (g)</td>
<td>Pb shot (g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background 1</td>
<td>21</td>
<td>(4 \times 10^{-3})</td>
<td>0</td>
<td>(4.2 \times 10^{-3})</td>
</tr>
<tr>
<td>Background 2</td>
<td>14</td>
<td>(3 \times 10^{-3})</td>
<td>0</td>
<td>(4.4 \times 10^{-3})</td>
</tr>
<tr>
<td>Background 3</td>
<td>31</td>
<td>(6 \times 10^{-3})</td>
<td>0</td>
<td>ND</td>
</tr>
<tr>
<td>Contaminated 1</td>
<td>4120</td>
<td>1.40</td>
<td>11.46</td>
<td>0.95</td>
</tr>
<tr>
<td>Contaminated 2</td>
<td>4050</td>
<td>1.53</td>
<td>14.71</td>
<td>0.64</td>
</tr>
<tr>
<td>Contaminated 3</td>
<td>3590</td>
<td>1.26</td>
<td>10.98</td>
<td>0.28</td>
</tr>
</tbody>
</table>

ND = Not detectable (< 2 µg L\(^{-1}\))
Pb Leached from Background lysimeters

Lead concentrations leached from the lysimeters containing background fine earth Pb concentrations were below 20 µg L⁻¹, and generally less than 5 µg L⁻¹ (Figure 6.16). One of the three lysimeters leached Pb at concentrations below the limit of detection (2 µg L⁻¹).

Pb Leached from Contaminated lysimeters

Concentrations of Pb in leachates from the contaminated lysimeters were substantially greater than those in leachates from background lysimeters. Over the period of the experiment, leachate Pb concentrations generally remained steady or increased, with typical concentrations ranging between approximately 0.1 and 1.0 mg L⁻¹, reaching maximums of 0.23-1.09 mg L⁻¹. Figure 6.17 shows the characteristic BTCs for Pb in the separate lysimeters, which indicate that soluble Pb is rapidly and repeatedly replenished in the soil solution during re-equilibration periods throughout the experiment.
Figure 6.17. Pb concentrations (mg L⁻¹) and pH of leachates from contaminated Waimakariri lysimeters.
6. Lead mobility

**Fine earth Pb fractionation**

Sequential fractionation of contaminated Waimakariri fine earth shows that <5% is present in the residual fraction, and the remaining Pb is proportioned relatively equally between the four other fractions (Figure 6.18). A relatively large proportion (19%) of the fine earth Pb was contained in the exchangeable fraction.

![Partitioning of Pb in contaminated Waimakariri soil (mean total fine earth Pb (sum of fractions) = 4000 mg kg⁻¹).](image)

**Modelling leachate speciation from contaminated lysimeters**

The speciation of leachate Pb predicted using the GEOCHEM-PC model is summarised in Figure 6.19. Results of the GEOCHEM-PC calculations indicate that over 70% of the total Pb released in the leachates was bound in soluble organic complexes in the first three leaching events. The dominance of organic-Pb species is predicted to have declined rapidly, after which free Pb²⁺ becomes dominant. This corresponds closely to the BTCs of SOC in the leachates, in which a rapid decline in concentration is observed (Figure 6.20). These trends in SOC and Pb speciation are very similar to those for the contaminated Lismore soil. The fractionation data (Figure 6.18) confirms that this soil has large pool of potentially labile Pb, particularly in the exchangeable fraction. The small proportion of Pb-hydroxy species (most likely as PbOH⁺) increased as the experiment progressed and corresponds with the increase in leachate pH.
Figure 6.19. GEOCHEM-PC model predictions for Pb speciation (as % of total soluble Pb) in selected leachates from Contaminated Waimakariri lysimeter 2.
In the contaminated lysimeters only 10-12% of the total Pb (fine earth Pb + Pb shot) at the site occurred as fine earth Pb (Table 6.5). Again, it is expected that a similar proportion of Pb present as Pb shot crust material has also contributed to Pb concentrations leached from the contaminated lysimeters. The fractionation data (Figure 6.18) indicated that >40% of the fine earth Pb is associated with the two most soluble fractions (exchangeable and carbonate/specifically adsorbed). The equivalent of <0.1% of the fine earth Pb leached during the experiment, again demonstrating that although the large pool of potentially soluble Pb was released relatively slowly, leachate Pb concentrations were maintained throughout the experiment.

Figure 6.21 shows the activity of Pb$^{2+}$ in the first leachate fraction of the leaching events selected for speciation modelling plotted versus leachate pH, compared to the solubility of various important Pb minerals. The activities of Pb$^{2+}$ in leachates from the background lysimeters are well below the lines of solubility for the Pb minerals shown, and are significantly different from those in leachates from the contaminated lysimeters. This indicates Pb solubility control by adsorption-desorption mechanisms. The predicted Pb$^{2+}$ activities in leachates from contaminated Waimakariri lysimeters are in a similar position to that from the contaminated Lismore lysimeters. As for the previous soils, Pb solubility in the contaminated Waimakariri soils is controlled by the dissolution of corrosion products.
Figure 6.21. Leachate-Pb data for Waimakariri lysimeters plotted with the solubility of important Pb minerals. Pb$^{2+}$ activity (mol L$^{-1}$) calculated using the GEOCHEM-PC model. Stability constants from Lindsay (1979). $[SO_4^{2-}] = 10^{-5}$ M, $[Cl^-] = 10^{-4}$ M, assumed PCO$_2(\text{g})$ of 0.03 atm.
6.3.4 General discussion

Leachate Pb concentrations

Lead shot deposited on soil acts as a pool of Pb that transforms into soluble Pb compounds with the potential to support long-term mobilisation of Pb with percolating water. In the contaminated soils studied, Pb was readily solubilised to replace that removed from the soil solution by leaching, and leachate Pb concentrations were sufficient to be easily measurable. The proportions of Pb leached from the contaminated soils during this experiment were very small: equivalent to <0.2% of the total fine earth fraction. Even so, maximum concentrations of Pb in leachates from the three soils were 1.6-3.4 mg L\(^{-1}\) (Motukarara), 0.4-0.5 mg L\(^{-1}\) (Lismore), and 0.2-1.1 mg L\(^{-1}\) (Waimakariri). In a study of contamination at a Canadian gun club, leachate from the soil contained elevated Pb levels, and exceeded 5 mg Pb L\(^{-1}\) in leachate from soil at the principal shot-fall zones* (Emerson, 1994, in Thomas, 1997). The maximum leachate Pb concentrations measured in the current study all exceed the Australasian water quality guidelines for Pb (Table 6.6). However, subsoil attenuation and dilution by receiving surface- or ground-water bodies would lessen the impact on water quality of the observed Pb concentrations leached from topsoil.

Table 6.6. Water quality guidelines for Pb.

<table>
<thead>
<tr>
<th></th>
<th>Drinking water</th>
<th>Raw water for drinking</th>
<th>Fresh water-bodies</th>
<th>Irrigation water</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZ Ministry of Health (2000):</td>
<td>10 µg L(^{-1})</td>
<td>50 µg L(^{-1})</td>
<td>1-5 µg L(^{-1})</td>
<td>200 µg L(^{-1})</td>
</tr>
<tr>
<td>ANZECC (1992):</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The greatest leachate Pb concentrations were generated by the Motukarara lysimeters. While SOC concentrations appeared to play a major role, the Motukarara lysimeters also contained the greatest concentrations of Pb shot (Table 6.3 cf. Tables 6.4 and 6.5). This would have given rise to the presence of the greatest amount of crust material available for dissolution and maintenance of leachate Pb concentrations.

* Method not known
6. Lead mobility

Of the total Pb at the sites, 7-12% is associated with the fine earth fraction, an estimated 10% is in crust minerals and the remainder is in elemental form that has yet to corrode. Currently, the source of mobile Pb is most likely the dissolution of corrosion products associated with the corrosion crust and fine earth, and possibly ion exchange. Because of the continual movement of Pb from corrosion products to the solution and solid phase, there may also be adsorbed Pb with a short residence time that is easily desorbed and leached. Garcia-Delgado et al. (1996) studied the mobilisation of Pb from artificially contaminated calcareous clay loam containing 91% of the 49,000 mg Pb kg\(^{-1}\) soil as PbCO\(_3\) by leaching repacked columns of the soil with deionised water. The Pb concentrations of collected leachates were <30 mg L\(^{-1}\) and generally <5 mg L\(^{-1}\). Significantly lower Pb concentrations were leached from this calcareous soil than from the lysimeters used in the present study, particularly when the relative amounts of Pb present as PbCO\(_3\) are considered.

Influence of soluble organic carbon

A strong relationship was observed between soluble organic matter and leachate Pb dynamics. The importance of soluble organic matter in Pb mobilisation in both the organic and mineral soils was confirmed by GEOCHEM-PC predictions of organic-Pb speciation dominance. Concentrations of soluble organic carbon with Pb were better-sustained in leachates from the organic soil. This was most likely due to the greater soil organic matter content (Table 6.1) and the higher leachate pH range of \(\approx 7-8\) which would favour organic matter solubility and the formation of organo-Pb complexes. Li and Shuman (1997) identified these factors to be critical for Pb solubilisation.

The organic soil produced the greatest leachate Pb concentration maximas and the greatest proportion of total soil Pb leached. In contrast, the influence of SOC in the mineral soils was relatively short-lived, most likely due to the inability of the lower soil organic matter levels (Table 6.1) to sustain soluble organic matter concentrations and lower leachate pH range (\(\approx 6-7\)). In field soils, SOC may have a more constant Pb-complexing role, due to the continual supply of SOC in the form of plant root exudates, which may have been exhausted under the intense leaching regime of the lysimeter experiment. The speciation calculations indicate that a lack of soluble organic complexes in the mineral soils may have reduced the concentration of Pb leached relative to the organic soil, but there was still a continuous release of Pb from the mineral soils for the duration of the experiment. The predicted
dominance of free Pb$^{2+}$ in leachates after soluble organic matter decline indicates that a proportion of the Pb present in the soil is sufficiently soluble that it equilibrates with the soil solution without the need for strong complexation (by soluble organic matter). This is most likely due to the multiple possible sources of solution Pb: potentially soluble corrosion products, ion exchange and specifically adsorbed Pb.

Camobreco et al. (1996) showed that soluble organic matter facilitated metal leaching. This concurs with the data from the present study. Tyler (1981b) found that Pb movement in a soil was favoured by high soil temperature and moisture conditions that favoured organic matter leaching. Regression analysis indicated that soil chemistry variables other than soluble organic matter had little value for predicting Pb leaching. Metal leaching can also be accelerated considerably by preferential flow that provides rapid movement of percolating water down the soil profile and increasing the depth of metal transport. The ponded water on the surface of lysimeters during leaching events is likely to have favoured preferential flow. Preferential flow paths may allow some Pb to bypass binding sites in the soil matrix and more rapidly reach greater depth in the profile, although some of this Pb would be readsorbed onto the walls of preferential flow paths.

**Degree of saturation of soil Pb sorption capacities**

Figure 6.22 shows that the sorption capacities of the three soils for Pb have yet to be exceeded, according to experimentally derived sorption isotherms. While these sorption isotherms may overestimate the field Pb sorption capacity, the data indicate that Pb is leaching from all three soils well before sorption capacity is reached. The dynamic equilibrium between Pb in aqueous and solid phases discussed in Chapter Five supports this process. That is, regardless of sorption capacity sufficient labile Pb exists in the soil, predominantly as corrosion products, to maintain soluble Pb concentrations when water percolates through the soil. Therefore, where Pb shot is in contact with soil, corrosion will occur and soluble Pb will be subject to transport down the profile. Even at relatively low levels of saturation of sorption sites, soluble Pb will be removed by percolating water. Therefore at the present time, at all CTS ranges, Pb will be leaching from the zone of contaminated topsoil into soil below.
Figure 6.22. Lead sorption isotherms for the three soils studied; Motukarara plots show sorption of Pb by 0-20 mm organic layer and 20-100 mm organic matter and sand; Current field level of Pb contamination in the fine earth fraction of each soil is indicated on the y-axis; Increase in Pb sorption by the soils resulted in a decrease in solution pH (Appendix D).

Implications of lysimeter data for the field

Leaching of the influent water added to the lysimeters most likely took place by preferential flow, followed by transport through the soil matrix in latter stages of each leaching event, as observed by Camobreco et al. (1996). Thus, the relatively rapid supply of Pb to solution observed in this experiment indicates that Pb can be supplied rapidly to percolating water during rainfall events. The total volumes of water collected after leaching each of the lysimeters was equivalent to approximately 500 mm of drainage. Table 6.7 shows the mean equivalent rate of Pb removal from lysimeters for each soil, and extrapolation of the data to indicate the potential magnitude of Pb transport by percolating water in the field. A typical annual drainage rate through freely-draining Canterbury soils is 400 mm (Dr H.J. Di, personal communication, July 2001). The possible impact of irrigation on the rate of Pb migration is indicated by the higher annual drainage volume of 1000 mm yr⁻¹.
Table 6.7. Rate of Pb removal by percolating water, and estimation by extrapolation of the rate of Pb migration from contaminated surface soil expected in the field.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Rate of Pb removal from lysimeters (µg mm(^{-1}) drainage)</th>
<th>Rate of Pb migration in the field (mg m(^{-2}) mm(^{-1}) drainage)</th>
<th>Annual amount of Pb migration (mg m(^{-2}) yr(^{-1}))</th>
<th>Annual drainage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motukarara</td>
<td>3.7</td>
<td>1.0</td>
<td>410</td>
<td>1030</td>
</tr>
<tr>
<td>Lismore</td>
<td>1.0</td>
<td>0.3</td>
<td>110</td>
<td>270</td>
</tr>
<tr>
<td>Waimakariri</td>
<td>1.3</td>
<td>0.4</td>
<td>140</td>
<td>350</td>
</tr>
</tbody>
</table>

* A typical annual drainage rate through freely-draining Canterbury soils (Dr H.J. Di, personal communication, July 2001).

The extent of the area containing high soil Pb contamination at each CTS range will vary, largely according to the number of individual trap and skeet ranges in use. Using Figure 4.10 it may be estimated that approximately 20,000 m\(^2\) of the shot-fall area at the Waikora CTC (where the Motukarara lysimeters were collected) contains a similar level of contamination to the lysimeters leached in this study. Assuming 400 mm of annual drainage, the loss of Pb from the surface soil could be in the order of 8 kg Pb yr\(^{-1}\). Based on similar club age, facilities and Pb deposition figures in (Lobb et al., 1997) it is estimated that the Mead-Te Pirita CTC (where the Lismore lysimeters were collected) has an area containing soil Pb concentrations >300 mg Pb kg\(^{-1}\) soil that is similar in size to that indicated by Rooney et al. (1999, >20,000 m\(^2\)). If an estimated 25% of this area (5,000 m\(^2\)) at the Mead-Te Pirita CTC sustains leachate Pb concentrations at a similar level to those measured from the lysimeters from the site, the annual amount of Pb migrating from the surface soil may be in the order of 550 g (assuming 400 mm of drainage).
6. Lead mobility

Subsoil attenuation will provide some degree of retardation in the rate of Pb encroachment down the soil profile and into groundwater. When soluble Pb moves into the subsoil it may be readsoorbed onto available exchange and adsorption sites, or precipitated onto subsoil surfaces. Bricka et al. (1998) found that Pb movement at selected American military small-arms ranges was limited in soil profiles containing clay layers, presumably as a result of attenuation and/or reduced drainage. These authors and others (Jørgensen and Willems, 1987a; Murray et al., 1997; Bricka et al., 1998) show that in some cases Pb entering the topsoil can lead to elevated subsoil Pb concentrations at depths of 1-2 m. The depth of subsoil and extent of subsoil development will greatly influence subsoil retention capacity. Subsoil attenuation is expected to delay Pb movement into groundwater for a limited period only. It is possible that, as for the topsoil, Pb leaching from subsoils could occur before subsoil Pb sorption capacity is reached.

The impact of Pb leaching from contaminated CTS ranges on local groundwater quality has not been quantified in this study. The concentration of Pb will be substantially reduced in groundwater compared to percolating water in the unsaturated zone of the soil. However, the potential movement of Pb into groundwater at the levels estimated above is certainly undesirable.

Factors affecting the risk of lead movement

Lead leaching is highly likely to occur at most CTS sites due to the constant supply of soluble Pb from the dissolution of corrosion products. The risk of Pb movement from the contaminated topsoil at CTS ranges is dependent on four main factors:

(i) Solubility of Pb compounds and soil solution Pb concentration
The rate of solubilisation of corrosion products (in the corrosion crust and associated with the soil solid phase) is low, but sufficient to maintain substantial leachate Pb concentrations. The solubility of Pb corrosion products will be determined by soil pH, and the equilibrium between solution Pb and sorbed Pb. The availability of soluble organic carbon will also influence solution Pb concentration.
(ii) **Volume and transport rate of percolating Pb-contaminated water**

The volume of percolating water (as indicated by annual drainage and/or mean annual rainfall (MAR) data) and the rate of water transport (largely determined by soil texture and macroporosity) will directly impact on Pb movement. Even slow transport through the soil may eventually lead to the contamination of groundwater. Higher annual rainfall would facilitate the transport of Pb through the soil, and therefore increase the risk of Pb leaching. Risk may increase further where high rainfall is coupled with other risk factors such as acidic, organic or coarse-textured soils. Percolating water from individual rainfall events would be expected to contain Pb speciation such as that predicted for the first few leaching events. Thus, organic-facilitated transport of Pb is likely to be very important in the field under natural rainfall conditions. Murray *et al.* (1997) has suggested that downward migration of lead may also be accelerated during or immediately following dry summer months as a result of desiccation and the formation of cracks in some soils. Such cracks create a significant secondary permeability that may extend to depths of 250 mm or more.

(iii) **The role of subsoil in attenuation of Pb leaching**

Subsoil attenuation will provide some degree of retardation in the rate of Pb encroachment down the soil profile and into groundwater. The depth of subsoil and extent of subsoil development will greatly influence subsoil retention capacity. The action of the subsoil is expected to delay Pb movement into groundwater for a limited period only. It is assumed that, as for the topsoil, Pb leaching from subsoils could occur before subsoil Pb sorption capacity is reached.

(iv) **Depth of groundwater below ground surface**

Depth to unconfined groundwater will be a significant factor in the time taken for Pb to reach groundwater and affect water quality.
6.4 CONCLUSIONS

While very small proportions of potentially soluble Pb were leached from all three contaminated soils during the experiment, leachate Pb concentrations were easily measurable. Solid-phase Pb, most likely Pb associated with the corrosion crust or precipitated in the soil matrix, rapidly replaced Pb removed from the soil solution by the relatively aggressive leaching regime. This indicates that Pb concentrations in percolating water related to individual rainfall events would remain relatively constant. Soluble organic matter has a substantial Pb-complexing, -solubilising and -transporting role, but Pb-transport is not facilitated by soluble organic matter alone; Pb will also leach readily as free Pb$^{2+}$ and inorganic-Pb complexes.

This experiment has shown that Pb can leach from the topsoils when only a small proportion of the total Pb burden has been transformed from the elemental state of intact Pb shot. This occurs irrespective of the level of saturation of a soil’s Pb sorption capacity. The amount of Pb leached will become greater as solution Pb concentration increases to equilibrium concentration, which will be influenced by soil chemistry parameters as discussed in Chapter Five. The large amount of intact Pb shot at CTS ranges that is yet to corrode will act as a source of chronic Pb leaching over a substantial period of time. Some degree of subsoil attenuation in most Canterbury soil is likely to delay movement of Pb down the profile. The degree of attenuation will vary depending on subsoil depth and development.
Chapter Seven
Management of lead mobility

7.1 INTRODUCTION

The potential for leaching of Pb from soil contaminated with Pb shot was established in Chapter Six. Intervention is required to reduce the environmental risk that contaminated shooting ranges pose, particularly in Canterbury where the quality of the groundwater resource needs to be protected. A common approach for dealing with contaminated soil at overseas shooting ranges is soil removal (for example, in Germany and the USA; F. Lang, personal communication, 29 August 2001; USEPA (2001)) and disposal in landfill. In New Zealand, resources for such comprehensive treatment of contaminated sites are limited, particularly in the short-term. Likewise, other techniques for the decontamination of sites, developed in the USA and Europe, such as soil removal, washing, and replacement, may also be unsuitable for use in New Zealand. Therefore, realistic remediation methods will be more desirable to parties dealing with contaminated New Zealand shooting ranges.

The environmental hazard at shooting ranges primarily consists of three components:

(i) the elemental Pb in the form of intact Pb shot which continually releases Pb to the soil environment via corrosion;

(ii) the Pb associated with the soil; and,

(iii) Pb movement associated with soil drainage.

Removal of the Pb shot from Canterbury shooting ranges as part of a comprehensive remediation strategy is unlikely to take place immediately. Left untreated, percolating water will continue to remove Pb from the soil solution, perpetuating the dissolution of corrosion products and the migration of Pb from the surface soil. Reducing the potential for Pb to leach from shooting ranges in order to limit adverse effects of Pb release into the wider environment is therefore of prime concern.
Methods for mitigating movement of Pb from shooting ranges by leaching need to be considered and applied as soon as possible. In situ stabilisation/immobilisation methods are potentially feasible remediation strategies that have been used to reduce the environmental risk at contaminated sites. Trace elements can undergo transformations or sorption reactions in soils that alter both speciation and concentration in solid and solution phases. Stabilisation methods utilise this principle to reduce metal mobility and toxicity. Desired transformation reactions have been promoted by the addition of various compounds to soils. Metal-stabilisation methods do not eliminate the hazard, but reduce it to a more acceptable level.

The objectives of this study were:

- To evaluate the suitability of various amendments for immobilising Pb at shooting ranges; to this end, a discussion of in situ immobilisation technology is given below, which focuses on a review of literature published on the use of phosphorus (P) amendments to immobilise soil Pb.
- To assess the Pb-immobilising performance of the most suitable amendment; Part I of the experimental approach aimed to assess the potential for P amendments to immobilise Pb in soils contaminated with Pb shot, and to establish an appropriate rate of P addition to each soil for effective Pb immobilisation. This information formed a foundation for the methods of Part II of the experimental approach, which describes the lysimeter experiment which was used to determine the effect of P addition on Pb mobility in undisturbed soil cores.
7. Control of lead mobility

7.1.1 Brief outline of in situ stabilisation technology

A brief discussion follows of commonly used soil amendments and management strategies, and their applicability to shooting range remediation.

Biosolids

Biosolids have been applied in various situations to stabilise contaminated soils and restore ecosystems disturbed by heavy metal contamination, particularly those involving mine tailings. Applications are effective where soil fertility improvement is required to establish vegetative cover on bare sites in order to reduce the risk of erosion. The addition of organic matter may also provide additional reactive surfaces to aid metal retention but increases in dissolved organic carbon in the soil solution could have undesirable mobilising effects on trace elements (Sauvé and McBride, 1998). The role of soluble organic matter in enhancing the transport of Pb in Pb shot-contaminated soils was demonstrated in Chapter Six. Sorption capacity can be increased further if Fe compounds have been used for dewatering the biosolids. Considerable concentrations of heavy metals are often present in biosolids, which may accumulate in soil with repeated applications. This material is not useful for remediating contaminated shooting ranges. Most sites have established vegetation and the potential for Pb movement by increased soluble organic matter (Chapter Six) should be avoided. There is no added benefit from Fe compounds, as New Zealand biosolids do not contain such additives.

Industrial by-products containing iron and/or manganese

Waste by-products from industrial processes that contain Fe have been used as soil amendments to increase the sorption of contaminant metals in soils, thereby reducing soluble metal concentrations. The addition of Fe and Mn oxides to Pb shot-contaminated soil could reduce the equilibrium solution Pb concentration (Figure 5.13), and therefore reduce potential leachate Pb concentrations. Hydrous Mn oxides have the desirable property that Pb$^{2+}$ is bound even under acid conditions, however Mn oxides are not readily available and are difficult to apply in the field (Knox et al., 2000). The Fe-containing by-products including steel shots (an iron grit) and red mud (a by-product of aluminium industry) are more prevalent in overseas countries than in New Zealand. The limited availability in New Zealand prevents the use of Fe/Mn oxide amendments, however they should be re-evaluated for use in the future if a suitable source becomes available.
7. Control of lead mobility

Lime
Agricultural lime may be applied to contaminated soil to increase the soil pH and so that metal adsorption to soil particles and the formation of hydroxide and carbonate precipitates is enhanced. However, Sauvé and McBride (1998) show that organic-Pb complexes solubilise at pH >7, actually increasing the concentration of soil solution Pb. Liming is generally considered potentially effective for soils that are naturally acidic or become acidic due the contamination or other treatment processes. In Chapter Five it was demonstrated that increasing the soil pH is somewhat beneficial, by reducing the rate of Pb shot transformation, but does not have a similar effect on the transfer of Pb to the soil solid phase. Heavy loadings of lime may affect surrounding surface and groundwater quality. The wide availability and ease of application makes lime relatively cheap to apply, and the compound may aid in the maintenance of optimum pH for other Pb immobilisation techniques at shooting ranges.

Phytoaccumulation
An increasing amount of research is being carried out on the use of metal-hyperaccumulating plant species to remove available metals from contaminated soils. While overall there is a growing number of species identified as hyperaccumulators, there is still a relatively small number of plants identified for the hyperaccumulation of lead. A more common approach is to enhance uptake of Pb using non-hyperaccumulator plants by mobilising soil Pb into solution using a chelating agent such as EDTA. The use of phytoaccumulation at shooting ranges will not be effective at present because the vast majority of the Pb is present as intact Pb shot, and is therefore unavailable for plant uptake. Poorly-applied chelating agents have the potential to cause substantial downwards movement, which is to be avoided. However, phytoaccumulation may be beneficial after the removal of Pb shot from the soil, particularly as EDTA chelates a large proportion of the fine earth Pb in soils contaminated with Pb shot (Manninen and Tanskanen, 1993; Rooney et al., 1999; Chapter Four).
7. Control of lead mobility

Phosphate immobilisation

The use of P compounds as soil amendments is based on the geochemical principle that many metals and radionuclides (e.g. Ac, Cd, Co, Eu, Pb, U, Zn) naturally and rapidly form phosphate (PO$_4$) minerals (Knox et al., 2000) which are stable under conditions likely to be present in the surface environment. Applying PO$_4$ amendments utilises this process by encouraging metal-PO$_4$ precipitation to reduce the mobility and bioavailability of contaminating metals. Studies of PO$_4$ amendments have shown there is great potential as an effective method of Pb immobilisation. Increasing the PO$_4$ supply sufficiently to provide ample PO$_4$ activity in solution should lead to the formation of Pb-phosphates, which are the least soluble Pb minerals in aerobic soils. In common with liming, many P compounds are relatively cheap, widely available and easy to apply, making them attractive and potentially successful amendments for shooting ranges.

Zeolite

Zeolites, natural or synthetic aluminosilicate minerals, have been applied to contaminated soils to increase sorption capacity in order to reduce available metal concentrations. Knox and Adriano (1999) showed that when equal quantities of zeolite and apatite (Ca$_3$(PO$_4$)$_2$) were applied to an artificially contaminated soil, zeolite was less efficient at reducing the solubility of Pb than apatite. The likely higher cost and lower availability relative to PO$_4$ compounds means zeolites are not the best amendment choice for shooting ranges.

Summary

Phosphorus amendments, possibly in conjunction with liming, are most likely to be effective at immobilising available soil Pb to reduce plant uptake and leaching. The considerable theoretical and experimental evidence that supports the consideration of P amendments as an effective method of Pb immobilisation in soil will be discussed in the following section. Further immobilisation techniques could be effective once Pb shot is removed from the shooting ranges, or if amendment availability improves (for example, Fe and Mn oxides).
7.2 PHOSPHATE IMMOBILISATION: THEORETICAL BACKGROUND

7.2.1 Interactions of lead and phosphorus in aqueous systems

Nriagu (1972) suggested that the interaction of Pb and PO₄ could be an important buffer mechanism controlling the migration and fixation of Pb in the environment. Since then there has been increasing interest in the role of PO₄ in the immobilisation of Pb in contaminated soil. Considerable theoretical and experimental evidence supports the consideration of P amendments as an effective method of Pb immobilisation in soil. Nriagu (1973; 1974) demonstrated that pyromorphite minerals (\(\text{Pb}_5(\text{PO}_4)_3X\), where \(X\) is Cl, OH, fluorine (F), bromine (Br)) have greater stability than other Pb minerals, such as PbSO₄, PbCO₃, PbOH, PbO, and Pb-orthophosphates in oxidising and moderately reducing environments. Table 7.1 gives solubility data for Pb minerals commonly found in the soil and various Pb-phosphate minerals. The study of Pb solubility in soils under experimental conditions by Santillan-Medrano and Jurinak (1975) supported Nriagu’s conclusions that Pb-phosphate formation would be an important sink for Pb in the environment, particularly where P was added to the system.

<table>
<thead>
<tr>
<th>Pb mineral</th>
<th>Stoichiometry</th>
<th>Log (K_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litharge</td>
<td>PbO</td>
<td>12.9</td>
</tr>
<tr>
<td>Anglesite</td>
<td>PbSO₄</td>
<td>-7.7</td>
</tr>
<tr>
<td>Cerussite</td>
<td>PbCO₃</td>
<td>-12.8</td>
</tr>
<tr>
<td>Hydroxypyromorphite</td>
<td>(\text{Pb}_5(\text{PO}_4)_3\text{OH})</td>
<td>-76.8</td>
</tr>
<tr>
<td>Fluoropyromorphite</td>
<td>(\text{Pb}_5(\text{PO}_4)_3\text{F})</td>
<td>-71.6</td>
</tr>
<tr>
<td>Bromopyromorphite</td>
<td>(\text{Pb}_5(\text{PO}_4)_3\text{Br})</td>
<td>-78.1</td>
</tr>
<tr>
<td>Chloropyromorphite</td>
<td>(\text{Pb}_5(\text{PO}_4)_3\text{Cl})</td>
<td>-84.4</td>
</tr>
</tbody>
</table>
Reduction of Pb concentrations in aqueous solutions after the addition of natural and synthetic apatite compounds (Ca$_5$(PO$_4$)$_3$X, where X is Cl, OH, F) has been reported frequently. Various authors (for example Ma et al., 1995; Zhang and Ryan, 1999) have identified that concomitant apatite dissolution and pyromorphite precipitation was the dominant mechanism for Pb immobilisation from aqueous solutions. Adsorption of Pb$^{2+}$ by hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH) and pyromorphites, or Pb$^{2+}$ substitution for Ca$^{2+}$ in hydroxyapatite is also possible (Ma et al., 1994a). Laperche et al. (1996) demonstrated that when solid PbO and PbCO$_3$ was reacted separately in solution with hydroxyapatite, hydroxypyromorphite formed at the expense of hydroxyapatite, PbO and PbCO$_3$, causing significant decreases in aqueous Pb concentrations. Ma and co-workers (1994a) have shown pyromorphite formation could effectively immobilise Pb$^{2+}$ in the presence of interfering anions and heavy metal cations (Ma et al., 1994b), although competing metal cations inhibited Pb immobilisation to some extent through the precipitation of other metal-phosphates. The following equations (Ma et al., 1994a) describe the dissolution of hydroxyapatite in the presence of Pb$^{2+}$ to form insoluble hydroxypyromorphite precipitate:

\[
\text{Ca}_5(\text{PO}_4)_3\text{OH} (c) + 7\text{H}^+ \rightarrow 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \tag{7.1}
\]

\[
5\text{Pb}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{Pb}_5(\text{PO}_4)_3\text{OH} (c) + 7\text{H}^+ \tag{7.2}
\]

The molar ratio of P:Pb is commonly used in the literature to describe the mass of P which is reacted with Pb, relative to the stoichiometric molar P:Pb ratio in solid pyromorphite (3:5).
7. Control of lead mobility

7.2.2 Pyromorphite formation in soil

It is known that pyromorphite minerals are able to form in soils, as many metals and radionucleides (actinium, cadmium, cobalt, europium, lead, uranium, zinc) naturally form PO₄ minerals which are stable over wide range of geochemical conditions (Knox et al., 2000). However there are few cases of naturally-formed pyromorphite in the literature. Cotter-Howells et al. (1994) identified the major Pb-bearing phase in soils formed from mine waste as a Ca-rich pyromorphite, indicating that pyromorphite will naturally form over time (ca. 200 years) in soils containing P. Small amounts of calcium-rich Pb-phosphates have been found in Pb-contaminated urban and roadside soils as a general weathering product (Cotter-Howells, 1996). Ruby et al. (1994) identified pyromorphite as a weathering product at a port site with prolonged moderate to gross Pb contamination by mining and smelting products and moderate to high P deposition from a nearby phosphoric acid factory. Sufficient evidence exists that pyromorphite formation in Pb-contaminated soils is commonly restricted by low availability of solution-P.

Reduced Pb solubility in soils has been achieved experimentally subsequent to the addition of PO₄ compounds. Ma et al. (1993) and Boisson et al. (1999) undertook experiments using synthetic hydroxyapatite at molar P:Pb ratios in excess of 200:5 which reduced Pb²⁺ solubility in contaminated soils by at least 90%. Zhang et al. (1998) recorded a 96% reduction in soluble Pb concentration in soil suspensions amended with synthetic hydroxyapatite at a molar P:Pb ratio of 4:5. Laperche et al. (1996) reported that after reacting the Pb-enriched fraction of a Pb-contaminated soil with hydroxyapatite for 9 days at pH 5, the concentration of dissolved Pb in a suspension was reduced by 79% at a molar P:Pb ratio of 3:5 and 99% at a molar P:Pb ratio of 6:5. Laboratory experiments using relatively insoluble phosphate rock (natural apatite) have also been successful at large (190:5 – Ma et al., 1995) and near-stoichiometric (10:5 – Lambert et al., 1997) molar P:Pb ratios.

Highly soluble PO₄ compounds have also been used experimentally (Davenport and Peryea, 1991; Berti and Cunningham, 1997; Hettiarachchi et al., 1997; Lambert et al., 1997; Christensen and Brown, 2001). Davenport and Peryea (1991) reported that the addition of monocalcium orthophosphate (Ca(H₂PO₄)₂; MCP) fertiliser to contaminated soil at molar P:Pb ratios of 1:5 and 3:5 reduced Pb leached by 1 pore volume displacement from repacked soil columns by 41% and 71% respectively. However, persistence of the immobilisation was not achieved in the second pore volume of leachate, most likely due to the inability of the MCP to maintain a sufficient supply of PO₄ to the soil solution. Christensen and Brown
(2001) added P to contaminated soils in the form of phosphoric acid (24:5 molar P:Pb ratio) and adjusted the soil pH to >7. A reduction of 99% was achieved in soil solution Pb in the P amended soil, but lettuce grown in the amended soil contained a greater amount of Pb than those in unamended soil.

Direct physical evidence of pyromorphite mineral formation in soil following reaction with PO₄ compounds has been provided by Laperche et al. (1996), Laperche et al. (1997), Zhang et al. (1998), Lambert et al. (1997), and Hodson et al. (2000) using XRD. Sequential fractionation of contaminated soils and slag reacted with K₂HPO₄ or apatite at molar P:Pb ratios ≤20:5 has shown redistribution of Pb from labile fractions (exchangeable and carbonate) to oxide, organic and/or residual fractions (Berti and Cunningham, 1997; Hettiarachchi et al., 1997; Lambert et al., 1997).
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7.2.3 Mechanisms controlling lead-phosphorus reaction

The primary mechanism of Pb immobilisation by P in aqueous and soil environments appears to be through P mineral dissolution and subsequent precipitation of pyromorphite minerals (Ma et al., 1993; Ma et al., 1994b; Ma et al., 1995; Laperche et al., 1996; Ma, 1996; Manecki et al., 2000). Other possible mechanisms of Pb immobilisation – precipitation of other less stable Pb-phosphate minerals, absorption onto P mineral surfaces and cation substitution – have been shown to be minor mechanisms (Ma et al., 1994b; Laperche et al., 1996; Valsami-Jones et al. (1998) in Hodson et al., 2000). Pyromorphite has been shown to nucleate on the surface of apatite grains, but this does not appear to restrict further apatite dissolution (Hodson et al., 2000; Manecki et al., 2000). The dissolution of hydroxyapatite and the formation of hydroxypyromorphite has been described in equations 7.1 and 7.2 (Section 7.21). Chen et al. (2001b) have described the transformation of PbCO3 to a pyromorphite-like mineral in the presence of soluble P using the equations:

\[
PbCO_3 + H^+ + H_2PO_4^- \rightarrow Pb^{2+} + H_2PO_4^- + HCO_3^- \quad (7.3)
\]
\[
10 Pb^{2+} + 6H_2PO_4^- + HCO_3^- \rightarrow Pb_{10}(PO_4)_6CO_3(s) + 13 H^+ \quad (7.4)
\]

Parameters affecting the reactions represented in equations 7.1-7.4 will affect Pb immobilisation by PO4 compounds. The precipitation of pyromorphite (Equation7.2) will be favoured by addition of P to the solution. Phosphate mineral solubility is therefore a primary parameter determining the effectiveness of Pb immobilisation. This is substantiated by various authors who have observed that more soluble P amendments increase pyromorphite formation and that the source of P appears to be more important than rate of application or reaction time (Hettiarachchi et al., 1997; Lambert et al., 1997; Laperche et al., 1997). This suggests that a rapid supply of P to the solution is more important than application rate (molar P:Pb ratio).

When a water-soluble P fertiliser particle is in contact with soil, soil moisture moves to the particle and forms a saturated solution in and around the particle, and an osmotic gradient occurs between the fertiliser solution and the soil solution (Sample et al., 1980). The saturated solution is constituted of concentrations of P and associated cations in the fertiliser compound. In a Pb-contaminated soil amended with P fertiliser, the P would be removed from a fertiliser solution by precipitation with Pb. If the fertiliser solution remains saturated with respect to associated cations in the fertiliser compound, no further fertiliser dissolution would occur and further P would not be released. In this way, calcium released into solution
7. Control of lead mobility

by the dissolution of calcium-phosphate compounds such as apatite and superphosphate could affect the formation of pyromorphite. If the system becomes saturated with respect to Ca (as at triple point solution), the P compound will not continue to be dissolved and P will not be released. In this situation soluble Pb would return to being controlled by minerals such as cerussite, regardless of the amount of Ca-containing amendment added (Zhang et al., 1998).

Effect of pH on pyromorphite formation

Data from Berti and Cunningham (1997; Table 7.2) and Ruby et al. (1994; Table 7.3) suggest that pyromorphite formation is more strongly influenced by soil pH than molar P:Pb ratio and that a much greater molar P:Pb ratio is required to achieve the same immobilising effect at higher soil pH. Laperche et al. (1996) studied pyromorphite formation in a highly contaminated soil at natural and adjusted pH (7.7 and 5.0 respectively). The dissolved Pb concentration in the sample at pH 7.7 was reduced 13% by P addition (3:5 molar P:Pb ratio). The same P addition at pH 5.0 reduced dissolved Pb by 79%.

Table 7.2. Reduction in exchangeable + carbonate Pb in soil by the formation of pyromorphite minerals (from Berti and Cunningham, 1997).

<table>
<thead>
<tr>
<th>Total Soil Pb (mg kg⁻¹)</th>
<th>Soil pH</th>
<th>Percent reduction in Exchangeable + Carbonate Pb</th>
<th>P:Pb molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,500</td>
<td>4.6</td>
<td>79</td>
<td>67:5</td>
</tr>
<tr>
<td>3,500</td>
<td>6.0</td>
<td>71</td>
<td>48:5</td>
</tr>
<tr>
<td>1,200</td>
<td>8.0</td>
<td>68</td>
<td>139:5</td>
</tr>
</tbody>
</table>

Table 7.3. Impact of pH on the formation of pyromorphite minerals in contaminated soil (from Ruby et al., 1994).

<table>
<thead>
<tr>
<th>Total Soil Pb (mg kg⁻¹)</th>
<th>Soil pH</th>
<th>Percent of Pb minerals as Pb-phosphates</th>
<th>P:Pb molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,900</td>
<td>4.2</td>
<td>60</td>
<td>30:5</td>
</tr>
<tr>
<td>183,000</td>
<td>5.8</td>
<td>41</td>
<td>1:5</td>
</tr>
<tr>
<td>10,200</td>
<td>7.4</td>
<td>17</td>
<td>16:5</td>
</tr>
</tbody>
</table>
Ruby et al. (1994) give the optimum soil pH for maximum formation of pyromorphite and minimum solubility of Pb as approximately pH 7. Sauvé and McBride (1998) concluded that the optimum range for the reduction of Pb in solution is pH 5.5 to 6.5. This corresponds to the optimum soil pH range (5.5 to 6.5) for PO₄ availability in the soil solution (McLaren and Cameron, 1996). Data from Sauvé and McBride (1998) further suggest that Pb-phosphates are not sufficiently insoluble to prevent groundwater contamination in moderately contaminated soils (ca. 500 mg kg⁻¹) at low and high pH (5>pH>7), but in more-contaminated soils Pb-phosphate formation and insolvency would be expected to be favoured. Laperche et al. (1996) observed that pyromorphite formation in soil appears to be limited by kinetic rather than thermodynamic constraints at pH >8, and that given sufficient time, significant formation of pyromorphite should also occur at higher pH.

Acidic pH would cause greater dissolution of Pb-carbonates and result in greater precipitation of pyromorphite minerals. Laperche et al. (1996) observed that hydroxyapatite added to the PbCO₃-rich high-density fraction of contaminated soil at a molar P:Pb ratio of 3:5 caused PbCO₃ dissolution and pyromorphite formation at pH 5, but had no similar effect at pH 7.7.

Effect of organic matter on pyromorphite formation

Data from Sauvé and McBride (1998) showed that in aqueous solutions secondary Pb-orthophosphate (PbHPO₄) was solubilised to form dissolved organic-Pb at alkaline pH. The authors hypothesised that at higher soil pH the strong complexation of Pb by SOC dissolves a fraction of the Pb-phosphate. Thus PO₄ addition to contaminated soils would not be completely successful in immobilising Pb. Although the solubilisation of pyromorphite by SOC at high soil pH warrants consideration, it is likely to be less of a concern because the secondary Pb-orthophosphates studied by Sauvé and McBride (1998) are less stable than pyromorphite (Nriagu, 1972).
Soluble organic carbon may also create coatings around pyromorphite crystals which limit crystal growth and lead to an increased Pb solubility. Lang and Kaufenjohann (2001) have studied the effect of SOC on chloropyromorphite formation. The authors found that SOC did not influence the formation of chloropyromorphite precipitates at pH 5-7, but did impair the reaction at pH 3 and 4. It was identified that carbon coatings on the chloropyromorphite crystals prevented crystal aggregation from solution at low pH. This suggests that SOC may be a major cause of the reduced efficiency of pyromorphite formation observed in soils compared to studies of aqueous solutions. In addition, the results suggest there is potential for colloidal pyromorphite to be leached from soils at very low pH where pyromorphite particle size is greatly reduced.

Effect of time on pyromorphite formation

Pyromorphite minerals have been found in a soil formed in centuries-old mine waste (Cotter-Howells et al., 1994), indicating that pyromorphite will naturally form as a weathering product over time in soils containing P and Pb. The effect of time on pyromorphite formation has been studied experimentally by a few authors. Laperche et al. (1996) observed that XRD peaks of hydroxypyromorphite that formed in soil material increased in intensity from 9 to 14 days, indicating further hydroxypyromorphite formation with time. Lambert et al. (1997) found that pyromorphite became more abundant in slag after 6 weeks reaction time with a P compound compared to 3 weeks reaction time, but little further immobilisation of Pb occurred over the extended time period. This suggested the possible formation of intermediary Pb-orthophosphates which transformed to pyromorphite over time. This is consistent with the behaviour of phosphate reaction products in soils discussed by Sample et al. (1980), in that initial reaction products may be metastable and change form with time.
7.2.4 Use of phosphorus immobilisation technology in the field

Of the studies during the past 20 years which have investigated the use of P compounds as soil additives with the goal of transforming existing soil Pb forms to pyromorphites, there is little data available from the use of P amendments in the field.

Application of P at large molar P:Pb ratios such as those used by Ma et al. (1993; 1995), Berti and Cunningham (1997) and Boisson et al. (1999) is unrealistic for use in field situations. Large volumes of P compound applied in the field would result in undesirably high potential for mobility of excess P. Other experimental studies suggest the amendment of highly contaminated soil at molar P:Pb ratios approximating the stoichiometry of pyromorphite may be adequate for Pb immobilisation.

Brown et al. (1999) applied P amendments to contaminated soil (2000-4000 mg Pb kg⁻¹ soil) in a field trial where the majority of the Pb was present as Pb-carbonates. Soil treatments included P amendments in the form triple super phosphate (TSP) or rock phosphate (Ca₃(PO₄)₂; RP). Three months after P application, lime was applied to bring the pH to approximately 7. The lowest molar P:Pb ratio (83:5) did not have any effect on plant uptake of Pb relative to the control. The amended plots of soil that had the highest resultant molar P:Pb ratios of the study (161:5 and 517:5) showed significant reductions in plant uptake of Pb. This indicated that soil Pb solubility had been reduced only by the higher molar P:Pb ratio treatments.

Chen et al. (2001b) applied in situ treatments of phosphoric acid (H₃PO₄), phosphoric acid + MCP, and phosphoric acid + RP to a heavily Pb-contaminated site at a molar P:Pb ratio of approximately 6:5. The formation of pyromorphite in soils that received P amendments was reflected in redistribution of soil Pb from the exchangeable and carbonate fractions to the residual fraction. Persistence of the immobilisation effect was limited however, with subsequent redistribution of Pb over time from the residual fraction back to carbonate, exchangeable and organic fractions. This may have been caused by inadequate maintenance of soluble soil P by the treatments – the supply rate being either too fast (phosphoric acid and MCP) or too slow (RP). Concentrations of Pb in groundwater increased dramatically after the application of P amendments. This was most likely due to inability of the amendments to supply sufficient P for immobilisation of the Pb as the soil pH decreased.
illustrates the issues involved in the implementation of immobilisation technology in the field, however, the success of P applied at a molar P:Pb ratio of 6:5, while of limited persistence in the form applied, suggests that relatively low molar P:Pb ratios may be effective provided P activity in solution is maintained. In contrast, Lang and Kaupenjohann (2001) observed no effect of in situ PO₄ application on Pb mobility at a contaminated shooting range, even though the molar P:Pb ratio in the soil solution was in the order of 500:5 (F. Lang, personal communication, 29 August 2001).

The field trials of Brown et al. (1999) and Chen et al. (2001b) appear to illustrate the influence of soil pH on the P effectiveness of amendments. Chen et al. (2001b) achieved reduced Pb solubility with a molar P:Pb ratio of 6:5 at a soil pH that can be assumed to be reasonably acidic because the soil pH was not altered following the addition of phosphoric acid P amendments. In contrast, at a soil pH of approximately 7, Brown et al. (1999) reported that amendment molar P:Pb ratios above 161:5 reduced Pb mobility, and that a molar P:Pb ratio of 83:5 showed no beneficial effect. Similarly, Christensen and Brown (2001) used a molar P:Pb ratio of 25:5 to achieve reduced Pb solubility in a pot trial where soil pH was adjusted to >7. During discussion at the ICOBTE* 2001 conference, Dr S. Brown stated that it is necessary to be more ‘heavy handed’ when transferring an effective rate of P application from the laboratory to field situations. However a ‘heavy handed’ approach may only be needed when soil pH is approximately neutral to alkaline, where a high concentration of soluble P would be required to favour the stability of pyromorphite over Pb-carbonates. A moderate soluble P concentration appears to be effective at acidic soil pH where the influence of Pb-carbonate is reduced. Maximum effectiveness of an in situ P amendment would be gained by maintaining soil pH at a level at which soil solution P activity is effective and which is sufficiently low to create instability of Pb carbonates, without creating considerably greater risk of Pb movement to groundwater.

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* 6th International Conference on the Biogeochemistry of Trace Elements, Guelph, Ontario.
7.2.5 Potential for phosphorus immobilisation of lead at shooting ranges

As discussed in Chapter Five, commonly occurring Pb minerals in Pb shot corrosion crusts and Pb shot-contaminated soil are cerussite \((\text{PbCO}_3)\), hydrocerussite \((\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2)\), anglesite \((\text{PbSO}_4)\), lead hydroxide \((\text{Pb(OH)}_2)\), and litharge/massicot \((\text{PbO})\). Laperche et al. (1996) and Zhang and Ryan (1999) have demonstrated that Pb-carbonate is effectively transformed to pyromorphite in the presence of soluble P. The results obtained in the field by Brown et al. (1999) indicate successful Pb-phosphate formation in a contaminated soil rich in Pb-carbonates. In addition, the presence of pyromorphite has been recorded in the crust material of Pb shot by Fahrenhorst and Renger (1990). Therefore P amendments appear to be very suitable for reducing the leaching potential of Pb at shooting ranges.

It is apparent that there is generally insufficient naturally-occurring soil solution P activity to support pyromorphite formation in shooting range soils, and it is proposed that addition of PO\(_4\) compounds to soils at sites contaminated by Pb shot has potential to immobilise Pb. It is proposed that:

(i) pyromorphite formation could remove existing solution-Pb capable of downwards movement;

(ii) the presence of soluble P could encourage the transformation of existing, less stable Pb-carbonate corrosion products on the Pb pellets to more geochemically stable pyromorphite minerals, thus reducing or eliminating the current supply of Pb to the soil solution;

(iii) pyromorphite formation could immobilise further Pb supplied to the soil solution from labile forms of fine earth Pb, namely Pb weakly adsorbed onto soil colloids.

7.2.6 Summary

Phosphorus supply appears to be the primary parameter determining the effectiveness of Pb immobilisation. Even where soil pH conditions are less than optimal for pyromorphite formation, Pb immobilisation is likely to occur provided there is sufficient PO\(_4\) to drive the reaction towards pyromorphite formation in those conditions.
7.3 **PART I: EFFECT OF PHOSPHORUS ADDITION ON LEAD SOLUBILITY**

### 7.3.1 **OBJECTIVES**

The main objectives of this experiment were:

- To assess the potential for P amendments to immobilise Pb in soils contaminated with Pb shot;
- To establish an appropriate rate of P addition to each soil for effective Pb immobilisation, in order to form a foundation for the methods of Part Two (lysimeter leaching).

### 7.3.2 **MATERIALS AND METHODS**

The three clay target shooting sites used for the study described in Chapter 6.2.1 were also used for this experiment. Soil cores (0-100 mm) were collected from an area of high contamination at each of the sites to obtain samples with approximate maximum soil Pb concentrations. Cores were divided into 0-50 mm and 50-100 mm samples, which were air dried and sieved (<1 mm). Any Pb shot was removed and their weight was recorded. Total fine earth Pb concentration of the samples were determined (Chapter 3.2).

Subsamples of 50 g of the contaminated fine earth fraction from the three sites were weighed into 200 mL PET jars. Diammonium phosphate (DAP; \((\text{NH}_4)_2\text{HPO}_4\)) was mixed into the soil samples to attain molar P:Pb ratios of P to total Pb in the fine earth-DAP mixtures of 3:5, 6:5, 12:5 and 30:5 – equivalent to 1, 2, 4 and 10 times the stoichiometric molar P:Pb ratio in pyromorphite (Table 7.4). The experiment was prepared with duplicate treatments and included untreated controls (no P added). Samples were incubated at 25°C and maintained at a gravimetric water content of approximately 30%.

After 7 days, samples were oven dried at 50°C and sieved (<1 mm). A 0.1M Ca(NO₃)₂ extraction was carried out to measure soluble and exchangeable Pb. Ten grams of air dried soil (three replicates) were shaken end-over-end in 100 mL polypropylene centrifuge tubes with 50 mL of 0.1 M Ca(NO₃)₂ for 16h. Samples were centrifuged for 10 min at 10,000 rpm. Supernatants were filtered (Whatman No. 50) and the concentration of Pb was determined by flame AAS. The concentration of PO₄-P in the Ca(NO₃)₂ extract was also determined using
7. Control of lead mobility

colorimetric analysis, by the Murphy-Riley method. Colour development of the phosphomolybdate complex was determined after 60 minutes at 882 nm using a Shimadzu double beam spectrophotometer.

Table 7.4. Phosphorus addition required for molar P:Pb ratios of 3:5 to 30:5 in the three soils studied.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth</th>
<th>Mean total fine earth Pb concentration (mg kg(^{-1}))</th>
<th>Required P addition (g P kg(^{-1}) soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mm)</td>
<td></td>
<td>3:5</td>
</tr>
<tr>
<td>Motukarara</td>
<td>0-50</td>
<td>13774</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>50-100</td>
<td>5408</td>
<td>0.5</td>
</tr>
<tr>
<td>Lismore</td>
<td>0-50</td>
<td>4251</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>50-100</td>
<td>4441</td>
<td>0.4</td>
</tr>
<tr>
<td>Waimakariri</td>
<td>0-50</td>
<td>3274</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>50-100</td>
<td>3232</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Statistical analysis

Analysis of variance was carried out using Minitab 13.1 software. The LSDs were calculated with a 95% confidence interval.
7.3.3 RESULTS AND DISCUSSION

The addition of DAP to the contaminated soils was effective in reducing Ca(NO₃)₂-extractable Pb at all treatment levels as shown in Figures 7.1-7.3. Lead solubility was reduced by 65-98% compared to controls. A large decrease in Ca(NO₃)₂-extractable Pb occurred where DAP was added at a molar P:Pb ratio of 3:5. Doubling the molar P:Pb ratio did not double the reduction in Pb solubility. This suggests that there may be a threshold P concentration which could be optimised so that excess P is minimised in the field situation. A similar relationship between soil Pb solubility and P addition was observed by Ma et al. (1993), who reported 90% reduction in Pb solubility at 10:5, and 98% reduction at 40:5. It was assumed that the reduction in Ca(NO₃)₂-extractable Pb indicated that immobilisation of Pb by pyromorphite formation had occurred. This was not confirmed by XRD due to the experiment being a brief study preliminary to the leaching of intact soils cores following P application.

The solubility trend observed in the 0-50 mm layer of the Motukarara soil is markedly different to the 50-100 mm Motukarara layer and the other two soils studied. The Motukarara 0-50 mm layer is dominated by peat; the 50-100 mm layer is dominated by mineral material. While not classified as an organic soil, the peat layer significantly influences soil solution chemistry, as was shown in Chapter Six. A greater proportion of solution Pb will be present as organo-Pb species in the Motukarara soil relative to the Lismore and Waimakariri soils. The solubility trend suggests that the effectiveness of the DAP additions was reduced by organo-Pb species, and suggests that P addition may be less effective at immobilising Pb in organic-rich soils.

However, Table 7.5 shows that the pH of the Motukarara soil decreased substantially at the 30:5 level of DAP addition. This was most likely caused by nitrification of the relatively large ammonium addition to this sample (2.5-4 times greater mass than that added to the other soils). Figure 7.1(a) indicates that DAP addition at 30:5 caused less reduction in exchangeable Pb than the 12:5 treatment, but this is likely to be the effect of the pH decrease on solution and solid phase Pb speciation. It is likely that Pb²⁺ activity in solution increased to a level at which the P supplied was only sufficient to immobilise a small proportion of solution Pb²⁺, causing the apparent reduction in immobilisation efficiency. This influence of soil pH on Pb mobilisation also appears to be the cause of reduced effectiveness of the 30:5 treatment in the 50-100 mm layer of Motukarara soil (Figure 7.1(b); Table 7.5).
7. Control of lead mobility

Figure 7.1. Effect of P addition on Ca(NO₃)₂-extractable Pb (mg kg⁻¹) in Motukarara fine earth; Total fine earth Pb concentration: 0-50 mm = 13800 mg kg⁻¹; 50-100 mm = 5400 mg kg⁻¹.

Figure 7.2. Effect of P addition on Ca(NO₃)₂-extractable Pb (mg kg⁻¹) in Lismore fine earth; Total fine earth Pb concentration: 0-50 mm = 4300 mg kg⁻¹; 50-100 mm = 4400 mg kg⁻¹.
7. Control of lead mobility

Figure 7.3. Effect of P addition on Ca(NO$_3$)$_2$-extractable Pb (mg kg$^{-1}$) in Waimakariri fine earth; Total fine earth Pb concentration: 0-50 mm = 3300 mg kg$^{-1}$; 50-100 mm = 3200 mg kg$^{-1}$.

Table 7.5. Mean soil pH of fine earth samples incubated with diammonium phosphate.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth</th>
<th>Soil pH of treatments</th>
<th>Molar P:Pb ratio</th>
<th>(mm)</th>
<th></th>
<th>0:5</th>
<th>3:5</th>
<th>6:5</th>
<th>12:5</th>
<th>30:5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(control)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Motukarara</td>
<td>0-50</td>
<td>6.5</td>
<td>6.6</td>
<td>6.6</td>
<td>6.8</td>
<td>3.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50-100</td>
<td>7.3</td>
<td>7.7</td>
<td>7.4</td>
<td>7.3</td>
<td>7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lismore</td>
<td>0-50</td>
<td>6.5</td>
<td>6.6</td>
<td>6.7</td>
<td>6.9</td>
<td>7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50-100</td>
<td>6.2</td>
<td>6.5</td>
<td>6.7</td>
<td>6.8</td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waimakariri</td>
<td>0-50</td>
<td>6.0</td>
<td>6.1</td>
<td>6.5</td>
<td>6.7</td>
<td>6.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50-100</td>
<td>5.5</td>
<td>6.4</td>
<td>6.5</td>
<td>6.6</td>
<td>6.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Apart from the Motukarara soil at the 30:5 molar P:Pb ratio treatment, soil pH generally increased relative to PO$_4$ addition (Table 7.5), indicating H$^+$ removal from the solution to replace surface charge after movement of exchangeable Pb$^{2+}$ into solution to equilibrate solution Pb removed as pyromorphite precipitates. The saturated solution of DAP has a pH of 8, and this also may have caused the pH increase.
The use of the Ca(NO$_3$)$_2$ extraction for assessing the effectiveness of P amendment on shooting range soils was probably not ideal, as the extraction considered only the most soluble Pb fraction, which made up just 0.3 – 3.3% the total soil Pb. Ma et al. (1993) commented that the ability of hydroxyapatite to immobilise exchangeable Pb is important in Pb-contaminated soils, since exchangeable Pb is likely to be more dominant than aqueous Pb. However, the large fraction of Pb present in these soils as carbonate corrosion products are of greatest importance, and were not considered by the Ca(NO$_3$)$_2$ extraction, and the effect of P addition on immobilisation or transformation of this fraction was not assessed.

The proportion of added P extractable by Ca(NO$_3$)$_2$ generally increased relative to increasing DAP addition (Table 7.6). In the field situation it is assumed the extractable P would be subject to leaching via percolation of water. The use of a relatively high molar P:Pb ratio may increase the leaching of excess P to environmentally unacceptable levels. The leaching of excess P needs to be minimised in order for P amendments to be acceptable for Pb immobilisation in the field. Further potential adverse effects arise from the use of DAP. While the compound was a useful source of highly-soluble P, the use of DAP fertiliser as an amendment for a field trial is undesirable as the introduction of ammonium into soil systems could result in nitrate leaching and soil acidification (Table 7.5).

<table>
<thead>
<tr>
<th>Soil depth (mm)</th>
<th>Molar P:Pb ratio</th>
<th>Extractable PO$_4$-P (%)</th>
<th>Motukarara</th>
<th>Lismore</th>
<th>Waimakariri</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-50</td>
<td>Control</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>3:5</td>
<td>7</td>
<td>5</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6:5</td>
<td>14</td>
<td>11</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12:5</td>
<td>32</td>
<td>17</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30:5</td>
<td>53</td>
<td>25</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>50-100</td>
<td>Control</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>3:5</td>
<td>23</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6:5</td>
<td>29</td>
<td>8</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12:5</td>
<td>34</td>
<td>15</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30:5</td>
<td>22</td>
<td>23</td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>

ND = not detectable
Using the results obtained from Part I of this study, a molar P:Pb ratio of 6:5 was determined as a suitable treatment to be used in Part II. While the effect observed at molar P:Pb ratios of 3:5 and 6:5 were not significantly different for all soils, it was considered that the 6:5 treatment was more likely to result in a measurable effect. This takes into consideration the comment by Dr S. Brown (personal communication, August 2001) that a more heavy handed approach to P application may be required in field situations. Table 7.6 shows that at a molar P:Pb ratio of 6:5, extractable P was generally below 15% and thus a balance is achieved between the reduction of Pb solubility and adverse effects of excess P.

7.3.4 CONCLUSIONS

The incubation experiment has demonstrated that addition of P to Pb shot-contaminated soil reduces soil Pb solubility in similar proportions to those observed by other authors studying Pb-contaminated soils. It is assumed that Pb immobilisation occurred in the same manner as that observed by other authors – by the formation of pyromorphite minerals. Results indicate that a molar P:Pb ratio of 6:5 is sufficient to apply as a soil amendment in Part II of this study. This level of treatment appears to provide considerable reduction in Ca(NO₃)₂-extractable Pb coupled with a relatively small amount of potentially excess P which may have the potential to leach from the topsoil.

The choice of Ca(NO₃)₂ as the extractant used to assess Pb immobilisation may have hindered more comprehensive assessment of the efficiency of treatment molar P:Pb ratios. Use of an extractant that allowed the measurement of Pb in the carbonate fraction could have been more relevant as the effectiveness of P amendment for the study soils depends largely on the transformation of the Pb carbonate fraction to pyromorphite minerals.
7.4 PART II: EFFECT OF PHOSPHORUS APPLICATION ON LEAD MOBILITY IN UNDISTURBED SOIL CORES FROM CONTAMINATED SHOOTING RANGES

7.4.1 OBJECTIVES

The main objectives of this experiment were:

- To determine the effect of P addition on Pb mobility in undisturbed soil cores.
- To assess applicability of P amendment to Canterbury clay target shooting ranges.

7.4.2 MATERIALS AND METHODS

Study soils

The three contaminated sites used for the studies described in Chapters 6 and 7.3 were also used for this experiment.

Lysimeter collection and preparation

Five intact soils cores (68 mm diameter, 100 mm deep) were collected from an area approximately 120-140m from the traps at each of the three sites so that soil cores contained the approximate maximum soil Pb concentration at each site. Lysimeter casings, method of sampling, edge-sealing, and preparation for leaching were the same as those described in Chapter 6.2.2, following the method described by Cameron et al. (1992). The cores were wet up to field capacity and stored at 4°C until required.
Experimental design

In order to estimate the Pb concentration of each lysimeter, a secondary soil core was collected adjacent to the position of each lysimeter for destructive sampling, using a soil corer. The secondary soil cores were air dried and prepared for analysis as described in Chapter 3.1.1. Total fine earth Pb concentrations were determined (Chapter 3.2.1) and used as an estimate of the fine earth Pb concentration of the lysimeters. Superphosphate (SSP) fertiliser (<2 mm) was mixed into the top 30 mm of three lysimeters from each site at a molar P:Pb ratio of 6:5, based on an estimate of the total fine earth Pb concentration and the dry weight of each soil core. This was estimated from the wet weight of the lysimeters using the wet:dry weight ratio measured for the secondary soil cores. The remaining two lysimeters from each site were left untreated as controls. All lysimeters were then maintained at field capacity and room temperature for 7 days to allow for some equilibration.

All lysimeters were leached with one pore volume of distilled water every second day in order to allow for a re-equilibration period between leaching events. The leachate was collected manually in fractions of one-fifth of a pore volume for 5 leaching events. After reviewing the mixed results obtained after 5 leaching events, all cores were left to equilibrate for a further 20 days; de-ionised water was regularly added to the top of the cores to maintain moist soil conditions. The results of the first 5 leaching events suggested that rapid flow rate may have been inhibiting Pb immobilisation, therefore the leaching rate was regulated using mixture of silica sand and silica flour held within a glass fibre filter placed on top of each soil core. The filter paper was edge-sealed with petroleum jelly. Leaching was then continued for a further 5 events as before. The filter paper was lifted slightly after each leaching to avoid the cores becoming anaerobic, and edge sealing was repeated immediately before the next leaching event.
7. Control of lead mobility

Analysis

All leachate fractions were analysed for pH, and fractions 1, 3 and 5 from each leaching event were filtered (<0.45 µm, cellulose acetate membrane) and analysed for concentrations of Pb (flame or graphite furnace AAS) and PO₄-P (malachite green colorimetry by FIA; Ohno and Zibilski, 1991).

After leaching, the cores were removed from their casings, air-dried, weighed and prepared as outlined in Chapter 3.1.1. The total fine earth Pb concentration of each lysimeter was determined. In order to confirm the formation of Pb-phosphates, soil from selected lysimeters was subjected to a density fractionation scheme described by Cotter-Howells (1993) to separate Pb minerals from soil for XRD analysis. This method was not successful, therefore, as a secondary measure, soil from selected lysimeters was subjected to sequential fractionation using the method described in Chapter 3.2.3.

Superphosphate (monocalcium phosphate monohydrate: Ca(H₂PO₄).H₂O, and sulphur: CaSO₄) was chosen as a source of P on the grounds that it is readily available and highly water-soluble. The elemental analysis for the SSP used was 9% P, 12% S and 20% Ca.

Phosphorus adsorption isotherms

Air-dried soil samples (3g, <2mm) were weighed into centrifuge tubes and mixed with various amounts of KH₂PO₄, a drop of toluene and enough CaCl₂ solution and water to bring the final volume to 30 mL and the final concentration of CaCl₂ to 0.01 M. The suspensions were shaken on an end-over-end shaker for 96 hours, then centrifuged and the P in the supernatant was determined using the Murphy-Riley molybdenum blue method after 60 minutes at 882 nm using a Shimadzu double beam spectrophotometer.
7.4.3 RESULTS AND DISCUSSION

The amount of Pb leached from SSP-treated lysimeters generally decreased during the 10 leaching events but the results were quite variable, as could be expected from the heterogeneous nature of a collection of intact soil cores. Concentrations of leachate Pb from treated lysimeters of the Lismore and Waimakariri soils did not initially appear to be substantially different to those from control lysimeters, however there was a small effect of PO₄ addition on Pb solubility.

While the aim of the experiment had been to apply P to approximate a molar P:Pb ratio of 6:5, in practice, a range of molar P:Pb ratios resulted (Tables 7.7-7.9). This was due to a combination of factors. The total fine earth concentration of secondary soil cores collected adjacent to each lysimeter did not accurately estimate the total fine earth Pb concentration in the actual lysimeter. In addition, the estimation of the dry weight of soil in each lysimeter was inaccurate due to the presence of varying masses of stones in the Lismore and Waimakariri lysimeters, and varying proportions of organic matter and mineral components in the Motukarara lysimeters.
### Table 7.7. Motukarara lysimeters: Fine earth Pb concentrations and phosphate treatment details.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Estimated fine earth Pb conc. (mg kg⁻¹)</th>
<th>P added to approximate a 6:5 molar P:Pb ratio (g)</th>
<th>Equivalent loading of P (kg ha⁻¹)</th>
<th>Measured fine earth Pb conc. (mg kg⁻¹)</th>
<th>Measured molar P:Pb ratio</th>
<th>Average flow rate (mL hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSP Lysimeter 1</td>
<td>15,000</td>
<td>1.13</td>
<td>418</td>
<td>8,157</td>
<td>14:5</td>
<td>4.0</td>
</tr>
<tr>
<td>SSP Lysimeter 2</td>
<td>15,300</td>
<td>1.02</td>
<td>292</td>
<td>19,937</td>
<td>4:5</td>
<td>28.5</td>
</tr>
<tr>
<td>SSP Lysimeter 3</td>
<td>7,200</td>
<td>0.50</td>
<td>132</td>
<td>17,288</td>
<td>2:5</td>
<td>17.5</td>
</tr>
<tr>
<td>Control Lysimeter 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control Lysimeter 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 7.8. Lismore lysimeters: Fine earth Pb concentrations and phosphate treatment details.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Estimated fine earth Pb conc. (mg kg⁻¹)</th>
<th>P added to approximate a 6:5 molar P:Pb ratio (g)</th>
<th>Equivalent loading of P (kg ha⁻¹)</th>
<th>Measured fine earth Pb conc. (mg kg⁻¹)</th>
<th>Measured molar P:Pb ratio</th>
<th>Average flow rate (mL hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSP Lysimeter 1</td>
<td>5,300</td>
<td>0.60</td>
<td>268</td>
<td>7,917</td>
<td>9:5</td>
<td>50.4</td>
</tr>
<tr>
<td>SSP Lysimeter 2</td>
<td>4,500</td>
<td>0.52</td>
<td>154</td>
<td>8,398</td>
<td>5:5</td>
<td>11.0</td>
</tr>
<tr>
<td>SSP Lysimeter 3</td>
<td>6,300</td>
<td>0.66</td>
<td>289</td>
<td>10,557</td>
<td>8:5</td>
<td>49.3</td>
</tr>
<tr>
<td>Control Lysimeter 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Control Lysimeter 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7.9. Waimakariri lysimeters: Fine earth Pb concentrations and phosphate treatment details.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Estimated fine earth Pb conc. (mg kg(^{-1}))</th>
<th>P added to approximate a 6:5 molar P:Pb ratio (g)</th>
<th>Equivalent Loading of P (kg ha(^{-1}))</th>
<th>Measured fine earth Pb conc. (mg kg(^{-1}))</th>
<th>Measured molar P:Pb ratio</th>
<th>Average flow rate (mL hr(^{-1})) 0-5 days</th>
<th>Average flow rate (mL hr(^{-1})) 5-10 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSP Lysimeter 1</td>
<td>4,500</td>
<td>0.40</td>
<td>113</td>
<td>7,099</td>
<td>4:5</td>
<td>14.8</td>
<td>8.1</td>
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<tr>
<td>SSP Lysimeter 2</td>
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<td>0.41</td>
<td>118</td>
<td>7,027</td>
<td>5:5</td>
<td>14.1</td>
<td>9.4</td>
</tr>
<tr>
<td>SSP Lysimeter 3</td>
<td>3,600</td>
<td>0.33</td>
<td>78</td>
<td>6,025</td>
<td>4:5</td>
<td>23.9</td>
<td>9.9</td>
</tr>
<tr>
<td>Control Lysimeter 1</td>
<td></td>
<td></td>
<td></td>
<td>6,287</td>
<td>0:5</td>
<td>6.5</td>
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<td></td>
<td></td>
<td>6,799</td>
<td>0:5</td>
<td>12.9</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Motukarara soil

**Pb concentration of leachates**

The Motukarara soil lysimeters treated with SSP displayed a leaching trend that was discernibly different from that of the control lysimeters. Figure 7.4 shows the Pb concentrations of leachates from the Motukarara lysimeters as a proportion of the initial leachate concentration for respective lysimeters. Lead leached from the Motukarara control lysimeters in increasing concentration during the first 4 to 5 leaching events, then lessened for the remainder of the experiment. The three treated lysimeters produced leachate Pb concentrations which reduced as leaching progressed. This indicates that the SSP addition to Motukarara maintained the soluble P at a level sufficient to precipitate some or all dissolved Pb, presumably as pyromorphite, under the leaching conditions of the experiment. The three Motukarara lysimeters treated with SSP contained molar P:Pb ratios of 14:5, 4:5 and 2:5, and Figure 7.4 indicates that the success of the SSP treatments in reducing leachate Pb concentrations followed the molar P:Pb ratio order (Lysimeter 1 > Lysimeter 2 > Lysimeter 3). The greatest molar P:Pb ratio treatment (Lysimeter 1) appeared to be particularly effective, as Pb was not detectable (<2 µg L⁻¹) in most leachate fractions (Figure 7.4). SSP-treated Lysimeter 1 also displayed the slowest natural leaching rate during the first five (unregulated) leaching events (Table 7.7). This may also have had an effect on the success of the treatment by providing contact time sufficient for substantial immobilisation.

![Figure 7.4. Pb concentrations of leachate fractions (Ci) from Motukarara lysimeters as a proportion of the initial leachate concentration (C) for respective lysimeters; MR = molar P:Pb ratio.](image-url)
Figure 7.5 shows leachate Pb concentrations (Pb\textsubscript{Total}) plotted versus leachate pH for each lysimeter, compared to the solubility of PbCO\textsubscript{3} and hydroxyapatite. Leachate Pb speciation was not modelled in this experiment, necessitating the use of Pb\textsubscript{Total} data. Therefore these plots will underestimate any immobilising effect of PO\textsubscript{4} addition on Pb solubility. The initial stability of hydroxyapatite with pH was calculated using the solubility of MCP (the P mineral in SSP), as determined by CaCO\textsubscript{3} solubility, using stability constants from Lindsay (1979). This was then adjusted for each lysimeter using the approximate initial PO\textsubscript{4} concentration measured in respective lysimeter leachates (Figure 7.6). This resulted in hydroxyapatite stability slightly below optimum.

The stability plots also show a significant alteration between control and treated lysimeters in the position of data in the plots. The molar P:Pb ratio achieved in SSP-treated Lysimeter 1 appeared to be sufficient to completely alter the Pb minerals controlling Pb solubility from Pb-carbonates and other similarly soluble minerals to pyromorphite. In comparison, the plots of the remaining two SSP-treated lysimeters suggest that the molar P:Pb ratios in these lysimeters achieved partial success in reducing Pb solubility. It is most likely that greater molar P:Pb ratios, and therefore greater initial soluble PO\textsubscript{4} concentrations would have been successful in reducing Pb solubility further.

The lysimeter data show that P addition can be effective in immobilising Pb in the Motukarara soil. Sauvé and McBride (1998) hypothesised that at higher soil pH the strong complexation of Pb by SOC can dissolved PbHPO\textsubscript{4}. However, PbHPO\textsubscript{4} is less stable than pyromorphite (Nriagu, 1972). In addition, SSP application caused pH to reduce which would have reduced the concentration of SOC and aided pyromorphite formation.

X-ray diffraction of soil minerals to confirm pyromorphite formation was unable to be carried out, therefore soil from all Motukarara lysimeters was subjected to sequential fractionation. Considerable redistribution of Pb from exchangeable and carbonate/specifically adsorbed fractions to the residual fraction is evident (Figure 7.7), which infers the formation of pyromorphite. This concurs with the observations of various authors, as discussed in Section 7.2.2.
Figure 7.5. Leachate-Pb\textsubscript{Total} data for Motukarara lysimeters plotted with the solubility of PbCO\textsubscript{3} and Pb\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}(OH). Hydroxypyromorphite solubility calculated for individual lysimeters using approximate initial leachate [PO\textsubscript{4}]. Stability constants from Lindsay (1979).
Figure 7.6. Leachate pH and PO$_4$-P concentrations for treated and control Motukarara lysimeters.
The persistence of the effect of SSP treatment appeared to be good, lasting at least 5 leaching events (equivalent to approximately 250 mm drainage), but this is not completely clear as Pb concentrations in leachates of the control lysimeters also reduced in the latter stage of the experiment. After the first leaching event, Pb was detectable in leachate from SSP Lysimeter 1 from only the sixth leaching event, after the 20 day equilibration period. Leachate Pb concentrations from the sixth leaching event were substantially lower than those from the first leaching event, probably indicating that the immobilising effect of P was continuing.

**pH of leachates**

The pH of leachates from lysimeters treated with SSP remained lower than control lysimeters (Figure 7.6), due to the effect of the acidic saturated fertiliser solution (triple point solution; TPS) during SSP dissolution (Sample et al., 1980). Decreased soil pH would have caused an influx of Pb$^{2+}$ into the soil solution, and effectively reduced the molar P:Pb ratio in solution. SSP lysimeter 1 displayed the greatest decrease in leachate pH but the P supply was still sufficient to cause Pb immobilisation.
**7. Control of lead mobility**

**P concentration of leachates**

Concentrations of PO₄-P in the leachates from treated lysimeters were substantially greater in the first few leaching events compared to controls. By the end of the experiment PO₄-P concentrations were approximately the same from treated and control lysimeters (Figure 7.6). When leachate PO₄-P concentrations are considered relative to P added to respective lysimeters, SSP Lysimeter 1 leached a much larger proportion of PO₄-P in the first leaching event than the other two treated lysimeters (Figure 7.6). The high concentration of available P in initial stages of SSP Lysimeter 1 may have increased the potential for removal of dissolved Pb by pyromorphite formation.

Figure 7.8 indicates that initial SSP dissolution dynamics in the three lysimeters was varied. Leachate pH may also give an indication of the SSP dissolution. SSP Lysimeter 1 displayed the most acidic leachate for the first 2 leaching events, corresponding to the much greater initial concentrations of PO₄-P leached and therefore SSP dissolved during that time. The most acidic leachate in lysimeters 2 and 3 occurred in the second and third (lysimeter 2) leaching events, possibly indicating that less SSP dissolution occurred during the 7-day equilibration period before leaching was begun.

![Figure 7.8](image)

**Figure 7.8.** PO₄-P concentration of leachate from Motukarara SSP-treated lysimeters relative to P addition to respective lysimeters (mg PO₄-P L⁻¹ g⁻¹ added P).
The much greater concentrations of PO₄-P leaching from the treated lysimeters compared to those from control lysimeters gives rise to potential for adverse effects from P leaching out of the soil in the field. There is general consensus that the transfer of even relatively small quantities of P from the terrestrial to the aquatic environment can pose a threat to water quality. The Waihora CTC, from which the Motukarara lysimeters were collected, is immediately adjacent to the Halswell stream (Figure 4.5), which drains into Lake Ellesmere. Given the magnitude of P concentrations leaching from the lysimeters, the use of P as an amendment at the site may have potentially serious implications. Any increase in the eutrophic state of the stream and lake needs to be avoided. That organic soils retain excess P to a lesser extent than mineral soils (Brookes et al., 1997) aggravates this risk. The relative P sorption capacities of the three soils studied are shown in Figure 7.9. The essentially level site, and the levee between the site and the stream would negate any surface runoff of P. Migration of P from the site into the stream via horizontal sub-surface flow is much more likely to occur.

Figure 7.9. Sorption of P in the fine earth fraction (0-100 mm) of the three soils studied.
The rate of P addition to the treated lysimeters was equivalent to 132 to 418 kg P ha\(^{-1}\) (Table 7.7). Given the potential risk and adverse effects of P losses from this site, it is particularly important to minimise the application of P required for Pb immobilisation. The volume of water leached through the lysimeters during the experiment was equivalent to approximately 500 mm of drainage. The annual natural drainage at the site would be dependent on the duration of seasonal waterlogging, but is estimated to be 400 mm. This suggests that an effective rate of P addition to the most contaminated area of the Motukarara site may be approximately 300 kg P ha\(^{-1}\) yr\(^{-1}\). Approximately 12-30% of the P added to the lysimeters was lost in the leachates. This is equivalent to approximately 16-125 kg PO\(_4\)-P ha\(^{-1}\). Based on an estimated annual natural drainage of 400 mm, this equates to losses in the order of 13-100 kg PO\(_4\)-P ha\(^{-1}\) yr\(^{-1}\). This is generally greater than P leaching losses calculated by Duxbury and Peverly (1978) in a number of fertilised organic soils (1-30 kg P ha\(^{-1}\)). However, Sinaj et al. (2002) state that preferential flow is especially pronounced under flood irrigation. Preferential flow is likely to have been the main mechanism for water transport through the lysimeters in the current study, which may lead to overestimation of the P losses in the field.
Lismore and Waimakariri soils

**Pb concentration of leachates**

Addition of SSP to Lismore and Waimakariri lysimeters did not have a clearly discernable effect on Pb mobility under the conditions of the experiment (Figures 7.10 and 7.11). Only the results from Lismore SSP-treated lysimeter 1 showed an indication of a reduction in Pb leached relative to controls (Figure 7.10). In this lysimeter the initial reduction in Pb concentration was more rapid than that of the controls, and the molar P:Pb ratio (9:5) was the greatest of the treated Lismore lysimeters, suggesting the treatment had some effect on Pb immobilisation.

Figures 7.12 and 7.13 show the stability plots of leachate Pb$_{Total}$ data. As for Figure 7.5 previously, the stability of hydroxypyromorphite was adjusted for each lysimeter using the approximate initial PO$_4$ concentration measured in respective lysimeter leachates (Figures 7.14 and 7.15). The stability plots show a significant alteration between control and treated lysimeters in the position of data in the plots, with the data points from the treated lysimeters being below the line of PbCO$_3$ solubility. These plots indicate that although Figures 7.10 and 7.11 suggest inconclusive results, the molar P:Pb ratios achieved did have some effect on reducing Pb solubilities below those in the untreated lysimeters. It appears that a combination of Pb minerals that included hydroxypyromorphite and Pb-carbonates controlled Pb solubility during the experiment. This suggests that greater molar P:Pb ratios could have raised soluble PO$_4$ concentrations sufficiently to allow Pb solubility control by pyromorphite alone.

Fractionation of soil from SSP lysimeter 1 (Figure 7.16) revealed a similar redistribution of Pb to that observed for the Motukarara SSP lysimeters, inferring that the formation of pyromorphite occurred. The proportion of Pb in the oxide and residual fractions increased at the expense of Pb in the exchangeable and carbonate/specifically adsorbed fractions, confirming a reduction in labile Pb available for leaching relative to the control lysimeters.

The most likely contributing factors to the overall poor effectiveness of the SSP treatment in both soils are insufficient P supply and/or insufficient contact time. Lower leaching rates during the latter half of the experiment (Tables 7.8 and 7.9) did not appear to encourage immobilisation in the Lismore and Waimakariri soils. However, the contact time may still have been a contributing factor, secondary to insufficient molar P:Pb ratios.
Figure 7.10. Lead concentrations of leachate fractions ($C_l$) from Lismore lysimeters as a proportion of the initial leachate concentration ($C$) for respective lysimeters; MR = molar P:Pb ratio.

Figure 7.11. Lead concentrations of leachate fractions ($C_l$) from Waimakariri lysimeters as a proportion of the initial leachate concentration ($C$) for respective lysimeters; MR = molar P:Pb ratio.
Figure 7.12. Leachate-Pb\textsubscript{Total} data for Lismore lysimeters plotted with the solubility of PbCO\textsubscript{3} and Pb\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}(OH). Hydroxypyromorphite solubility calculated for individual lysimeters using approximate initial leachate [PO\textsubscript{4}]. Stability constants from Lindsay (1979).
Figure 7.13. Leachate-Pb$_{\text{Total}}$ data for Waimakariri lysimeters plotted with the solubility of PbCO$_3$ and Pb$_5$(PO$_4$)$_3$(OH). Hydroxypyromorphite solubility calculated for individual lysimeters using approximate initial leachate [PO$_4$]. Stability constants from Lindsay (1979).
Figure 7.14. Leachate pH and PO₄-P concentrations for treated and control Lismore lysimeters.
Figure 7.15. Leachate pH and PO4-P concentrations for treated and control Waimakariri lysimeters.
The indication that higher molar P:Pb ratios were required for the Lismore and Waimakariri soils in order to induce Pb immobilisation would appear to concur with Dr S. Brown’s statement (personal communication, August 2001) that a more ‘heavy handed’ approach to P application is required in the field compared to controlled experimental conditions. If the preliminary incubation experiment (Part I) had been designed differently, the optimum molar P:Pb ratio required for Pb immobilisation may have been more accurately predicted. The level of P addition required to reduce Pb solubility determined in the preliminary incubation experiment was not directly transferable to the lysimeters. Calculations of the amount of P required for Pb immobilisation in the lysimeters were based on the data from the preliminary incubation experiment, which only considered the fine earth Pb component of the soils. In contrast, the contaminated soil in the lysimeters also contained Pb shot with corrosion crusts. Given the role of corrosion crust minerals in the control of Pb solubility in the soils, effective P treatments are unlikely to be predicted accurately from fine earth Pb concentrations. Therefore more Pb would have been supplied to soil solution in the lysimeters than in the incubation soils and a greater addition of P to lysimeters would have been required to achieve the same reduction in solubility as that measured in the incubation experiment. This parallels the use of total soil metal concentration as the sole indicator of metal availability and toxicity to organisms and the environment, which is well known to be an inaccurate, out-dated method. The incubation experiment may have given a more accurate assessment of the required P addition if the crust-Pb had been exfoliated from the pellets during soil preparation and incorporated into the fine earth fraction used for the experiment.
7. Control of lead mobility

**pH of leachates**

The pH of leachates from Lismore and Waimakariri lysimeters treated with SSP remained lower than control lysimeters for the respective soils (Figures 7.14 and 7.15) due to the acidifying effect of SSP dissolution. Increases in leachate Pb concentrations from most of the treated lysimeters relative to controls may indicate a significant influx of Pb$^{2+}$ into the soil solution. In contrast to the organic soil, this appears to have reduced the molar P:Pb ratio in solution to a level insufficient to immobilise the Pb to any great extent. In this light a treatment molar P:Pb ratio of 6:5 is below optimum for Pb immobilisation in the Lismore and Waimakariri soils. The volume of water leached through the lysimeters during the experiment (500 mm) is similar to a typical annual drainage rate through a Canterbury soil (400 mm; Dr H.J. Di, personal communication, July 2001). Considering the P fixation capacity of the subsoils, an annual addition of P to field sites at a molar P:Pb ratio $>$10:5 is expected to be more effective for Pb immobilisation.

**P concentration of leachates**

Concentrations of PO$_4$-P in leachates from SSP-treated lysimeters reached maximums of approximately 500 mg L$^{-1}$ for the Lismore soil (Figure 7.14) and 250 mg L$^{-1}$ for the Waimakariri soil (Figure 7.15). Leachate PO$_4$-P concentrations from treated lysimeters were much greater in the first few leaching events compared to controls. At the end of the experiment leachate PO$_4$-P concentrations were substantially reduced but remained approximately 5 to 10 times greater than that of controls. Phosphorus sorption isotherms show that the Lismore and Waimakariri soils retain significantly greater amounts of P than the Motukarara soil (Figure 7.9). This effect can be seen when comparing the magnitude of PO$_4$-P concentrations from the control lysimeters of the three soils – PO$_4$-P concentrations from Motukarara control lysimeters are approximately twice that of the Lismore and Waimakariri soils. The poor success of the Pb immobilisation reaction in the latter two soils may have been partly due to their greater P sorption capacity, in that P sorption could effectively reduce the intended molar P:Pb ratio in the soil solution. This is supported by the proportions of added P leached from treated Lismore and Waimakariri lysimeters, which were generally less than that leached from treated Motukarara lysimeters. Lismore lysimeters leached approximately 2.6-7.8% of added P and Waimakariri leached approximately 6.9-21.1% of added P (cf. Motukarara: 12-30% of added P).
The rate of P addition to the treated lysimeters was equivalent to 154 to 289 kg P ha⁻¹ for Lismore lysimeters (Table 7.8) and 78 to 118 kg P ha⁻¹ for Waimakariri lysimeters (Table 7.9). The volume of water leached through the lysimeters during the experiment was equivalent to approximately 500 mm of drainage. Phosphorus loss from the treated lysimeters is calculated to be equivalent to approximately 4-23 kg PO₄-P ha⁻¹ for Lismore soil and 5-25 kg PO₄-P ha⁻¹ for Waimakariri soil. Based on a typical annual drainage rate of 400 mm yr⁻¹ (Dr H.J. Di, personal communication, July 2001) this equates to a P loss of approximately 3-20 kg PO₄-P ha⁻¹ yr⁻¹. Condron et al. (2000) observed maximum losses in the order of 1-2 kg P ha⁻¹ yr⁻¹ from lysimeters containing Lismore soil (0-70 cm) under relatively natural rainfall conditions. As noted earlier, this current experiment created a ponded water effect, so that preferential flow is likely to have predominated. This is likely to have caused rapid removal of soluble P, and lead to overestimation of the P losses that can be expected from the P application rates used. In addition, Sinaj et al. (2002) observed that while P was very mobile in the topsoils of Templeton and Lismore soils, almost all P lost from the topsoils was retained very efficiently, due to very high subsoil P-retention capacities. This demonstrates the risks associated with predicting potential P losses on the basis of P mobility in the topsoil alone. Alluvial mineral soils in Canterbury commonly contain Fe and Al oxides in the subsoils that provide substantial P-retention capacity.

The potential risk to groundwater quality of applying P amendments to shooting ranges with mineral soils is expected, in most cases, to be substantially reduced by the subsoil P retention capacity. This should allow greater P application rates, sufficient to increase molar P:Pb ratios to levels at which immobilisation is successful. Increased subsoil concentrations of P may lead to the immobilisation of any Pb that subsequently leaches from the top soil, providing a secondary chemical ‘barrier’ for Pb movement. However, the countering effect of acidifying PO₄ compounds reducing the P fixation potential due to dissolution of Fe oxides may need to be considered.
Practical aspects of effective field application of phosphorus amendments

This chapter illustrates the complexities of phosphate immobilisation when applied to the field with the current level of knowledge. Further study in a number of areas of this technique would improve the understanding of the complete system and the success of the technique in the field. The collection of further soil solution chemistry data after P addition to assess soil solution dynamics would be particularly useful. Much of this work could be carried out in a field trial of phosphate immobilisation of Pb.

Many PO$_4$ compounds have shown potential for immobilisation of Pb in contaminated soils, but those with higher solubility and purity are more effective (Ma et al., 1993; Ma et al., 1995; Hettiarachchi et al., 1997; Lambert et al., 1997; Singh et al., 2001). Agricultural fertilisers that offer high solubility and ready availability at relatively low cost appear to be a useful source of P. Laperche (2000) has discussed the solubility of PO$_4$ compounds in relation to the choice of an appropriate compound for phosphate immobilisation of Pb in contaminated soils. The author discounts the use of P fertilisers such as triple super phosphate (TSP), mainly due to high solubility and the production of phosphoric acid on reaction with water, which has the potential to mobilise Pb and counteract the immobilisation process. Less-soluble RP is offered as a more environmentally sound P amendment. While the low solubility of RP has reduced the effectiveness of Pb immobilisation in experimental trials (Lambert et al., 1997; Chen et al., 2001b), the particle size distribution of RP can be manipulated in order to maintain acceptable dissolution rates and soluble Pb concentrations. The slow-release of P from RP may be employed in order to minimise the potential for loss of excess P. Finely crushed bonemeal has been suggested as a more soluble and cost-effective source of P, with solubility intermediate to that of phosphate rock and KH$_2$PO$_4$ (Hodson et al., 2000). However insufficient quantities of bonemeal in many areas would limit the use of this material.

Lime may need be applied to the soil to counteract acidifying P amendments to maintain optimum soil pH for pyromorphite formation. Soil solution saturation with Ca$^{2+}$ would limit the dissolution of Ca-phosphate compounds applied to the soil. The addition to the soil system of further Ca$^{2+}$ from lime would need to be carefully considered. Christensen and Brown (2001) and Chen (2001b) have successfully used applications of phosphoric acid + lime to immobilise Pb in contaminated soils. This combination avoids the potential for limitation of the dissolution of Ca-phosphates.
7. Control of lead mobility

If concentrations of P in the soil solution are allowed to reduce with time, dissolution of pyromorphite and release of Pb may occur. While it is not possible to demonstrate that remobilisation will never occur, the literature indicates that maintaining an excess of P in solution will discourage this. To this end, the quantification of the concentration and rate of supply of P and Pb to the soil solution will be particularly important. Less soluble phosphorus amendments such as rock phosphate may be useful for providing a longer-term supply of solution P.

It is important to convey to interested parties that phosphate immobilisation is useful only as an interim measure to reduce the imminent leaching of Pb from shooting range sites. The total concentration of Pb in the soil will remain at elevated levels and comprehensive remediation will be required in the future in order to restore environmental quality.
Potential adverse effects of phosphorus amendments

The persistence of the effect of P amendments in the field is central to the success of the Pb immobilisation technique. Mench and Vangronsveld (2001) state that most failures of various in situ amendments arise when trace element removal from solution initiates release from previously strongly-adsorbed trace element pools. This mechanism appears to have been the reason for increased movement of Pb observed in a column leaching experiment (Davenport and Peryea, 1991) and a field trial (Chen et al., 2001b) where P amendments applied to the soils initially reduced Pb mobility. Reduced soil pH caused by acidifying PO₄ compounds may enhance this release of Pb. However, provided that soluble P is maintained at a level sufficient to sustain the system in pyromorphite-forming mode, the release of Pb would be beneficial as it would lead to a greater proportion of the soil Pb being transformed into non-labile pyromorphite minerals. A relatively insoluble P source, such as RP could be used in conjunction with a soluble P source to allow long-term maintenance of effective soluble P concentrations after initial immobilisation reactions. Alternatively, regular application of a more soluble P compound such as superphosphate could be managed successfully, however the effect of associated cations, such as Ca, on maintenance of P supply needs to be considered.

Results obtained by Laperche et al. (1997) strongly suggest that plants can induce the dissolution of pyromorphite in the absence of other sources of P, so that Pb becomes available for plant uptake. To prevent the dissolution of pyromorphite, it is necessary to maintain a level of soil-P available for plants that is in excess of that needed to immobilise Pb

The effect of changes in soil chemistry on other metals introduced to the soil by Pb shot oxidation needs to be considered. Tanskanen et al. (1991) states that Pb pellets contain approximately 97% Pb, 0.5% As and 2% Sb*. If a typical shooting range soil with a total fine earth Pb concentration of 5000 mg kg⁻¹ is considered, the associated release of As into the soil would be approximately 26 mg kg⁻¹, and of Sb would be approximately 100 mg kg⁻¹. The ANZECC guideline limit for both these elements is 20 mg kg⁻¹ soil (ANZECC/NHMRC, 1992).

* As and Sb make the Pb shot harder than pure lead; As also improves the properties of the molten material.
A positive relationship between arsenic release and added P concentration was observed by Peryea (1991). Arsenate (AsO$_4^{3-}$) and phosphate (PO$_4^{3-}$) have chemical and physical similarities, and compete for the same specific adsorption sites in soil, so that arsenic solubility is determined by P concentration. In a column leaching experiment Peryea and Kammereck (1997) found that soluble P fertiliser applied at a molar rate of 50:5 caused 96% of the soil As (82 mg kg$^{-1}$) to leach within 10 pore volumes (cf. <1% of soil As for unamended soil). Competition between P and arsenate could lead to increased transfer of As to groundwater. Increased As solubility in P-fertilised orchard soil has been found to increased As phytoavailability to apple trees (Peryea, 1998) and apricot seedlings (Creger and Peryea, 1994). Boisson et al. (1999) recorded increased plant uptake of As in maize with increasing hydroxyapatite addition to a contaminated smelter soil. Soil pH increases, such as those produced by lime additions have an undesirable mobilising effect on As, therefore the use of lime in conjunction with P amendments will need to be carefully considered.

The soil chemistry of Sb is not well characterized. Antimony has moderate mobility in soil relative to other heavy metals and it is assumed that a major proportion of Sb remains in a labile form with only low adsorption by clays, hydrous oxides and humates in soils (Alloway, 1990). The metal probably occurs as antimonate (SbO$_5^-$) in soluble form (Alloway, 1990), thus P amendment may mobilise soil Sb.

The effect of P amendment on As and Sb oxyanions in shooting range soils will need to be quantified and assessed before widespread amendment of shooting ranges with P. Phytoaccumulation may be successful in reducing potential adverse effects of increased As and Sb solubility. A plant that successfully hyperaccumulates arsenic has been developed (Tu and Ma, 2001).

Annual inputs of fertiliser impurities, especially cadmium, added to the soil by P amendments would be greater than that on agricultural soils receiving fertiliser due to the greater application rates required. The potential cadmium accumulation in a soil receiving 500 kg P ha$^{-1}$ year$^{-1}$ is in the order of 42 g Cd ha$^{-1}$ yr$^{-1}$ (calculated using the Cd content of Sechura phosphate rock; Syers et al., 1986).

Introducing large amounts of P to the soil system increases the potential risk to water quality if not properly managed, due to the eutrophic nature of P. Heavy applications of fertiliser, especially acidifying compounds, may kill vegetation at the sites and lead to increased erosion risk.
7. Control of lead mobility

7.4.4 CONCLUSIONS

The results of the lysimeter leaching experiment indicate that phosphate immobilisation of Pb can be successful in contaminated soil from clay target shooting ranges. Overall success of the P treatments in reducing Pb mobility was varied due to the variation in molar P:Pb ratio at which P was applied to lysimeters. Phosphorus amendments applied to the Motukarara lysimeters established molar P:Pb ratios sufficient to maintain soluble P at a level sufficient to precipitate soil solution Pb, most likely as pyromorphite, under the leaching conditions of the experiment. Results from the Lismore and Waimakariri soils suggest greater molar P:Pb ratios would have established similar Pb-immobilising conditions. Treatment molar P:Pb ratio appeared to have a greater influence on Pb immobilisation than contact time as determined by leaching rate.

The main limitations to the suitability of P amendments at Canterbury shooting ranges are the site-specific factors of soil vulnerability to P loss and potential adverse effect on the quality of local water-bodies. This experiment indicates that the application of P to the Waihora CTC site (Motukarara soil) is undesirable due to the low P retention of the organic soil and the relative sensitivity to P additions of the adjacent stream. Phosphorus-retaining subsoils present in most Canterbury soils will provide conditions more suitable for the use of P amendments.

On the basis of the experimental results, further investigation in the form of a field trial is warranted. Of particular benefit would be data for the leaching dynamics of Pb and P under ambient drainage conditions in profiles which consider the influence of subsoil P retention. In addition, the long-term efficacy of phosphate immobilisation in the field requires further conformation. Such data would contribute significantly to the advancement of international knowledge on the use of P amendments for Pb immobilisation in the field. The review of literature and experimental results confirm that pyromorphite formation is influenced by a complex combination of soil pH, P dynamics, and time. Reduction in soil pH may be particularly useful at shooting ranges, as it would favour dissolution of Pb-carbonate crust material on Pb shot and formation of pyromorphite. In addition, soil acidity reduces the potential for the movement of Pb in soluble organic complexes.

Above all, P amendment does not eliminate the need for the removal of Pb shot at shooting ranges and adoption of non-toxic alternatives to Pb shot. Amendment should be considered to be only a stop-gap measure, with a potentially useful lifetime in the order of 10 years, while more comprehensive remedial options are considered and planned.
Chapter Eight
General Discussion

8.1 INTRODUCTION

This thesis contributes significantly to current knowledge by elucidating the mechanisms of Pb solubility control and transport in contaminated shooting range soils, and will contribute substantially to the practical management of shooting ranges. This chapter integrates these issues and discusses implications and applications of the information. Related issues surrounding Pb contamination at shooting ranges are also discussed. Finally, some general conclusions and recommendations for future research are presented.

8.2 GENERAL SUMMARY

The magnitude, and spatial and vertical distribution of Pb contamination at four CTS ranges in Canterbury was investigated. Fine earth Pb concentrations at all four sites were elevated above the guideline limit, to a similar extent to those reported overseas. Vertical distribution of Pb indicated Pb transport down the profile at the Waihora CTC. The maximum shot-fall zone occurred in approximately the same area at each site, and total Pb loadings (soil Pb + Pb shot) of up to 20% indicate that gross levels of contamination are possible at New Zealand clay target shooting ranges. A high proportion of the Pb present at the site was in the form of intact Pb shot, even at the Waihora CTC where shooting began over 50 years ago, suggesting that pellet decomposition is a relatively slow process. A large proportion of the fine earth Pb was extracted by EDTA, a reagent commonly considered to indicate the potentially ‘bioavailable’ portion of a heavy metal in soil. The survey showed that overseas research and conclusions about such soil Pb contamination are not a result of “focus on extreme situations such as heavily used target ranges” (Fish and Game New Zealand, 2000a), but are comparable and applicable to New Zealand CTS ranges.
An incubation experiment was conducted using uncontaminated soil to which Pb shot was added in order to investigate the rate of corrosion of Pb shot and transfer of Pb to the soil. Rapid onset of Pb shot corrosion was observed. Results showed that soil pH, moisture and temperature affected both processes, and the percentage of Pb shot affected the latter process. In addition, the soil chemical data obtained allowed predictions of solution Pb speciation and pCO₂ using GEOCHEM-PC. This aided the elucidation of the mechanism of interaction between soil and the Pb shot corrosion crust. The dissolution of corrosion products, particularly PbCO₃, supplies Pb to the soil solution. The rate of dissolution is controlled by soil pH, and soil Pb sorption capacity and kinetics. The rate of corrosion and corrosion product dissolution is initially rapid until equilibrium solution concentration is achieved, after which the dissolution rate slows considerably as it becomes controlled by removal of Pb from the system. The build up of corrosion crust material appears to significantly reduce further corrosion. Thus a high proportion of elemental Pb remains as undecomposed Pb shot, such as that observed during the initial survey of the four CTS ranges.

The initial survey of four Canterbury CTS ranges confirmed the transfer of Pb from intact Pb shot to the soil solid phase, and EDTA extraction of fine earth Pb indicated a high proportion of potentially ‘bioavailable’ Pb. This prompted investigation of the potential for leaching of Pb from soils contaminated with Pb shot. Leachate Pb concentrations from lysimeters collected from contaminated areas of three CTS ranges were significantly elevated above background concentrations. High Pb mobility was a result of the high solubility of corrosion compounds (associated with both the corrosion crust and soil solid phase). However, only a very small proportion of the total Pb present in each lysimeter was leached. The large pool of corrosion compounds and the much greater pool of undecomposed Pb shot gives rise to the potential for chronic leaching of Pb. Stability diagrams suggested that control of Pb solubility was via a variety of Pb-carbonates, -oxides, -hydroxides, or related mixed Pb minerals. This differs from the incubation experiment, however under the experimental incubation conditions precipitates may have been formed in more distinct phases.
The lysimeter leaching study concurs with the mechanism of Pb shot corrosion and
dissolution established from soil chemical data from the incubation study. Once equilibrium
solution concentration is achieved, the rates of corrosion and crust dissolution become
controlled by the very slow removal of Pb, largely by percolating water. Thus, information
gained from the incubation and lysimeter leaching data allows estimation of the time required
for total decomposition of a Pb pellet. The time is largely dependent on annual rainfall, but is
in the order of $10^4$ yrs. This is substantially different to earlier estimations that complete
decomposition of a Pb pellet in the soil would take in the order of 100-300 years (Jørgensen
and Willems, 1987b; Lin, 1996). These earlier estimates were largely based on the reactivity
of the highly soluble crust material alone, and did not consider the equilibrium that becomes
established. Table 8.1 shows the calculated estimations for complete decomposition of the
current Pb shot in the lysimeters used in the leaching study. Cultivation would be expected
to increase the rate of decomposition by causing exfoliation of the corrosion crust. Further
corrosion is then likely to occur, reforming the pellet corrosion crusts and effectively
increasing the proportion of total Pb present as corrosion products. Jørgensen and Willems
(1987b) studied the partitioning of Pb between pellet, crust and soil at four sites
contaminated with Pb shot. The two cultivated sites had approximately three times more Pb
associated with the crust and soil fractions than the two uncultivated soils.

Table 8.1. Estimated time for complete decomposition of the Pb shot contained in the
lysimeters used in the study described in Chapter Six.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Lysimeter data</th>
<th>Time for drainage from rainfall to completely remove existing Pb shot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rate of Pb removal (µg mm⁻¹)</td>
<td>Proportion of total Pb shot removed (% mm⁻¹)</td>
</tr>
<tr>
<td>Motukarara</td>
<td>3.7</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Lismore</td>
<td>1.0</td>
<td>$7.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Waimakariri</td>
<td>1.3</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

* A typical annual drainage rate through freely-draining Canterbury soils (Dr H.J. Di, personal communication, July 2001).
The final objective of this research was to identify techniques that could be effective in the management of soil contamination by Pb shot. The information gained from the incubation and lysimeter studies aids enormously the evaluation of such techniques. By considering mineral solubility trends, it is evident that PO₄ application is likely to be more effective in reducing Pb mobility than application of lime to increase soil pH. Superphosphate addition to lysimeters containing contaminated soil significantly reduced Pb leachate concentrations where the molar P:Pb ratio was sufficient. Presumably, soluble Pb was precipitated as pyromorphite. The results indicate there is significant potential for the successful use of phosphate immobilisation at contaminated CTS ranges. In addition, phosphate immobilisation theory suggests that PO₄ addition to range soils would favour the formation of a corrosion crust dominated by pyromorphites, provided sufficient PO₄ is applied. Eusden et al. (2002) observed bulk mineralogical transformations in the reaction rinds of tailings particles rich in PbS and PbCO₃ following the addition of PO₄. Such transformation of Pb shot corrosion crusts could substantially reduce the solubility of corrosion products and consequently reduce solution Pb concentrations, transfer of Pb to the soil matrix and Pb mobility. The over-riding site-specific considerations for the suitability of using PO₄ immobilisation will be soil vulnerability to Pb and P loss, and sensitivity of the local environment to P.
8.3 IMPLICATIONS FOR NEW ZEALAND RANGES

All New Zealand CTS ranges are expected to have elevated soil Pb concentrations. Even sites used by clubs with comparatively small membership numbers have been shown to have substantially elevated soil Pb concentrations (Chapter Four; Lobb et al., 1997; McLaren and Clucas, 1998). Concern about the environmental effects of Pb shot corrosion in soil extends to CTS ranges on private properties for commercial and personal use (Chapter 1.1). Outdoor static target (rifle) ranges, which are also common in New Zealand, are expected to experience similar solubility control by Pb corrosion compounds and associated environmental effects.

The data collected from the laboratory experiments in this thesis provide substantial information about the behaviour of Pb shot in soil and has substantial application in the field. The theory of corrosion leads to the conclusion that potentially soluble corrosion crust Pb compounds will develop whenever Pb shot is in contact with particles of soil or sand in moist environments. As discussed in Chapter Six, the main risk factors that will determine the environmental effect of Pb shot contamination at ranges will be:

- Solubility of Pb compounds and soil solution Pb concentration;
- Volume and transport rate of percolating Pb-contaminated water;
- Degree of subsoil attenuation; and,
- Depth of groundwater below ground surface.

The factors which are expected to control the solubility of Pb compounds and soil solution Pb concentration (soil pH, Pb sorption capacity and amount of soluble organic carbon) will vary greatly between soils throughout New Zealand. Volume and transport rate of percolating water will vary with climate and soil drainage efficiency.

Climatic and soil parameters expected to accelerate or reduce the rate of release of Pb into the environment are summarised in Tables 8.1 and 8.2 respectively. Broad examples are given of geographic areas in New Zealand where such effects may be expected. Rates of Pb shot corrosion and corrosion crust dissolution will also vary seasonally, due to variations in temperature and rainfall.
Table 8.2. Climatic and soil parameters expected to accelerate the rate of release of Pb into the environment, related to geographic areas of New Zealand.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low soil moisture deficit</td>
<td>Greater presence of corrosion electrolyte.</td>
<td>Determined by combination of annual rainfall and temperature dynamics, and soil drainage; Southland.</td>
</tr>
<tr>
<td>High rainfall</td>
<td>Greater removal of corrosion crust products by leaching;</td>
<td>West Coast (South Island); Northland; Higher altitudes.</td>
</tr>
<tr>
<td></td>
<td>Elevated soil Pb concentrations at depth attained relatively rapidly.</td>
<td></td>
</tr>
<tr>
<td>High temperature</td>
<td>Greater rate of soil Pb sorption;</td>
<td>Northern New Zealand.</td>
</tr>
<tr>
<td></td>
<td>increases rate of corrosion crust dissolution;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>increases rate at which equilibrium solution concentration is attained.</td>
<td></td>
</tr>
<tr>
<td>High soil organic matter</td>
<td>Facilitation of Pb transport by SOC;</td>
<td>Podzols and organic soils.</td>
</tr>
<tr>
<td></td>
<td>Increased soil sorption capacity for Pb increases potential for high equilibrium solution Pb concentrations.</td>
<td></td>
</tr>
<tr>
<td>Low soil pH</td>
<td>Greater solubility of corrosion crust minerals.</td>
<td>In New Zealand, mainly dependent on soil type and buffer capacity.</td>
</tr>
<tr>
<td>Free-draining soils</td>
<td>Facilitation of Pb transport.</td>
<td>Recent soils, sandy-textured or very stony soils, well structured soils;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lack of soil pans.</td>
</tr>
<tr>
<td>Low subsoil attenuation</td>
<td>Low interception of transported Pb by sorption in subsoil layers;</td>
<td>Recent soils; Shallow soils.</td>
</tr>
<tr>
<td></td>
<td>Little retardation of groundwater Pb contamination.</td>
<td></td>
</tr>
</tbody>
</table>
Table 8.3. Climatic and soil parameters expected to reduce the rate of release of Pb into the environment, related to geographic areas of New Zealand.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>High soil moisture deficit</td>
<td>Reduced presence of corrosion electrolyte.</td>
<td>Central Otago; Determined by combination of annual rainfall and temperature dynamics and soil drainage.</td>
</tr>
<tr>
<td>Low rainfall</td>
<td>Low rate of removal of corrosion crust products by leaching;</td>
<td>Central Otago.</td>
</tr>
<tr>
<td></td>
<td>Elevated soil Pb concentrations at depth attained relatively slowly.</td>
<td></td>
</tr>
<tr>
<td>Low temperature</td>
<td>Lower rate of soil Pb sorption reduces rate of corrosion crust dissolution and rate at which equilibrium solution concentration is attained.</td>
<td>Southern New Zealand.</td>
</tr>
<tr>
<td>Low soil organic matter</td>
<td>Reduced potential for Pb transport by SOC;</td>
<td>Recent soils.</td>
</tr>
<tr>
<td></td>
<td>Reduced soil sorption capacity for Pb reduces potential for high equilibrium solution Pb concentrations.</td>
<td></td>
</tr>
<tr>
<td>High soil pH</td>
<td>Lower solubility of corrosion crust minerals.</td>
<td>Calcareous soils (parts of Central Otago and North Canterbury); Otherwise, in New Zealand, mainly dependent on soil type and buffer capacity</td>
</tr>
<tr>
<td>Poorly-draining soils</td>
<td>Reduced potential for vertical Pb transport (but may encourage horizontal movement into water bodies)</td>
<td>Soils in low position in landscape; textural, structural and morphological factors which impede water movement; high water table</td>
</tr>
<tr>
<td>High subsoil attenuation</td>
<td>High interception of transported Pb by sorption in subsoil layers;</td>
<td>Recent soils; Shallow soils.</td>
</tr>
<tr>
<td></td>
<td>Retardation of groundwater Pb contamination.</td>
<td></td>
</tr>
</tbody>
</table>
Relatively high risk areas can be identified where such parameters occur in combination. High humidity in northern New Zealand will support the combined effects of high rainfall and temperature. In podzolic soils, high rainfall will exacerbate the effect of SOC facilitation of Pb mobility. Two of the sites studied in this thesis (Canterbury and Waihora CTCs) provide examples of high risk of Pb movement where some parameters from both Tables 8.1 and 8.2 occur in combination. These ranges are discussed in the following section.

Phosphate immobilisation is a promising technique for the management of Pb solubility and mobility at New Zealand ranges. Site-specific considerations for the suitability of phosphate immobilisation will be soil vulnerability to Pb and P loss, and sensitivity of the local environment to P. Where phosphate immobilisation cannot be used, the only method to control Pb solubility and transport may be the use of an impermeable barrier or surface cover to prevent contact between Pb shot and the soil.
8.3.1 Canterbury clay target shooting ranges

In Canterbury, the majority of CTS ranges, listed in Table 4.1, are situated on freely-draining alluvial soils underlain by gravels. The depth at which groundwater is found varies throughout the region, but Lobb et al. (1997) identified the following CTS ranges as having groundwater levels <10 m below ground surface: Amberley, Ashburton, Canterbury (McLeans Island), Ellesmere, Mead-Te Pirita, the old North Canterbury site (Rangiora), Timaru and Waihora. Lead-retaining subsoils will be present in most Canterbury soil profiles, where Fe/Mn oxides are relatively abundant and some subsoils contain significant amount of clay. The subsoil depth is not great at some of the CTS ranges, and a number of the sites are situated on soils classified as Recent soils which have minimal subsoil development.

Canterbury CTC, McLeans Island

The CTS range that is considered to be most at risk of Pb leaching and it’s effect on groundwater quality is the Canterbury CTC at McLeans Island. Lobb et al. (1997) estimated that at least 69 tonnes of Pb was present at the Canterbury CTC. At an estimated input of 9.8 t yr⁻¹, the site has the highest annual deposition rate of Pb shot in the region. The range is regularly used for regional and national shooting events, and during a recent World Championship event, over 1 t Pb day⁻¹ is estimated to have been deposited on the range (From data in Dew, 2002).

The soil is classified as a Waimakariri stony loamy sand, shallow in depth (50-150 mm) and underlain by very stony sand and gravels (N.Z. Soil Bureau, 1967). The soil has relatively little sorption capacity for Pb, as noted in Chapter Four, due to few weathering products and relatively low organic carbon content (2.7 %; Table 4.4). The soil pH in the contaminated area of the range was measured at 7.2, which suggests control of the equilibrium solution Pb concentration by Pb corrosion compound solubility rather than soil sorption capacity (Figure 5.12). The soil pH in this Recent soil would generally be expected to be relatively low due to poor buffer capacity. As observed and discussed in Chapter Five, the dissolution of Pb corrosion compounds are likely to be causing the high soil pH.
Soil profile sampling from a contaminated area of the McLeans Island site (Chapter 4.3.3) suggested that Pb leaching has already elevated soil Pb concentrations at depths >100 mm from <10 mg kg\(^{-1}\) to 10-30 mg kg\(^{-1}\). Although the soil carbon content of the soil is low, the mobility of Pb at the McLeans Island site will be facilitated by the relatively high hydraulic conductivity of the soil due to coarse-textured alluvial deposits. A lack of subsoil to attenuate vertical Pb movement significantly increases the risk of Pb reaching groundwater in a relatively short period of time.

A typical annual drainage rate through freely-draining Canterbury soils is 400 mm (Dr H.J. Di, personal communication, July 2001). Data from Chapter Six suggests that the Pb concentration of leachate at the site will be in the order of 10\(^{-1}\) mg Pb m\(^{-2}\) mm\(^{-1}\) drainage. Thus, 400 mm yr\(^{-1}\) of drainage at the McLeans Island range is likely to result in at least 40 mg Pb m\(^{-2}\) transported from surface soil in the more contaminated areas of the range. Figure 4.8 indicates that the area of soil with fine earth Pb concentrations >300 mg kg\(^{-1}\) is not that large (approximately 2000 m\(^2\)). However the high intensity of Pb shot deposition at this site and the probable use of all existing individual ranges during national and international competitions is expected to rapidly create a much larger area of land where equilibrium concentration will exist. Thus, the amount of potentially soluble Pb available to be leached from the site is expected to be substantial. Significant vertical migration of Pb from the surface soil is inevitable over the next 100 years under the current conditions at the range. Collection and analysis of soil solution samples from the range is recommended in order to validate the assumptions made about equilibrium concentration and the amount of Pb leached.

Groundwater in the immediate area of the range occurs at a depth of approximately 6 m below ground surface in an unconfined aquifer (Little, 1997; Lobb et al., 1997). It is upgradient of the confined aquifer used for the Christchurch city water supply (Talbot and Bowden, 1986). At a site in the Christchurch Airport area, approximately 8 km from the McLeans Island CTS range, 40% of the rainfall recorded during the period May 1999-March 2001 became groundwater recharge (D. Scott, personal communication, 15 January 2002). Assuming a mean annual rainfall (MAR) of 640 mm, this corresponds to approximately 250 mm of annual rainfall contributing to groundwater recharge. Continuing the assumed values in the previous paragraph, the annual input of Pb to groundwater recharge is likely to be at least 25 mg Pb m\(^{-2}\).
Phosphate immobilisation is expected to be effective in reducing Pb solubility and mobility at the McLeans Island range. However, the soil is also expected to be vulnerable to P loss due to relatively little development of soil components responsible for the retention of P (Fe/Al oxides) and the lack of subsoil. Given the unconfined groundwater resource underlying the range, the site environment would be considered potentially sensitive to P. Any application of P would need to be carefully considered and, if carried out, thoroughly managed and monitored. There are no known adverse effects of P in drinking water on human health (unlike Pb; Brookes et al., 1997). However, movement of P into groundwater may still be considered undesirable due to its eutrophic effect, and may preclude the use of phosphate immobilisation at the range.

Within approximately a 10km radius of the McLeans Island range is located the West Melton military firing range and a public pistol shooting range. It is expected that the soil type at the at both sites is very similar to that at the public range, and high loadings of Pb are assumed to be present. These factors are expected to create significant risk for Pb migration.

Yaldhurst site, former Christchurch CTC

Also within 10 km of the McLeans Island CTC range is the former Christchurch CTC. Soil from the Yaldhurst site was used for the lysimeter studies of Chapters Six and Seven. The site and soil is described in Chapter 6.2.1. In summary, the soil is a Waimakariri stony sandy loam and unconfined groundwater occurs at a depth of 10-15 m below ground surface. As for the McLeans Island site, the area is up-gradient of the confined aquifer used for the Christchurch city water supply (Talbot and Bowden, 1986). Data from Chapter Six indicates that the Pb concentration of leachate from the most contaminated area of the site will be 0.4 mg Pb m^{-2} mm^{-1} drainage. Assuming drainage of 400 mm yr^{-1} it is likely that 140 mg Pb m^{-2} yr^{-1} could be transported from surface soil.
8. General discussion

**Waibora CTC, Motukarara**

Samples of Motukarara soil from the Waibora CTC were studied in Chapters Six and Seven. The soil consists of accumulated organic matter (30-40 mm) over gleyed estuarine sands, and experiences seasonal waterlogging. Lead loadings of up to 20%, significantly elevated fine earth Pb concentrations, and relatively high availability of soluble organic carbon are factors which give rise to high potential for Pb mobility at this range. This was indicated in Chapter Four by elevated soil Pb concentrations at a depth of 600 mm in the profile of the Motukarara soil (Table 4.4), and confirmed in Chapter Six. Some retention of Pb has occurred in the subsoil, and may be due to sorption onto the few Fe/Mn oxide mottles observed in the sand and/or precipitation of Pb compounds or reprecipitation of organic and inorganic Pb compounds. In general, the Motukarara subsoil is expected to provide relatively little Pb retention capacity. The coarse subsoil texture also provides macropores which aid rapid transport of Pb down the profile.

Data from Chapter Six indicates that the maximum Pb concentration of leachate at the site will be approximately 1 mg Pb m⁻² mm⁻¹ drainage. If 400 mm yr⁻¹ of drainage from the surface soil is assumed, approximately 400 mg Pb m⁻² yr⁻¹ may be transported from surface soil in the most contaminated areas. Groundwater in the area is largely present in a confined aquifer >50 m below ground level (Lobb et al., 1997) and is not expected to receive Pb leachate. However, there is potential for horizontal subsurface flow of drainage water containing elevated concentrations of Pb into the adjacent stream.

Phosphate immobilisation is expected to be effective in reducing Pb solubility and mobility at this range; however, the soil is also expected to be vulnerable to P loss due to the influence of soil organic matter. The local environment is considered to be particularly sensitive to P due to the potential for horizontal flow from the site into the adjacent Halswell Stream. This stream flows into Lake Ellesmere, which is susceptible to eutrophic inputs such as P. Once again, phosphate immobilisation would be considered unsuitable for reducing the solubility and movement of Pb from this site.
8.4 IMPLICATIONS FOR CURRENT RANGE MANAGEMENT GUIDELINES

Material has been published on the management of Pb shot and bullets at shooting ranges by the U.S.A. National Shooting Sports Foundation (NSSF; 1997) and the USEPA (2001). A German report into contamination at CTS ranges also considers possible management practices (Laender Ministers for the Environment, 1998).

Management strategies and technologies for static target (rifle) shooting are further developed than those for CTS shooting, and have been implemented in the U.S.A and possibly other countries (National Shooting Sports Foundation, 1997; USEPA, 2001). The anomaly is most likely due to contamination effects of rifle shooting being confined to a relatively small area close to the berm behind the static targets. Clay target shooting presents a more difficult management prospect due to the widespread deposition of Pb shot over a much larger area. Sporting clay facilities present more difficulties since the hilly terrain and established vegetation are preferred, and Pb shot deposition patterns are more variable.

The identification of the influence on soil Pb chemistry of PbCO$_3$ and other Pb corrosion compounds with similar solubility in soil will lead to more effective management of Pb solubility and transport. The results of this thesis supply substantial information that will allow more scrutiny of the effectiveness of best management practices contained in manuals produced by the National Shooting Sports Foundation (1997) and the USEPA (2001). To be most effective, management practices will need to be compatible with the natural system controls of PbCO$_3$ solubility and soil Pb sorption capacity, and consider the role of soluble organic matter in Pb transport. Published management guidelines will need updating to reflect the new information contained in this thesis. These are discussed in the following sections.

However, the identification of the role of soluble corrosion crust minerals in the Pb shot-soil system allows greater certainty about the effectiveness of management techniques suggested by the USEPA and NSSF. Successful control of Pb contamination in New Zealand will therefore be easier to achieve.
8.4.1 Management practices requiring reconsideration

_After the soil Pb sorption capacity by organic matter addition, to reduce Pb mobility_

- Organic matter addition to soils is suggested.
- Mulch or compost addition is also suggested in order to reduce contact of Pb shot with water.

**Comments**
- Increasing sorption capacity has the potential to reduce equilibrium solution Pb concentration, particularly at low soil pH (Figure 5.12).
- Organic matter has the potential to increase SOC supply and facilitate Pb mobility, which is undesirable.

_After the soil pH by lime addition to reduce Pb mobility_

- The ideal soil pH is recommended to be between 6.5 and 8.5, in order to reduce potential for Pb migration, by lowering solubility of Pb-carbonates and -hydroxides.

**Comments**
- Although the Pb concentration of leachate moving through the soil will be reduced, increasing soil pH is not sufficient to eliminate Pb mobility.
- Lime addition alone is insufficient to control Pb mobility, particularly in environments sensitive to Pb.
- Lime addition may have some benefit in areas with acid soil pH or rainwater acidity.
- Organic matter solubility increases proportional to pH, therefore the potential for SOC-facilitated Pb mobility will increase with lime addition.
- Transfer of Pb to the soil (soil Pb sorption) is increased by pH increase.
- Soil pH adjustment may be a requirement of phosphate immobilisation in order to optimise pyromorphite formation.
Periodic Pb recovery and recycling

- Periodic Pb shot recovery is advocated, principally so that CTS clubs in the U.S.A. avoid deposited Pb shot being legally defined as abandoned, hazardous waste and management requirements associated with this definition.

Comments

- Rapid onset of corrosion and transfer of Pb to the fine earth fraction precludes even annual removal of Pb shot from limiting accumulation of potentially soluble Pb corrosion compounds.
- Soil solution Pb concentrations are likely to remain high after Pb shot recovery, and potential for Pb leaching may be maintained for decades, similar to that if Pb shot remains in the soil:
  (i) A large proportion of the fine earth Pb at CTS ranges is likely to be associated with potentially labile exchangeable and carbonate soil fractions;
  (ii) Exfoliation of the existing corrosion crust is likely to occur during processing and remain in the soil.
- At active CTS ranges, this management technique would be negated by the continued use of Pb shot. Corrosion of newly deposited pellets will occur, but dissolution will be controlled by the existing equilibrium Pb concentration. Subsequent Pb recovery will again exfoliate corrosion crust material and add to the pool of potentially soluble Pb in the soil.
- Periodic removal is suggested in the U.S.A., and a 7-year recovery interval has been suggested by an Australian company in order to minimise environmental damage of Pb shot accumulation at ranges (E. McClelland, personal communication, 5 February 2002). These practices are unlikely to have significant impact on minimising the adverse effects of Pb shot.

Cultivation

- Suggested as a method of limiting the availability of Pb shot to wildlife and migratory birds in North America.
- The NSSF publication (1997) notes that the use of tilling may have negative consequences and should be evaluated on a case-by-case basis.
8. General discussion

Comments

- Cultivation is likely to increase the total proportion Pb in the soil that is potentially soluble, by causing exfoliation of the existing corrosion crust. This is likely to induce further corrosion products to accumulate on the pellet surface.
- Recovery of Pb shot at any later date will be more difficult, as Pb shot will become spread throughout the depth of the plough-layer.
- Cultivation of the shot-fall zone is not recommended for New Zealand ranges.

Sand traps

- The EPA considers a layer of sand may be appropriate for managing Pb shot at CTS ranges (Petrucelli, 1996).
- This system is used at some US ranges to aid the recovery of Pb shot by machine (V. Thomas, personal communication, 3 August 2001).

Comments

- A sand layer would make Pb shot recovery faster and easier (particularly by physical separation).
- Contact between Pb shot and sand would still initiate corrosion, and sand would provide minimal retention of solubilised corrosion crust material, possibly leading to greater potential for Pb mobility.
- Therefore, a sand layer would require hydraulic isolation from underlying soil, and runoff control and treatment would be necessary.

Reducing shot-fall area by relocation of ranges

- The characteristic wide distribution of Pb shot at CTS ranges will be minimised if individual ranges at a site are angled slightly relative to one another. This causes greater overlap of each shot-fall zone.

Comments

- Beneficial if the main consideration is the financial cost of processing a volume of soil to remove spent ammunition in the future.
- Higher loadings of Pb in the concentrated shot-fall zone have the potential to reduce the time required to achieve equilibrium solution Pb concentration and therefore accelerate rate of elevation of soil solution and fine earth Pb concentrations. These effects were indicated in Chapter 5.3.6.
8.4.2 Management practices with continued potential effectiveness

The following range management techniques, either individually or in combination, are considered to be potentially effective in controlling adverse effects of Pb shot deposition on soil:

**Removal of Pb shot**

- Removal of Pb shot from the soil will remove contamination source

  **Comments**

  - Most beneficial at former ranges or at active ranges when shooters change to exclusive use of non-toxic shot.
  - Given that elemental Pb as Pb shot makes up 70-95% of the total Pb burden at most clay CTS ranges, recovery of Pb shot would substantially reduce the amount of Pb shot available for future transformation into potentially soluble Pb compounds.
  - Highly soluble exfoliated crust material may be returned to the site in the soil.
  - Soil washing, used after and in conjunction with Pb shot removal will substantially reduce the continued influence of exfoliated crust material and potentially labile fine earth Pb.

**Impermeable barriers and surface covers**

- Used to break hydraulic connection between the surface soil and underlying soil layers or groundwater, in order to eliminate adverse effects of Pb migration.

  **Comments**

  - At existing ranges, contaminated soil could be removed and replaced on top of an impermeable barrier.
  - At new ranges, a cover could be laid on the soil surface and protected from wind damage with a layer of sand.
  - Potential lining materials could include compacted clay, high density polyethylene sheeting, such as that used for landfills (designed to last more than 50 years), geotextiles and asphalt.
  - The design would need to incorporate a drainage and collection system for the management of Pb-contaminated drainage water generated within the contaminated soil mass, and to ensure no movement of Pb to surrounding permeable soil.
8. General discussion

- An impermeable barrier would be an appropriate management technique at ranges where phosphate immobilisation is determined to be unsuitable due to environmental sensitivity to P.
- An impermeable barrier covering soil containing Pb shot is likely to be ineffective, as percolation can still occur, and the soil chemistry may be adversely affected by the development of anaerobic soil conditions.

**Phosphate immobilisation**

- A management technique currently in a developmental stage.
- Potential for substantial reduction in Pb mobility through precipitation of soluble Pb with phosphate.

**Comments**

- Chapter Seven has confirmed that phosphate immobilisation has the potential to mitigate Pb mobility and leaching. Lime addition may also be required to optimise chemical conditions for pyromorphite formation.
- Phosphate application may possibly cause bulk transformation of corrosion crust materials leading to significantly reduced equilibrium Pb concentrations and transfer of Pb to the soil solid phase.
- Soil vulnerability to P loss and sensitivity of the local environment to P must be a prime consideration in the suitability of the phosphate immobilisation technique for individual sites.

**Alteration of soil Pb sorption capacity by clay, to reduce Pb mobility**

- Clay addition to soils is suggested;

**Comments**

- Increasing sorption capacity has the potential to reduce equilibrium solution Pb concentration, particularly at low soil pH.
- Movement of Pb is possible regardless of the sorption capacity, due to continual presence of Pb in the soil solution.
**Lime addition to reduce Pb mobility**

- The ideal soil pH is recommended to be between 6.5 and 8.5, in order to reduce potential for Pb migration, by lowering solubility of Pb-carbonates and -hydroxides.
- Discussed in previous section (Chapter 8.4.1).

**Comments**

- Phosphate immobilisation is likely to be more cost-effective and achieve greater reduction in Pb mobility.
- Soil pH adjustment may have some benefit where phosphate immobilisation cannot be used to counteract the effects of low soil pH on equilibrium solution Pb concentration.

**Runoff control**

- Recommendations include vegetative ground cover, mulches and compost, filter beds of crushed lime or other Pb-neutralising material, and retention ponds.

**Comments**

- Runoff control is potentially useful at ranges where slope creates the potential for migration of Pb in surface runoff, and may have particular application to sporting clays ranges, where sloping terrain is desirable.
- Mulch and compost should be avoided due to the potential for Pb mobilisation by SOC.
- Filter beds constructed with phosphate compounds rather than lime would be expected have superior Pb-retention capabilities.
- Vegetative cover will also reduce the potential for wind erosion.

**Capture ponds**

- A pond of water constructed in the shot-drop zone to minimise deformation of Pb shot to increase the potential for reuse after periodic recovery.

**Comments**

- Effective in minimising adverse environmental effects of Pb shot corrosion, provided capture pond is hydraulically isolated from soil, groundwater, and other natural water bodies at a range.
- Potential risk of waterfowl using the pond and developing Pb toxicosis due to ingestion for grit.
8.4.3 Recommendations for general management practices at New Zealand clay target shooting ranges

At present there is no management of Pb contamination at CTS ranges in New Zealand. If Pb shot is deemed essential, its deposition should be managed in such a way as to minimise any further soil Pb contamination. For all shooting activities, on a daily basis, gun safety requirements are considered paramount. Similar precaution and prevention considerations also need to be integrated into all shooting activities in terms of environmental stewardship. In addition to the best management practices discussed above, consideration of the following points would contribute to a comprehensive contamination management strategy:

- Land use and management, particularly the risks associated with agricultural and horticultural production on shot-fall areas;
- Location of all land that has received Pb shot deposition, including closed, abandoned, private and commercial ranges;
- Awareness and reduction of possible Pb shot deposition outside range perimeters;
- Record keeping at individual ranges, to document the number of rounds shot per meet and the type and size of shot used, including % antimony;
- Regular soil and groundwater analysis and reporting to monitor the rate of Pb transport from sites;
- Distribution of accurate environmental and technical information for shooters and local authorities;
- Arrange club environmental funds in order to accumulate some financial resources for site management and/or remediation;
- Comprehensive strategy for avoiding soil contamination at new CTS ranges;
- Elimination of further Pb contamination through introduction of truly non-toxic shot (see overleaf).
8. General discussion

8.5 Alternatives to Lead Shot

Regulation of Pb shot use has occurred in various countries in order to reduce the incidence of waterfowl Pb toxicosis. This has prompted manufacturers to increase production and development of ‘non-toxic’ alternatives to Pb shot. There are a variety of commercially available non-toxic alternatives, including bismuth, tungsten-iron, hevi-shot, and steel shot (Fish and Game New Zealand, 2000b). The ballistic properties and price of these alternatives differ from that of Pb shot to various degrees. Steel shot is generally considered the main alternative, and although myths about its performance persist (Fish and Game New Zealand, 2000b; Forsyth, 2002), many technical difficulties experienced in the past with steel shot have been overcome by manufacturer research and development. It appears that most of the current resistance to non-toxic alternatives is due to poor shooter education.

Adverse effects from the corrosion of steel shot deposited onto soil are documented (Laender Ministers for the Environment, 1998), but little information is available. The rate of corrosion of steel is approximately five times that of Pb (Uhlig, 1971). Corrosion resistant, lacquer sealed steel shot produced by Winchester Ammunition (2002) may eliminate this potential problem. Small but significant amounts of copper (Cu), nickel (Ni) and chromium (Cr) may also be contained in steel shot (Winchester Ammunition, 2002).

Frangible ammunition is a Pb-free product developed recently in the U.S. Although judged to be of low toxicity, the frangible bullet is described as a metal-composite bullet (Oak Ridge National Laboratory, 2001), made of mixtures of tungsten and other metals or alloys, including copper and zinc (Oak Ridge National Laboratory, 2001; Winchester Ammunition, 2002). Therefore, research is required to establish the environmental effects of these potentially corrosive metals.
8.6 **CONCLUSIONS**

The following conclusions can be drawn from the results of this study:

- The fate of Pb in soil is determined by site-specific parameters, particularly:
  
  (i) Soil chemistry: particularly soil pH, Pb sorption capacity, equilibrium position, SOC concentration, and subsoil attenuation;
  
  (ii) Climate: particularly temperature and rainfall;
  
  (iii) Soil drainage characteristics, including soil properties and presence of surface- and ground-water;

- The rate of transformation of metallic Pb shot and release into the soil environment is defined by:
  
  (i) an initial rapid period of corrosion and dissolution until equilibrium concentrations are obtained; followed by
  
  (ii) slower transformation controlled by the removal of Pb from the system by water percolation through the soil;

- A significant proportion of the fine earth Pb in contaminated samples is associated with Pb-carbonates, adding to the pool of potentially soluble Pb;

- Potential for Pb transport from all surface soils contaminated with Pb shot is high, due to the maintenance of elevated solution Pb concentrations by dissolution of corrosion compounds associated with the corrosion crust and soil solid phase;

- Determination and development of effective management or remedial strategies is significantly aided by the information in this thesis;

- The identification of the dominance in the Pb shot-soil system of PbCO$_3$ and other similarly soluble Pb corrosion compounds rationalises the use of phosphate instead of lime, where possible, to manage the environmental effects of Pb shot corrosion;

- The time required for complete decomposition of Pb shot is in the order of $10^4$ years.
Lead contamination of soils is most commonly attributed to automobile emissions, atmospheric deposition and paint residues (World Health Organisation, 1977 in Bruell et al., 1999). Greater public and regulatory awareness of the sources of Pb contamination in the past few decades has lead to the elimination or substantial reduction of Pb released into the New Zealand environment from commonly recognised sources. It is possible that recreational shooting has become one of the principal means of Pb input to the environment.

In the 1970s, awareness of the adverse health effects of airborne Pb (primarily from Pb-containing cartridge primers) on shooters at indoor firing ranges lead to modification of the ammunition used. The Pb toxicosis of waterfowl via the ingestion of spent Pb shot in wetlands had become an issue by the 1990s. This has been addressed by many countries with regulatory requirements for hunters to use non-toxic alternatives to Pb shot. Both of these issues had highly visible effects. In approximately the last decade, a growing amount of data has made visible the adverse environmental effects of Pb shot and bullet deposition onto soil at outdoor clay target and rifle ranges. The environmental effects of Pb shot deposition onto soil are different to those observed for Pb shot deposition into wetlands. The potential for environmental exposure to Pb is greater due to the highly soluble nature of transformed Pb. Mitigation and control measures have been developed in the U.S.A. for Pb bullet use at rifle ranges, but the more widespread deposition of Pb shot at CTS ranges is largely still to be addressed.
8.7 Recommendations for future research

Further work is required on soil contamination at shooting ranges by Pb and other metallic ammunition:

_Pb shot:_
- Further study of the formation and dissolution characteristics of Pb shot corrosion crust material, with particular focus on the apparent dominance of the less soluble Pb₃(CO₃)₂(OH)₂ over PbCO₃;
- Measurement of Pb concentrations in groundwater down-gradient of CTS ranges;
- Direct measurement of free Pb²⁺ concentrations (e.g., using an ion selective electrode) and Pb speciation in the soil solution of field soils.
- The effectiveness of mechanical Pb shot recovery, the fate of Pb remaining in the soil, and the potential for soil washing following Pb shot recovery to remove fine earth Pb.
  
  Note: To avoid poor analytical precision, it is advisable that soil + Pb shot samples be processed so that corrosion crust material is exfoliated during sample sieving, and the soil sample ground finely to homogenise crust material and fine earth.

_Phosphate immobilisation:_
- Field trials of phosphate immobilisation of Pb at CTS ranges, with particular focus on soil solution chemistry;
- The persistence of the Pb-immobilising action of phosphate;
- The effect of elevated soil-P concentrations on the mineral composition of corrosion products; investigation of the hypothesis that phosphate addition will lead to bulk mineral transformation of current corrosion compounds into pyromorphite;
- Calculation of required molar P:Pb ratio by analysis of all potentially soluble Pb (crust Pb + fine earth Pb) as opposed to fine earth Pb alone.

_Non-toxic alternatives to Pb shot:_
- Steel shot – The fate in soil of Fe and other constituents of steel shot when in contact with soil;
- Frangible ammunition – The potential for soil contamination by potentially corrosive metallic components;
- The potential for a non-toxic shot alternative made from rubber, that is environmentally stable or has no toxic transformation products.

_Static target ranges and military firing ranges in New Zealand:_
- Confirm soil contamination and level of mobility of Pb and other heavy metals present in ammunition;
- Potential application at New Zealand ranges of environmental protection measures in use in the U.S.A. and elsewhere (for example, bullet traps)
References


ANZECC/NHMRC (1992). *Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites*. (Australian and New Zealand Environment and Conservation Council (ANZECC)/ National Health and Medical Research Council (NHMRC), Canberra).


References


References


References


References


References


References


Ma, Q.Y., Logan, T.J., Traina, S.J. and Ryan, J.A. (1994a). Effects of NO\textsuperscript{3}, Cl\textsuperscript{-}, F\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, and CO\textsubscript{3}\textsuperscript{2-} on Pb\textsuperscript{2+} immobilization by hydroxyapatite. *Environmental Science and Technology* **28**, 408-418.


References


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Appendices

Appendix A. Personal Communications

Appendix B: Preliminary pH adjustment study for Chapter 5

Appendix C: Development of crust material on Pb shot removed from Temuka soil

Appendix D: pH of Pb sorption equilibrium solutions

Appendix E: Data used to construct PbX solubility plots

Appendix F: Inputs into GEOCHEM-PC modelling software
Appendix A: Personal Communications

Dr. S. Brown, August 2001

Research Assistant Professor, Forest Resources
Director, Soils Laboratory
Ecosystem Sciences Division
University of Washington
Seattle, USA

Discussion at the 6th International Conference on the Biogeochemistry of Trace Elements (ICOBTE), 30 July - 2 August, 2001, Guelph, Canada.

G.B. Davis, 22 August 1997

Ministry of Agriculture and Fisheries (MAF)
Hastings Office

Telephone communication giving a first hand account of a cattle poisoning case that was reported in The Dominion, 8 September, 1978 (Page 1).

Summary of communication

Mr G.B. Davis attended the case in 1978 as MAF Veterinary Advisory Officer.
Stock owner: Jim Robertshaw
Veterinarian: Dave Quinliven

The shot fall area of a clay target shooting club in the Hastings area was used as a 'loafing pad' over winter for a herd of in-calf cattle. Apples were trucked in as extra feed, and spread in lines on the pasture.

At the end of winter, the cattle were removed from the shot fall area and walked 'home'. This was an easy walk (maximum 10km /day) that took 3 days.
Mr Davis visited the farm to carry out TB testing on the cattle herd (Friday). On the Sunday the veterinarian contacted Mr Davis to report dead and dying cattle. On the Monday, symptoms evident in the herd included blindness and semi-consciousness. An autopsy found Pb pellets accumulated in the reticulum and abomasum, and scattered thinly through the small intestine. Kidney and liver samples were sent away for a toxicology report, the result of which showed Pb concentrations that were abnormal, but not as high as had been expected. An inspected foetus indicated stress. Cattle were treated with epsom salts to flush pellets out of the digestive system, and severely poisoned cattle were treated with EDTA.

Inspection of the shooting range site was carried out on the Tuesday. Apples were found to contain pellets (picked up from soil surface)
The delayed effect of Pb ingested at the shooting range during winter was attributed to:

- The accumulation of pellets in the cattle over the winter period
- Pb poisoning is aggravated by exercise. Three-days walk was equivalent to considerable exercise in comparison to that which would have been possible in the confines of the shooting range paddock during winter.
- Possible aggravating effect of the stress caused by the TB testing.

Data from this case has not been published in any form, and MAF records relating to the case were destroyed in 1996 after a move to smaller offices. Laboratory records may be available at the Palmerston North Animal Laboratory or the Central Animal Laboratory at Wallaceville. These have not been obtained for this study.

Dr. H.J. Di, July 2001

Senior Research Scientist/ Lecturer
Lincoln University
Canterbury

Annual drainage of a typical Canterbury soil = 400 mm

Dr. F. Lang, 29 August 2001

Institute of Soil Science
University of Hohenheim
Germany

E-mail correspondence

E. McClelland, 10 August 2001

Leadex Australia

E-mail correspondence: leadex@netcon.net.au. Subject: Re: Green Machine query.

E. McClelland, 5 February 2002

Leadex Australia

E-mail correspondence: firesteel@useoz.com. Subject: Re: Lead Shot Machine.

K. Nicolaysen, 2 March 2002

Professor of Neurobiolgy (also a recreational shooter and hunter)
Norwegian University of Sport and Physical Education
Oslo, Norway

E-mail correspondence: kaare.nicolaysen@nih.no. Subject: Steel pellets.
Appendix A

O. Osbourne (deceased), 1999

Landowner – Waihora Clay Target Club
Bethels Rd
Leeston

Telephone conversation

D. Scott, 15 January 2002

Groundwater Hydrologist
Environment Canterbury
Christchurch

E-mail correspondence
Institute of Geological and Nuclear Sciences / Dr Hugh Thorpe (Canterbury University) / Environment Canterbury

V. Thomas, 3 August 2001

Professor of Zoology (also a recreational clay target shooter)
Department of Zoology
University of Guelph
Ontario, Canada
Appendix B: Preliminary pH adjustment study for Chapter 5

<table>
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<tr>
<th>Soil</th>
<th>Lime addition (g 100g soil(^{-1}))</th>
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<th>Resultant soil pH</th>
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<td>12</td>
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<td>4.3</td>
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</table>
Appendix C: Development of crust material on Pb shot removed from Temuka soil

Development of crust material over 24 months on Pb shot removed from Temuka soil incubated at field capacity and 25°C; soil pH = 5.2 ± 0.1 (6× magnification).
### Appendix D: pH of Pb sorption equilibrium solutions

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH of equilibrium solutions containing added Pb (mg L⁻¹)</th>
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<tr>
<td></td>
<td>0</td>
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<tr>
<td>Motukarara (0-20 mm)</td>
<td>6.5</td>
</tr>
<tr>
<td>Motukarara (20-100 mm)</td>
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</tr>
<tr>
<td>Lismore</td>
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<tr>
<td>Waimakariri</td>
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### Appendix E: Data used to construct PbX solubility plots

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<th>Pb compound</th>
<th>Equilibrium equation</th>
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</thead>
<tbody>
<tr>
<td>PbCO₃</td>
<td>( \log \text{Pb}^{2+} = 4.65 - 2\text{pH} - \log \text{CO}_2(g) )</td>
</tr>
<tr>
<td>Pb₃(CO₃)₂(OH)₂</td>
<td>( 3\log \text{Pb}^{2+} = -17.51 - 2\log \text{CO}_2(g) - 6\text{pH} )</td>
</tr>
<tr>
<td>PbSO₄</td>
<td>( \log \text{Pb}^{2+} = -7.79 - \log [\text{SO}_4^{2-}] )</td>
</tr>
<tr>
<td>Pb(OH)₂</td>
<td>( \log \text{Pb}^{2+} = 8.16 - 2\text{pH} )</td>
</tr>
<tr>
<td>PbO</td>
<td>( \log \text{Pb}^{2+} = 12.72 - 2\text{pH} )</td>
</tr>
<tr>
<td>PbCO₃·PbO</td>
<td>( 2\log \text{Pb}^{2+} = 17.39 - 4\text{pH} - \log \text{CO}_2(g) )</td>
</tr>
<tr>
<td>PbCO₃·Cl₂</td>
<td>( \log \text{Pb}^{2+} = -1.8 - 2\text{pH} - 2\log [\text{Cl}^-] - \log \text{CO}_2(g) )</td>
</tr>
<tr>
<td>Pb₅(PO₄)₃(OH)</td>
<td>( 5\log \text{Pb}^{2+} = -62.79 - 3\log [\text{PO}_4^{3-}] - \text{pH} )</td>
</tr>
</tbody>
</table>

Calculations made using:

- Equilibrium constants from Lindsay [, 1979 #417]: based on ion activities, therefore constants hold true for all ionic strengths, \( T = 25^\circ \text{C} \).
- Assumed constant \( \text{CO}_2(g) \) of 0.03 atm
- For Chapter 5 (soil solution): \( [\text{SO}_4^{2-}] = 10^{-3} \text{ M} \)
- For Chapter 6 (leachate): \( [\text{SO}_4^{2-}] = 10^{-5} \text{ M}, [\text{Cl}^-] = 10^{-4} \text{ M} \)
Appendix F: Inputs into GEOCHEM-PC modelling software

The following numbers refer to the GEOCHEM-PC program (on accompanying CD-ROM) to allow reference to critical data used in the model.

Metals:
1 Ca\(^{2+}\)
2 Mg\(^{2+}\)
4 K\(^{+}\)
5 Na\(^{+}\)
15 Pb\(^{2+}\)

Ligands:
1 CO\(_3^{2-}\)
2 SO\(_4^{2-}\)
3 Cl\(^{-}\)
9 PO\(_4^{3-}\)
17 Citrate
19 Salicylate
32 Phthalate
33 Arginine
34 Ornithine
35 Lysine
42 Valine
57 NO\(_3^{-}\)
60 Maleate
61 Benzylsulfonate