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Sustainable Restoration of Mine Sites

A thesis
submitted in partial fulfilment
of the requirements for the Degree of
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by

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A sustainable approach to restoration of the post-mining landscape involves creating conditions where a viable growth medium can be established with the minimal amount of fertiliser inputs over a period of time. Ideally, this growth medium should comprise a combination of minerals, organic matter, and biological components with have the capacity to retain and release nutrients over time. When combined with a re-vegetation scheme appropriate to the biogeographic area, a self-sustaining ecosystem can be established. Regulatory requirements for mine restoration typically require the use of topsoil, which is often in limited supply. However, overburden is commonly present in vast quantities and has the potential to be used as a restoration substrate with appropriate amendments. There are significant gaps in our understanding of factors relating to the use and amendment of overburden as a growing medium. The main objective of this study was to investigate and quantify the effects of inorganic and organic amendments and weathering on nutrient availability and plant growth in topsoil and overburden material obtained from the OceanaGold Globe Progress mine at Reefton, New Zealand. A series of glasshouse experiments were carried out on topsoil, fresh overburden and mullock (old waste rock) amended with biosolids, green manure, sawdust, lime and mineral fertiliser nutrients (nitrogen (N) and phosphorus (P)). Results demonstrated that 300 kg N ha\(^{-1}\) was sufficient to overcome N deficiency in topsoil, while 100 kg P ha\(^{-1}\) was required to overcome P deficiency. Addition of biosolids to topsoil and overburden increased plant biomass production, without increasing heavy metal concentrations. Amendment of overburden significantly affected weathering rates by accelerating the formation of secondary minerals. In particular, lupin green manure accelerated the formation of organic iron (Fe) and aluminium (Al) organic complexes, resulting from the decomposition of the green manure and release of Fe from primary minerals. Results revealed that wineberry and red beech required 200 kg N ha\(^{-1}\) for optimum growth. Overall, the findings of this research identified key parameters for effective utilisation
of overburden as a restoration substrate. A sustainable restoration method for managing the 
topsoil and/or any overburden or waste rock material remaining at mine sites can be achieved 
by careful selection of organic amendments and allowing an initial weathering period.

**Keywords**: metal availability; nutrient availability; weathering; red beech (Nothofagus fusca); 
wineberry (Aristotelia serrata); lupin (Lupinus angustifolius).
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Chapter 1
Introduction

In response to concern about the disturbance of land due to mining, many countries have imposed state restoration laws requiring mined land to be restored after mining closure (Sengupta, 1993). These regulations for restoration processes imply that the physical and/or chemical properties of reconstructed mine soil may be less favourable for vegetation establishment compared to the original vegetation; for example Barnhisel (1988) cited poor post-mining tree growth compared to the original forest.

Vegetation cover is an important part of environmental management after mining closure (Maiti, 2007), because restoration of a vegetation cover can fulfil the objectives of stabilization, pollution control, visual improvement and the removal of environmental threats to the surrounding population (Wong, 2003). Mining industry produces a large amount of waste rock and overburden material, ranging from tens to hundreds of millions of tonnes that can have a detrimental impact on environmental conditions (Izquierdo et al., 2005). However, a major issue is that the waste material effectively represents a growth medium which is usually uncultivable on its own. Furthermore, topsoil is the most favourable growth medium for rehabilitation purposes, but is often unavailable in sufficient quantities to cover the whole restoration area. Regulations often dictate the use of topsoil for mine restoration (Sydnor & Redente, 2002). Thus, there is a gap between what is required under regulations and the quantity and type of materials which are actually available for rehabilitation. Management of any available topsoil and of the overburden, as growth mediums for mine restoration is the key to successful, sustainable restoration.

Rehabilitation, reclamation, remediation, and re-vegetation activities are part of the suite of restoration processes which can be used to up-grade and return the post-mining landscape to a close approximation of its condition prior to disturbance (Bradshaw, 2000; Clewell et al., 2005; Harrington, 1999; Norton, 1991). In restoration practice, a speeding up or compression of the natural processes is often conducted in order to restore the site in as short a time period as possible (Bradshaw, 1987). Overcoming physical, chemical, toxicity problems on these materials has to be done first to support viable growth medium for initial plant. This can be achieved through addition of fertilizer to the substrate, which can be in the form of organic or inorganic chemical amendments (Bradshaw, 2000; Marrs, 2002). Furthermore, when dealing with the issue of long-term sustainable restoration, weathering processes can be taken into
account. Weathering processes resulting in the breakdown of primary minerals will release nutrients as well as any heavy metals if present. Formation of secondary minerals such as clays will aid in the formation of regolith and soils and hence conditions more favourable to creating and maintaining a viable growth medium. Amendments and conditions favourable for promoting weathering will thus help to promote long-term sustainable restoration.

Thus, a restoration method (amendments to add, effect on weathering and plant species to use) which is effective for a particular site, is important to determine. However, there is a lack of information about methods for managing gold mine overburden material for creating a viable growth medium in the short-term and the long-term. There is also a lack of knowledge concerning effects on nutrient availability and plant bioavailability of both nutrients and heavy metals released during overburden weathering processes. This is important to determine as it will ultimately affect the long-term sustainability of the mine restoration process.

Thus, this study aimed to determine a number of key initial parameters essential in a sustainable restoration method for managing the topsoil and overburden or waste rock material remaining at gold mine sites. This was achieved by determining the effect of both amendments (organic and inorganic) and weathering processes on the substrate nutrient and heavy metal availability, plant bioavailability, and plant growth of selected species. The gold mine used in this study is the OceanaGold Globe Progress mine at Reefton.

Herewith the hypotheses tested in this research project together with the related objectives.

Hypotheses:

- Nutritional status of topsoil, overburden and mullock as well as plant biomass (Red beech, *Nothofagus fusca*; and Wineberry, *Aristotelia serrata*) will be improved by the addition of organic and inorganic amendments;

- Un-amended topsoil will limit Red beech plant growth due to nitrogen (N), phosphorus (P) deficiency and acid soil;

- Application of high rate of N fertilizer will hamper the Wineberry and Red beech growth; Wineberry as a pioneer species will have a lower internal N requirement compared to Red beech as a later successional species;
- Weathering in combination with amendments will improve the nutritional status of overburden and hence, plant biomass production.

Objectives:

- To characterize the nutrient status of growth mediums and plants after the application of amendments (Chapter 4);

- To characterize the impact of N, P and lime amendments on plant biomass and nutrients status of the topsoil (Chapter 5);

- To determine the N rate for optimal plant growth of Red beech and Wineberry in topsoil and overburden (Chapter 6);

- To investigate the effects of short-term weathering regimes in combination with amendments (both organic and inorganic) on the overburden and hence, the production of a viable growing medium from waste rock (Chapter 7).
Chapter 2
Literature Review

Chapter 1 identified that there is a real issue with the spatial extent of the post–mining landscape to be restored, and the quantity of any stockpiled material to achieve this. While topsoil is often the material of choice and specified in regulations, it is commonly in short supply. Overburden is often available in sufficient quantities, but its value as a viable growth medium is poorly understood. The first part of this review will examine the issue of mine processes, the accompanying environmental impacts and the associated restoration practices. Creating a viable growth medium is essential for successful restoration; and is next considered in the review. The effects of overburden weathering and nutrient release from inorganic and organic sources are then reviewed. Finally, the literature which reviews approaches to the assessment of successful restoration is examined.

2.1 Mine restoration

In New Zealand, minerals had been used for the first time by Maori for making weapons, ornaments and tools from hard, durable rocks, such as greenstone (nephrite, or jade). Furthermore, in the beginning of 19th century and by 1830 coal had been discovered in Otago, followed by gold in the 1840s. These minerals were the main products initially and remain so today (Barker & Hurley, 1997).

 Generally, gold ore occurs in narrow veins or seams. Previously, most of New Zealand’s gold and coal was extracted by underground mines. In the present day, most mines in New Zealand use surface extraction methods such as open pit mines, opencast mines or quarries (Barker, 1996). The surface extraction methods are used widely due to improvements in mining technology, thus reducing operating costs. In addition, the amount of mineral deposit that can be extracted is higher for open pit mine operations (Barker, 1996). The Reefton Goldfield is located near Reefton, north-west coast of the South Island of New Zealand. This historical goldfield produced over two million ounces since the discovery of alluvial gold in 1866. The last productive mine was closed in 1950. Mining operations re-commenced at the Globe-Progress mine in early 2005 by OceanaGold. The Globe Progress mine consists of four open pits which extract near-surface refractory gold ore.
Mining operations clears the land of surface vegetation and leads to the loss of biodiversity (Porter-Bolland et al., 2007), nutrient cycle disruption (Negrete-Yankelevich et al., 2006), organic matter depletion (Teixeira et al., 2007), and losses of more than 70% of the original soil organic carbon pool (Akala & Lal, 2001). Once the vegetation is removed from the ecosystem, this triggers several events. Nutrient uptake, the translocation of nutrients from senescent tissue, the return of nutrients in litter, the decomposition of litter on the forest floor and mineral soil, and the mineralization of nutrient from organic matter will disappear and essential ecosystem processes will all be stopped (Barnes et al., 1998). Mining operations also result in the stock piling of overburden that can cause the destruction of landscape, degradation of the visual environment, disturbance of watercourses and destruction of agricultural and forest lands (Sengupta, 1993). In addition, there are specific issues: 1) toxicity and mobility of metal which can leach to ground water and affects plants, animals and human; 2) acid mine drainage (AMD); 3) alkalinity, salinity; 4) deficiency soil nutrients; 5) soil moisture depletion; 6) soil temperature; 7) soil compaction; 8) lack of diversity, declining productivity (Sengupta, 1993).

In the 19th century and in the early 20th century, little attention had been given to the effects of land uses following mining, particularly the deliberate attempts to rehabilitate or restore land to productive, protective land uses after mining (Ross & Mew, 1995). All material remaining following mineral extraction, such as waste rocks and tailings, were commonly deposited in the nearest river or valley. In the last 30 years, attention has been focused on the way mining operates, and to regulations which impose a promotion of sustainable management of natural and physical resources. The purpose of these regulations are to control activities on the basis of their effects on the environment (Barker, 1996).

In restoration processes, rehabilitation, reclamation, remediation, re-vegetation are considered holistic solutions (Bradshaw, 2000). Restoration covers those activities which are to up-grade and return the derelict land to a close approximation of its condition prior to disturbance (Bradshaw, 2000; Clewell et al., 2005; Harrington, 1999; Norton, 1991). Rehabilitation processes involve returning the site to a stable and permanent use in relation with a pre-mine plan. Reclamation processes entail that the area is re-shaped close to the precise contour; plant and animal communities are re-established to previous levels. Re-vegetation processes returns the original vegetation to that which has vanished (Bradshaw & Chadwick, 1980; Hossner, 1988). The damage to the land resources is repaired, the structure and the functions of the ecosystem are recreated in order to achieve successional target (Figure 2.1) (Marrs, 2002).
Furthermore, the goal is to re-create a natural, functioning, self-regulating system which existed before the impact of mining damage (Marrs, 2002; Reay & Norton, 1999).

Figure 2.1 Ecosystem complexity to time for restoration ecology (Marrs, 2002).

In New Zealand, restoration practices will be different for each mining site, dependent on the dominant mine restoration issue at each site. For example, at Golden Cross Mine (Waihi), among the four principal post-mining land uses proposed (pastoral use, production forestry, assisted regeneration to a natural forest cover, and a natural landscape designed and managed for recreation) the Waihi site was returned to pasture (Golden Cross Mining Project, 1987). The Golden Cross mine was underground and waste rock volume was not an issue; the topsoil could be managed. In addition, The Golden Cross mine also conducted some open cast mining, however the waste rock was retained and used for building the embankment for the tailing pond. In this way, the issue of acid mine drainage could be maintained properly. In a similar approach to the Waihi site, the Martha Mine progressively rehabilitated any disturbed land back to pasture and grazing (Brodie et al., 2003). At the OceanaGold-Reefton mine, the main issue in the recent phase of exploration has been maintaining the overburden and waste rock stockpiles within the surrounding mining site (as the mine site is within the Victoria Park conservation area). The ore rock is crushed on site and transported to the Oceana-Gold mine at Macraes, Palmerston, Otago, where it is processed. No issues of processing-related heavy metal contamination or acid mine drainage occurs, as the processing occurs offsite. However, often the soil and water surrounding old mines like Reefton are elevated in heavy metals, derived from 18th and 19th century mining operations (Taylor & Smith, 1997).
In relation to mine restoration practices, public law in the USA requires grading of overburden, topsoil replacement and lime and fertilizer application when necessary to achieve productivity level equal to or greater than for pre-mined conditions. The law implies that the physical and/or chemical properties of reconstructed mine soils may be less favourable for tree establishment and growth than the original forest (Barnhisel, 1988). In New Zealand, alluvial gold mining is regulated under The Crown Minerals Act 1991. The Act controls the allocation and administration of mining rights. In addition, the Resource Management Act 1991 (RMA) is designed to provide an integrated policy framework for managing the resources of mine sites, such as controls on the excavation of land, and water and discharge permits for the use and discharge of water, and topsoil mining that might affect soil fertility in the future (Christchurch Community Law Centre, 1998; Hart et al., 1999). The regulations are designed to protect the environment for future generations and sustainably manage. Thus, it is mandatory to contour tailings, strip and salvage topsoil, re-spread topsoil and re-vegetate the site (Parker, 1991).

Any reconstruction of an ecosystem and mine soil will not only depend on the quality of the growth medium but will also depend on vegetation for increasing the soil physical, chemical, and biological condition of disturbed sites (Bradshaw, 1997; Tordoff et al., 2000). Planting vegetation in degraded areas will generate an input of organic substances and initiate nutrient cycling, and is an effective way to reduce surface erosion, because the roots bind the substrate (Teixeira et al., 2007). Vegetation can also return a large proportion of percolating water to the atmosphere through transpiration, thus reducing the concentration of soluble heavy metals entering water systems (Adriano et al., 2004). However, if plant establishment is slow, erosion may occur prior to development of vegetation cover. Furthermore, the run-off from sites that contain heavy metals in the surface horizons will pollute the water systems. Plant establishment is also inhibited by the absence of metal-tolerant population of legumes that would maintain a supply of N through symbiotic fixation. In addition, P deficiency may also occur due to the formation of insoluble heavy metal-P complexes (Bradshaw, 1987).

The main issue to address for re-vegetation of mine waste is the selection of appropriate plant species that can cope with the physiochemical properties of mine wastes (Maiti, 2007). These plant species also need to be able to alter soil properties in specific processes, (such as enhancing soil N availability by planting N fixation species) and to produce large amounts of biomass for increasing organic matter levels in the soil. These plants also need to take up high amounts of cations from the subsoil (Harrington, 1999). Often, the common practice in re-
vegetation is choosing plants that are drought resistant, fast growing trees which can grow in nutrient-poor, acidic conditions, and metal contaminated soils (Maiti, 2007).

Even though physical factors may severely limit vegetation establishment due to spoil materials/waste rock having very poor water holding capacity, chemical properties are also recognized as inhibiting plant growth (Maiti, 2007; Marrs, 2002; Tordoff et al., 2000). Many mine re-vegetation efforts focus on establishing rapid-growing non-native species which can control erosion. Establishing native tree and shrub species on unmodified mine spoils is difficult (Davis & Langer, 1997b). It is necessary that the correct site preparation occurs, in order to overcome such issues like poor drainage and substrate infertility (Davis & Langer, 1997b).

In New Zealand, Wineberry, Pepperwood (*Pseudowintera colorata*), and *Coprosma* species are recommended to be used as potential rehabilitation species in the West Coast forest, along with beech species which is dominant in New Zealand forest (Davis & Langer, 1997a). Furthermore, potential species which can be used for restoration planting specifically for the Grey-Inangahua biogeographic region (Reefton-Westland) are listed in Table 2.1 (Norton, 1991). This is the same biogeographic region as the Globe Progress mine at Reefton. The unit B1-B5 indicates the major landform-vegetation units, ranging from flat (B1) to sloping land (B5). The phase 1-4 indicates the serial species at the start of restoration programme. While Kamahi and Manuka often exist as pioneering scrub species in these forests, Wineberry and Red beech indicate their suitability for all phases of land surface, and have the potential to grow into mature forest as part of a self-sustaining forest ecosystem.
Table 2.1 Potential species for restoration in Grey-Inangahua biogeographic region (Westland-NZ).

<table>
<thead>
<tr>
<th>Unit B1:</th>
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<tbody>
<tr>
<td>Phase 1:</td>
<td>wineberry, tutu (<em>Coriaria</em> sp), red beech, karamu (<em>Coprosma robusta</em>)</td>
</tr>
<tr>
<td>Phase 2:</td>
<td>wineberry, tutu, red beech, karamu, putaputaweta (<em>Carpodeus serratus</em>)</td>
</tr>
<tr>
<td>Phase 3:</td>
<td>wineberry, silver beech (<em>Nothofagus menziesii</em>)</td>
</tr>
<tr>
<td>Phase 4:</td>
<td>flax, purei (<em>Carex secta</em>), raupo (<em>Typha orientalis</em>)</td>
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<th>Unit B2:</th>
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<tbody>
<tr>
<td>Phase 1:</td>
<td>wineberry, kamahi (<em>Weinmannia racemosa</em>), toro, red beech</td>
</tr>
<tr>
<td>Phase 2:</td>
<td>wineberry, kamahi, toro, red beech, hard beech (<em>Nothofagus truncata</em>)</td>
</tr>
<tr>
<td>Phase 3:</td>
<td>manuka (<em>Leptospermum scoparium</em>), mountain beech (<em>Nothofagus solandri</em>), <em>Quintinia</em> species</td>
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<tr>
<th>Unit B3:</th>
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</thead>
<tbody>
<tr>
<td>Phase 1:</td>
<td>manuka, quintinia, hard beech</td>
</tr>
<tr>
<td>Phase 2:</td>
<td>manuka, silver pine (<em>Dacridyum colensoi</em>), mountain beech</td>
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<th>Unit B4:</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Phase 1:</td>
<td>wineberry, red beech, kamahi, toro, karamu</td>
</tr>
<tr>
<td>Phase 2:</td>
<td>wineberry, kamahi, toro, hard beech</td>
</tr>
<tr>
<td>Phase 3:</td>
<td>kamahi, toro, hard beech</td>
</tr>
<tr>
<td>Phase 4:</td>
<td>mahoe (<em>Melycitus ramiflorus</em>), wineberry, tutu, karamu, putaputaweta, silver beech</td>
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<tr>
<th>Unit B5:</th>
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</tr>
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<tbody>
<tr>
<td>Phase 1:</td>
<td>wineberry, tutu, red beech</td>
</tr>
<tr>
<td>Phase 2:</td>
<td>wineberry, kamahi, toro, red beech</td>
</tr>
</tbody>
</table>

2.2 Characteristics of the growth medium

The main issue of any potential growth medium is nutrient deficiency and potential toxicity. Poor physical conditions and poor biological activity are also critical issues. Analysis of the growth medium will help to determine fertilizer requirements and identify any potential toxic or otherwise intractable layers which may have to be selectively handled (Sengupta, 1993).

2.2.1 Topsoil

Topsoil is the ideal ecosystem for plant growth, as it contains a higher percentage of organic matter than underlying B and C horizons. Topsoil also contains communities of microorganisms, fungi and soil fauna that drive soil processes, such as nutrient cycling. The biologically active topsoil is thus fundamental for soil development, and the sustainability of the whole ecosystem (Carrick & Kruger, 2007). Topsoil is beneficial for restoration, as it can be used for covering spoil materials; spreading topsoil above spoil materials may enhance water holding capacity, nutrient status of mine waste, and provide a source of soil organisms (Sydnor & Redente, 2002). In addition, spreading topsoil becomes a source of seed and beneficial microorganisms and is an effective method for plant establishment (Jasper et al., 1988).
In contrast, removing and re-spreading the topsoil over mine waste could reduce the physical and chemical quality of the topsoil, such as the destruction of soil aggregates, increase the soil mineralization, leading to a decrease in the soil organic carbon and by implication, reduce the N level (Ingram et al., 2005). In addition, in most areas there may be insufficient quantities of topsoil available to cover the spatial extent of the whole restoration site. In that case, mixing the topsoil with the B horizon and even the C horizon becomes an alternative to provide a sufficient quantity of suitable medium for re-vegetation. However, this technique can lead to an increase in the rates of mineralization, erosion, and leaching from exposed topsoil (Shukla et al., 2004). In high rainfall environments, replacement of mixed soil with B or C horizons results in poorer drainage, rush species invasion, and reduced growth of planted native species (Langer et al., 1999). Furthermore, the difficulty with the soil cover approach is that the chemical contaminants from waste materials still remain on the site (Cairney, 1987), and also the quality of topsoil, subsoil and overburdens are extremely variable (Marrs, 2002). Thus, it is difficult to see soil cover as an effective long term remedial solution in cases where the contamination is mobile (Cairney, 1987). Other geotechnical problems from spreading topsoil is that dissimilar underlying material can cause hydraulic discontinuity, and lead to dangerous slope instability (Bradshaw, 1987). Bradshaw (1987) also stated that the subsoil material has little structure, and even when mixed with topsoil and organic material from the forest floor, drainage remained restricted. Tensiometer and oxygen diffusion test results showed that the mixed soil treatment remained saturated with water and deficient in oxygen for long periods after rainfall vents, in contrast to the layered soil treatment (Bradshaw, 1987). Soils at the Globe Progress site in Reefton are dominated by podzols and acid brown soils (acid soils with low base saturation) The podzols are formed under humid to super humid environments with annual rainfalls between 1,000 mm and 3,500 mm and usually associated with forest species which produce an acid litter. Profile horizons are unevenly developed and commonly grade into strongly leached acid brown soils (Gibbs, 1980; Hewitt, 1992).

2.2.1.1 Physical properties

The process of topsoil removal and topsoil replacement by heavy vehicles can destroy substrate structure. This causes soil particles to become packed closely together and results in the loss of pore space by compaction (Harrington, 1999; Lyle, 1987). This problem can be overcome to a certain extent by growing deep rooting plants which form macro pores and channels when the roots die and decay. Compaction can also be alleviated by adding organic matter to the topsoil; enhancing soil aggregation into small, loose and porous lumps (Lyle, 1987). Perennial grasses and legumes are advocated as the best crops to grow, due to their
strong root penetration in the soil that will increase the soil volume, thus reducing soil compaction (Lyle, 1987). Reduction of compaction will increase the amount of water and nutrients available to the roots (Lyle, 1987). However, solving the compaction problem by growing specific plants is dependent on the growth period of the plant. Alternatively, compaction can be alleviated by mechanical techniques, such as ripping with deep tines to a depth of 60-80 cm or by running over the soils with tracked vehicle or even a roller; however this operation is costly (Bradshaw, 2000).

2.2.1.2 Chemical properties

Generally, topsoil is free from pH, salinity or toxic metal problems that inhibit plant growth (Kost et al., 1998). However, several researchers have found that topsoil from mining sites was low in pH, and acidity is a major issue in many New Zealand soils (Kooijman et al., 2008; Ross & Mew, 1995; Sydnor & Redente, 2002). Therefore, in these instances it is necessary to raise the soil pH, since soil reaction will affect element availability and toxicity, microbial activity, and root growth that will ultimately affect soil fertility and plant growth (Foth & Ellis, 1997). For example, N mineralization will be optimum between pH 6 and 8; meaning that N will be available for plant growth. Increasing the pH of acidic soils improves plant-availability of macronutrients while reducing the metals solubility, such as aluminium (Al) and manganese (Mn) (Whalen et al., 2000). However, even though the topsoil is suitable for plant growth, the soil material underneath of the topsoil may have pH, salinity and toxicity problems (Kost et al., 1998).

2.2.2 Overburden

The mining industry produces a large amount of waste rock and overburden material, ranging from tens to hundreds of million tons that damage environmental conditions (Izquierdo et al., 2005). In this instance, overburden and waste rock are removed from the site in order to access and extract the ore (Marshall, 1982). Waste rock is defined as the material that is removed from above or adjacent to the ore. This material contains both non-mineralized and low-grade mineralized rock, and usually is piled up close to the mine. Potentially these materials can impact surface and ground water quality, due to the nature and level of mineralization of the waste rock, prevailing climatic conditions, and the buffering capacity of the waste rock pile. Overburden is defined as the substrate which is removed from above the ore, consisting of soil, sand, clay, shale, gravel and boulders (Gregorich et al., 2002; Marshall, 1982). Usually, overburden is chemically immobile, apart from the removal of fines which
can contribute to surface runoff turbidity. Apart from a turbidity effect, these materials usually do not present any risk to water quality (Marshall, 1982).

Specifically, the overburden from Reefton sites is categorized as a meta-sedimentary rock consisting of sandstone and mudstone. The sandstone contains quartz, rock fragments, and muscovite mica. Plagioclase feldspar and biotite mica \((K(Mg,Fe)_2AlSi_3O_{10})\) have been altered to albite and chlorite, respectively, during metamorphism. Furthermore, through metamorphic hydrothermal process the sandstone is transformed to K-mica, carbonate (dolomite, ankerite, ferroan magnesite and magnesian siderite), chlorite, pyrite and arsenopyrite (Christie & Brathwaite, 2003; Smith et al., 1996). These characteristics indicate that as a part of the Greenland group, the overburden from Reefton has a potentially promising source of nutrients for plant growth, but they need to be released from the primary minerals (solid phase) by weathering processes which result in secondary minerals. Nutrients can be released from these secondary minerals into the liquid phase via surface exchange reactions. The processes releasing nutrients from solid to liquid phase can be achieved through natural weathering processes; however, this can take a long time to achieve. The addition of organic or inorganic amendments to the overburden can provide sufficient nutrients for growing plants (Bradshaw, 2000; Lyle, 1987; Marrs, 2002). However, the presence of organic acids and organic chelating complexes derived from organic matter decomposition are important factors in weathering processes (Drever & Stillings, 1997; Kabata-Pendias & Pendias, 2001; Wardle, 1991), by activating the breakdown of the primary minerals and releasing interlayer cations and by the formation of organic matter-metal chelate complexes. Thus the addition of organic matter can aid in the release of nutrients from primary minerals.

### 2.2.2.1 Physical properties

Overburden has different characteristics in different areas, due to the type of material being mined and the geology of the associated strata. Types of overburden minerals can range from weathered sub soils or deeper un-weathered overburdens. Often these overburden materials are characterized by a high rock fragment content (35 to >70 %), low clay content, low moisture retention capacity, and high bulk density (Haering et al., 2004; Maiti, 2007; Tordoff et al., 2000).

In disturbed land, soil texture is the most important physical factor of concern, because texture determines water holding capacity and the entrance and flux of air and water. The proportion of sand, silt and clay affects water absorption. Soil with high clay percentage holds
more water, but most of the water is held within the clay lattice structure and unavailable for plants. This situation can be modified by ameliorating the structure (Lyle, 1987). Overburden will often have very poor water holding capacity that will lead to surface drought and which will make vegetation hard to establish. This problem can be alleviated by the spreading and surface incorporation of organic matter, such as sewage sludge that can improve the physical structure of substrate and contribute nutrients in slow release form to both encourage sward establishment (Tordoff et al., 2000) and enhance weathering processes (Lyle, 1987).

Generally, mine wastes are coarse and open textured, and subject to erosion due to unstable materials. Preventing or controlling erosion can be done by two methods which are 1) maintaining stable slope angles by building mechanical structures and 2) covering the mine waste with vegetation (Lyle, 1987; Tordoff et al., 2000). Vegetation controls erosion by preventing raindrops from striking the substrates, absorbing water from substrates, and stabilizing the substrates by means of the plant’s root system. Roots bind soil particles together and reinforce the soil by increasing soil shear strength (Phillips, 2005). In the early stages of re-vegetation, drainage is required to support the plant growth. However, after a period of time, the water supply for vegetation will depend on the rainfall. Water availability (too much or too little) also causes a problem in mine restoration processes. Saturated soil can lead to an-aerobic conditions and vegetation mortality. Introducing wetland species can contribute to biodiversity, especially when open pits fill with water, or by providing the drainage system for managing re-vegetation programs. Dry conditions can also lead to the death of vegetation. In this situation, understanding the moisture requirements for plant establishment is required; an application of organic mulch can be effective in maintaining adequate moisture (Bradshaw, 1997a). Organic material such as sewage sludge, domestic refuse, peat and topsoil are typically used not only for solving physical problems of overburden, but also to enhance the chemical properties of overburden by improving the physical nature of the rooting medium, increasing water and nutrient-holding capacity, improving the presence of cations, providing slow-release nutrients, and reducing metal complexity (Tordoff et al., 2000).

2.2.2.2 Chemical properties

Most overburden material is low in nutrients, pH, but elevated in metal concentrations (Bradshaw, 1997; Maiti, 2007). Thus, using overburden as a growth medium requires a high degree of maintenance. For example, to develop a pool of organic and inorganic nutrients in the raw material there are two major strategies that can be used; (1) based on man-modified succession processes (using time, the natural accumulation of nutrients, N fixation, fertilizer);
(2) accumulating organic matter and nutrients from other resources (using topsoil, sewage sludge, green manures, etc) (Marrs, 2002).

In mining sites, the total sulfur level (often present as pyritic mineral) causes acidity in overburden (Hossner, 1988). When initially deposited, these minerals are generally neutral to alkaline; after 2 to 4 months, the materials will oxidise, particularly pyrite and generate acidity. The characteristics of the material changes, becoming unstable and very dry, as a result there will be a little vegetation growth. The two main processes that generate acidity are commonly represented by the following reactions (Seoane & Leiros, 1997):

\[
\begin{align*}
\text{FeS}_2 (s) + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} & \longrightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2 \text{H}^+ \\
\text{FeS}_2 (s) + 14 \text{Fe}^{3+} (aq) + \text{H}_2\text{O}(l) & \longrightarrow 15 \text{Fe}^{2+} (aq) + 2 \text{SO}_2^{-4} (aq) + 16 \text{H}^+ (aq)
\end{align*}
\]

The presence of Al and/or Fe sulfates as well as hydroxysulfates release more hydrogen ions and cause the substrates to become strongly acidic by the following reactions (Seoane & Leiros, 1997):

\[
\begin{align*}
\text{Al}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{O} & \longrightarrow \text{AlOHSO}_4 + \text{H}^+ \\
\text{K}^+ + 3\text{Al}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} & \longrightarrow \text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ \\
\text{Fe}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{O} & \longrightarrow \text{FeOHSO}_4 + \text{H}^+ \\
\text{K}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} & \longrightarrow \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+
\end{align*}
\]

With time, a combination of natural weathering and leaching will lead to the disappearance of the pyrite (FeS2) and the associated hydrogen ions. The rate of pyrite oxidation to generate sulphuric acid is catalysed by the presence of *Thiobacillus ferooxidans*. In cool climates, the acidity takes around 30-50 years to disappear. However in other environments, such as the gold mine wastes in South Africa, the processes can take around 10 years (Bradshaw, 1987).

One approach to cut the natural weathering and leaching time and to reduce levels of pyrite generated acidity is to neutralize the acid by application of lime (Bradshaw, 1997; Sengupta, 1993). The calculation of net acid generation potential allows the estimation of the amount of lime required to neutralise this generated acidity. The source of lime can be calcite (CaCO3), burnt lime (CaO), slaked lime (Ca(OH)2), dolomite (CaMg(CO3)2), and slag (CaSiO3); their ability to neutralize the acidity will also vary (Bolan & Duraisamy, 2003). Application of CaCO3 in soils produces Ca²⁺, HCO₃⁻, and OH⁻ and Mg²⁺ if the lime was added as dolomite. The acidic cations on soil particles are substituted by Ca²⁺, Mg²⁺, and the hydrolysis products are subsequently neutralized by OH⁻ (Hossner, 1988). Application of up to 400 t ha⁻¹ CaCO₃ may need to be applied to acid soil, this large amount will need to be incorporated by soil
ripping into the surface layers. This will address the existing low pH, but also the hidden or reserve acidity which will be produced by continued pyrite oxidation (Marrs, 2002).

In addition to the acidity issue, overburden material is often characterized by high salinity, which is derived from the parent rock (Ross & Mew, 1995). Salinity is defined as the presence of soluble salts in water or soil (Shaw, 2005), which can cause a decrease in the relative growth rate and water uptake in shoots and roots (Misra & Dwivedi, 2004; Nathawat et al., 2007; Shaw, 2005). Furthermore, saline conditions can affect N uptake. These conditions can also significantly decrease dry matter production; can decrease the concentration of potassium (K\(^+\)), calcium (Ca\(^{2+}\)) in leaves; and increase the sodium (Na\(^+\)) and chloride (Cl\(^-\)) content in leaves (Nathawat et al., 2007). As a result, saline conditions could hamper reclamation schemes. This problem can be solved through installing drainage systems that will remove the excess of salts by leaching, and applying non-saline irrigation water to help leaching processes. Applying topsoil or mulches to the overburden surface will help vegetation establish and reduce surface soil evapotranspiration (Marrs, 2002).

2.2.2.3 Managing metal toxicity

Most of the waste material or soil that is found in or near metalliferous sites is highly contaminated with heavy metals, including cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) (Boularbah et al., 2006). These have the potential to affect food quality, plant growth and environmental health (McLaughlin et al., 2005; Tordoff et al., 2000)

Metal ions can be retained in soil by: (1) adsorption (charged solute metal ions are attracted to the charged soil surface by electronic attraction and/or through the formation of specific bonds); (2) precipitation; (3) complexation reactions (organic components have a high affinity for metal cations because of the presence of ligands or groups that can chelate metals (Adriano et al., 2004). In addition, metals ions can be occluded in oxides and secondary clay mineral phase, and occur as residual forms, within the primary mineral lattice phase (Speir et al., 2003).

Behaviours of metals would be different in different types of soils and often more dynamic in surface soils, due to the surface soil containing an increased microbial population, a higher organic matter content, and a higher cation exchange capacity than the subsoil (Adriano et al., 2004). The mobility and solubility of metals in soil is affected by the pH, redox potential, water regime, presence of organic and inorganic materials (Achiba et al., 2009; Vega et al.,
Heavy metal activity in acid soil decreases with an increasing pH, which is attributed to an increase in cation exchange capacity (Bolan et al., 2008a). This process can be explained through: (1) an increase in pH increases the variable-charge of the soil, along with an increase in surface negative charge (attributed to the dissociation of H\(^+\) from weakly acidic functional groups of organic matter and some clay minerals), resulting in an increase in cation adsorption; (2) an increase in soil pH results in the formation of hydroxyl species of metal cations that have a greater affinity for adsorption sites than just the metal cation alone (Bolan & Duraisamy, 2003).

Since the concentration of metals in the soil solution is mainly affected by the pH and the nature of organic and inorganic anions, Adriano et al. (2004), demonstrated that liming could reduce the concentration of Cd in soil. This is because Cd adsorption mostly depends on the relative change in pH and Ca\(^{2+}\) concentration in soil solution. Furthermore, the uptake of Pb by plants is often found to decrease with liming, which is attributed to increased adsorption/precipitation at high pH and competition between Pb and other cations for uptake. In addition, high pH may decrease heavy metal mobility by the formation of precipitates, by increasing the number of adsorption sites and decreasing the competition of H\(^+\) for adsorption, and by increasing the metal stability with humic substances (Achiba et al., 2009).

Organic matter has direct and indirect effects on metal fractionation in soils, due to metal adsorption on solid and particulate soil organic matter and complexation with dissolved organic matter. In addition, organic matter forms stable, complexes with heavy metals, thus affecting the dissolution and translocation of heavy metals in the soil profile (Busenelli et al., 2009; Vega et al., 2004). Organic matter like sewage sludge can immobilize trace element by metal oxide fixation. In contrast, sewage sludge can also mobilize trace element by interaction of metal-complexes and small organic molecules. It has also been reported that the long-term use of inorganic fertilizer, such as phosphate fertilizer can cause an increase in Cu, while not increasing the concentration of As, Cr, and Pb (Kabata-Pendias & Pendias, 2001).

To a large extent, the guidelines for metal limits in soil currently used in New Zealand and Australia for agriculture is summarized in Table 2.2 (NZWWA, 2003).
Marrs (2002) stated that to alleviate toxicity issues, there are two main approaches: (1) by soil amelioration or physical separation from growing crops; (2) by using tolerant species, particularly hyperaccumulator species (Bolan et al., 2008b; Keeling et al., 2003). For soil amelioration, the common way is to add inorganic materials, such as phosphate compounds, liming material, or organic material like sewage sludge, straw, wood chipping, sawdust, bark, fly ash to either the topsoil (A horizon), subsoil (B, C horizons) or overburden which has already been stripped from the site. However, care must be taken to ensure that these materials do not contain any toxic materials and are sufficient for plant restoration needs. Addition of these materials should not only alleviate toxicity problems but also enhance surface root systems (Marrs, 2002).

While excessive metals in waste rocks inhibit plant growth (Tordoff et al., 2000), metals can also be removed from soil through plant uptake - by utilizing metal-tolerant plants (Bolan et al., 2008b; Keeling et al., 2003), such as using *Berkheya coddii* (an asteraceous perennial plant) to extract Co and Ni from metalliferous media (Keeling et al., 2003; Robinson et al., 1997), or using agricultural species (mustard, radish, turnip, rape, and amaranth) to accumulate metals, such as Cd, Cr, Cu, Ni and Zn (Kabata-Pendias & Pendias, 2001). Using metal-tolerant plants is an economical approach; requiring direct seeding to the substrate with the addition of standard NPK fertilizer (Tordoff et al., 2000).

A plant's ability to uptake heavy metals will depend on the concentration of the metal in the soil solution, the varieties and the age of the plants, the organic content of the soil, and the addition of any materials to mine soils which can increase the natural concentration of metals (Vega et al., 2004). The processes associated with heavy metal uptake by plants are summarised in Figure 2.2. The “A” indicates that there is a metal interaction in rhizosphere; “B” and “B’” shows the processes of metal transported to plant; “C” is the transport of metals

### Table 2.2 Critical limits of selected metals in soil.

<table>
<thead>
<tr>
<th>Element</th>
<th>Critical limits (mg kg(^{-1}) dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>20</td>
</tr>
<tr>
<td>Cd</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>600</td>
</tr>
<tr>
<td>Cu</td>
<td>&gt; 300*</td>
</tr>
<tr>
<td>Co</td>
<td>100</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>80-5000*</td>
</tr>
<tr>
<td>Ni</td>
<td>60</td>
</tr>
<tr>
<td>Pb</td>
<td>300</td>
</tr>
<tr>
<td>Zn</td>
<td>300</td>
</tr>
</tbody>
</table>

* Gonzales & Gonzales-Chavez (2006)
across root membrane; “D” indicates circulation within the plant, accumulation in target tissue and associated toxic effects (Adriano et al., 2004).

Figure 2.2 Summary of soil-plant system interactions during heavy metal bioavailability processes (Adriano et al., 2004).

The bioavailability of heavy metal both in and to plants is also affected by the interaction of heavy metals with themselves (Figure 2.3) and/or major chemical elements (Table 2.3) (Kabata-Pendias & Pendias, 2001). The interaction between the chemical elements and trace elements can be both antagonistic and synergistic, and imbalances in any interaction may cause chemical stress in the plant. The interactions affect the ability of one element to reduce or increase the absorption of other elements in plant. These interactions are variable and can occur inside plants cells, within the plant membrane surface, and at the plant root interface. However, the mechanism of the interactions is still poorly understood (Kabata-Pendias & Pendias, 2001).
Figure 2.3 Trace elements interactions within plants and adjacent to plant roots (Kabata-Pendias & Pendias, 2001).

Table 2.3 Main and heavy metals interactions in plants (Kabata-Pendias & Pendias, 2001).

<table>
<thead>
<tr>
<th>Main element</th>
<th>Antagonistic elements</th>
<th>Synergistic elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Cu and Mn</td>
<td>Cu and Fe</td>
</tr>
<tr>
<td>P</td>
<td>Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn</td>
<td>Al, Cu, Fe, Mn, and Zn</td>
</tr>
<tr>
<td>K</td>
<td>Al, Cd, Cr, and Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>S</td>
<td>As, Fe, Pb and Zn</td>
<td>Cu and Fe</td>
</tr>
<tr>
<td>Ca</td>
<td>Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn</td>
<td>Cu, Mn, and Zn</td>
</tr>
<tr>
<td>Na</td>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>Al, Cr, Mn, and Zn</td>
<td>Al and Zn</td>
</tr>
</tbody>
</table>

2.3 Weathering processes in the overburden

Rocks as a geologic material differ from each other in two major aspects: (1) chemical and mineralogical properties, which influence chemical weathering processes; (2) physical properties, which may encourage or resist both physical and chemical weathering mechanisms (Bland & Rolls, 1988). Rocks and soil minerals, in their chemical structure contain plant nutrients, however in forms unavailable to plants. As a result of weathering process, nutrients (except N) are slowly released from the primary minerals in geologic materials. Secondary minerals, such as clays, are formed as a result of these weathering processes (Barnes et al.,
The parent rocks that have been exposed for some periods of time through weathering and pedogenic processes generates soil mineral material, and become a source of soil nutrients, such as P, Ca, Mg, Na, and K. As a result, weathering processes play a vital part in the success of restoration.

The presence of water, oxygen, carbon dioxide and organic acids are vital factors in weathering processes (Drever & Stillings, 1997; Wardle, 1991). Weathering will be intense and rapid in the zone where the availability of water and air is balanced, and also by the presence of organisms that produce organic acids, chelating agents and carbon dioxide. In contrast, under saturated conditions, weathering processes will be slower, and weathering products will be removed by ionic diffusion. In a wetting and drying situation, weathering processes still occur, but will be dependent on precipitation processes (Ollier, 1984). The presence of salt can also contribute to physical and chemical weathering processes; salt exerts physical pressure by thermal expansion, hydration and crystallization; and chemically, salts can act as catalysts for reactions (Pope et al., 2002).

Reefton has an average annual rainfall of 1920 mm per year, and receives little wind. Summer weather is often fine and cold, while frosts and fogs are common in winter (Barry, 1993). The Globe Progress mine is located near Reefton and would receive 1920 mm precipitation per year as a minimum. This indicates that overburden from the Reefton mine site receives sufficient water to enhance weathering processes. The amount of water in contact with the rock surface and its affect on weathering will depend on the porosity and permeability of the rocks; with small pores holding more water and lowering the overall permeability (Ollier, 1984). The overburden is coarse and open textured, thus having poor water holding capacity and high permeability, which may hamper the nutrient release from primary minerals. This condition will affect the redox state of elements, and hence their mobility in the soil system.

### 2.3.1 Physical weathering

A physical (or mechanical) weathering process is the disintegration of rock without changing the chemical composition (Bland & Rolls, 1988). The breaking down and alteration of minerals into smaller fragments are affected by temperature, rock pressure, water availability (wetting-drying), saline solution, and plant growth. In many cases, weathering responds to low temperature, low pressure, and the presence of air and water (Ollier, 1984). The effects of physical weathering are closely connected to chemical weathering because chemical alteration
may reduce the strength of a rock to a stage where mechanical weathering is sufficient to cause the rock to break down (Bland & Rolls, 1988).

In mining areas, the breakdown of overburden material exposes a large surface area of fresh material to further physical and chemical weathering processes; the rate of physical weathering will thus depend largely on the characteristics of the overburden. For example, shales (particularly those composed of expanding lattice clays and siltstone) will break down into smaller fragments relatively quickly, mainly by physical processes; in contrast, limestone generally breaks down chemically. Physical weathering of 20 year old coal mine spoils in Kansas, USA, has caused a measurable increase from 38.5 to 46.9% of rock fragments (defined here as clasts noticeably smaller than the original coal mine spoil) (National Research Council, 1981).

### 2.3.2 Chemical weathering

Chemical weathering changes the chemical and/or mineralogical composition of the original rock and minerals. The type of chemical weathering depends on the chemical characteristics of the elements combined to form the primary minerals in the rock; because each chemical element has a different ion radius and ionic charge it reacts differently to weathering agents (Carol, 1970). There are several processes involved in chemical weathering of common rocks and minerals, which are: hydrolysis (H⁺ or OH⁻ replaces an ion in the mineral); leaching (when ions are removed from mineral into solution by dissolution processes); oxidation (when oxygen reacts with minerals to change the oxidation state of an ion); hydration (addition of H₂O) and and ion exchange (Birkeland, 1999). In addition, organic compounds like organic acids (formed from the CO₂ released during organic matter decomposition) and organic chelates also affect chemical weathering (Kabata-Pendias & Pendias, 2001). For example, the release of cations from rocks and minerals during weathering is caused by the interaction of soluble mineral and natural organic chelates (Kabata-Pendias & Pendias, 2001). In mining sites, chemical weathering processes can be greatly speeded up by the mechanics of the mining operation, due to materials being exposed to the air during excavation.

Weathering begins when the weakest bond in a mineral is altered and broken. Ion release is the first step in weathering reactions that leads to the formation of new material products. Chemical weathering causes the development of the colloidal components of soils which are largely made up of clay minerals. The various processes of chemical weathering decompose the relatively stable primary minerals to yield a large array of alteration, or secondary products (Carol, 1970). Some of these are soluble, and so are quickly lost from the immediate
weathering environment by leaching (the downward movement of ions in solution); others are quite readily precipitated, such as calcite in limestone voids, while yet others are relatively insoluble (Nahon, 1991).

**Phosphorus:** Compared to other nutrients (Ca, Mg, and K), the labile P concentration in soil is low, whether in alkaline, neutral or acidic soil condition (Barber, 1995). The concentration of the primary mineral, apatite decreases with an increase in soil age; however levels of occluded P will increase as P is retained at iron and aluminium hydrous oxide exchange sites on the soil exchange complex (Fe and Al phosphate in Figure 2.4). This is the key process that affects P availability. With an increase in soil development, the soil progressively looses Ca, Mg and other base cations, and becomes more acid. In addition, an acid soil will have more positive surface charge and will thus bind more P by non-specific adsorption as well as by specific absorption from the iron and aluminium hydrous oxides. In this system, soil organic P initially increases but then decreases as it becomes progressively immobilised within organic complexes. At this stage, levels of available and soluble P are inadequate for biological growth (Figure 2.4) (Foth & Ellis, 1997).

![Figure 2.4 Distribution of soil phosphate form to time of soil development (Foth & Ellis, 1997).](image)

Phosphorus released to the soil solution by mineralization of organic matter, can be taken up by the microbial population and plants, transferred to the soil inorganic pool, or lost by leaching and runoff (Sanchez, 2007). However, it has been observed that organic matter may hinder P sorption, thus enhancing P availability. This is due to humic acids and other organic acids which may reduce P fixation through formation of complexes (chelates) with the presence of Fe, Al, Ca and other cations that react with P (Sanchez, 2007). Phosphorus ion in soil solution mainly occurs either as $\text{H}_2\text{PO}_4^-$ or $\text{HPO}_4^{2-}$ depending on soil pH (Barber, 1995).
**Base cations:** All base cations in the soil consist of three fractions: non-exchangeable, exchangeable, and water-soluble fractions. Calcium (Ca) is the dominant exchangeable base on the exchange sites of clay minerals. In the primary minerals, Ca is present as calcium carbonate (calcite), and as a combination of Ca and Mg carbonates (dolomite). In the early stages of weathering, Ca is lost first from the minerals and becomes available for plant uptake (Pilbeam & Morley, 2007).

Magnesium (Mg), in addition to existing as exchangeable and water soluble fractions, also exists as non-exchangeable fractions of Mg in primary minerals and many of secondary minerals (Merhaut, 2007).

The main source of potassium (K) in the soil is alkali feldspar, muscovite (K-mica), biotite (Mg-mica), and illite. The release of K⁺ during mineral weathering is associated with an opening of the interlayer in the crystal lattice structure. Prior to weathering of the primary mineral, the free negative charges of the interlayer can be occupied by hydrated cationic species (Ca²⁺, Mg²⁺, Na²⁺, cationic Al species), it follows that the interlayer K⁺ is exchangeable. Removal of the interlayer K⁺ by hydrated cations, along with cationic aluminium species, leads to the formation of a new secondary mineral. As K⁺ has no specific binding sites with organic matter; therefore K⁺ is loss to leaching. Thus, soils with contain high organic matter may be generally lower in potassium (Mengel, 2007).

**Heavy metals:** Initially, at the early stages of weathering and pedogenic processes, the heavy metal composition of the soil will be inherited from the parent material. With time however, the heavy metal status of soil will become different due to the influence of predominating pedogenic and anthropogenic processes. The presence of humus also affects the accumulation or migration of heavy metal during weathering and soil formation (Kabata-Pendias & Pendias, 2001; Violante *et al.*, 2002).

### 2.3.3 Weathering products

Weathering alters the substrate particle size into progressively smaller sizes that leads to an increase in the surface area of the substrate, thus increasing the ion release from the substrate into the soil solution from secondary minerals; and eventually leading to soil formation. Materials released from the system by removal or leaching of the materials are converted into a variety of forms of crystalline and amorphous secondary products. The common observation of weathering products is the presence of clay minerals and hydrous oxides of aluminium and iron. Identification of these products is necessary as they influence many soil properties and
also reflect the long-term effect of the chemical and leaching environment (Birkeland, 1999). In terms of the restoration process, the presence of clay minerals is important to identify since the internal surface area of clays can hold a high water content, accumulate and preserve organic matter, thus increase the cation exchange capacity, and as a result support vegetation for sustainable restoration.

Previously, attention had been focused on the presence of phyllosilicate clay minerals in soil; nowadays the importance of short-range order (SRO) minerals and the metal oxides and hydrous oxides of Fe, Al and Mn as non-crystalline products have been realized (Birkeland, 1999; McLaren & Cameron, 2004). SRO clays are characterized as minerals of variable composition and a predominance of Si-O-Al bonds (Buol, 1997). The differences between this SRO mineral and phyllosilicate clay minerals is that SRO’s have a very large surface area in comparison. For example, imogolite has a large specific surface area of 430-900 m$^2$g$^{-1}$ compared to geothite (feOOH) that has specific surface area of 12-132 m$^2$g$^{-1}$ (Wada, 1980).

The most common products of SRO clays (non-crystalline aluminosilicate) are allophane/imogolite (Birkeland, 1999; McLaren & Cameron, 2004; Parfitt et al., 1988), ferrihydrite, and/or other metal-humus complexes (Eger, 2007). Identification of SRO clays is important due to their widespread occurrence, special structures, and the specific effects on soil properties (Lowe, 1993), such as having a large surface area and reactive surface groups. Furthermore, the importance of allophane/ferrihydrite in the soil development processes is presented in Figure 2.5 (Lowe, 1993). The small amount of allophane and ferrihydrite in soil indicates that the soil has a large surface area and reactive surface groups, thus affecting the soil properties (Lowe, 1993).

![Figure 2.5 Relative surface area of three size components in a hypothetical soil compromising approximately equal quantities of sand, silt and clay, and containing 1 % allophane/ferrihydrite (Lowe, 1993).](image)
Drouza et al. (2007) stated that the formation of SRO is affected by pH; at pH 5.0-7.0, Al and Fe form allophane, imogolite and crystalline phyllosilicate minerals, but not Al and Fe-humus complexes. Furthermore, the high pH in combination with low organic matter content results in a low solubility of Al and Fe, and thus the absence of Al and Fe-humus complexes. In a study of aspect-related factors driving pedogenesis in high country soils in Canterbury, Eger (2007) stated that there was a relationship between the lack of short-range order minerals and free Al and Fe needed for the formation of metal-humus complexes. This was reflected in the lower amount of carbon on the northern slope aspect of the study sites; lack of carbon may hinder the mineralization of organic substances and ability to stabilize organic matter.

Allophane is defined as a group of clay-sized minerals (Wada, 1980). Allophane formation is related to organic matter supply relative to the amount of Al released by weathering of volcanic ash (Wada, 1980). However, since the amount of Al will increase by increasing the amount of total carbon, then the proportion of Al may be absorbed in humus accumulation and thus will inhibit allophane formation (Wada, 1980). The synthesis of allophane is also inhibited by Al and Fe-humus (Broquen et al., 2005). In addition, at pH < 5 the allophane formation is inclined to change in the ratio of SiO₂/Al₂O₃ (Wada, 1980). Even though the occurrence of allophane is closely related to soils from volcanic parent material (volcanic ash, pyroclastic deposits, basalt), Childs et al. (1983) found that allophane and imogolite was also present in a Canadian podzolic soil. Allophane has also been discovered New Zealand podzols from non-volcanic parent material, such as loess, argillite and ferralitic weathering products (Eger, 2007).

A clay sample from the Mairoa site in the Hamilton region-New Zealand contained up to 80% allophane (Parfitt et al., 1983). The allophane content of the clay fraction increases with increasing annual rainfall and increasing leaching through the soil (Drouza et al., 2007; Parfitt et al., 1983); even though strong leaching occurred in the Mairoa soil no moisture deficits occurred during summer season (Parfitt et al., 1983).

The amount of allophane and imogolite in soil can be estimated by using the Al/Si ratio and Si. A ratio of Al/Si close to 2 corresponds to allophane (Broquen et al., 2005; Drouza et al., 2007; Duncan & Franzmeier, 1999; Eger, 2007; Egli et al., 2006; Lilienfein et al., 2003; Parfitt & Kimble, 1989; Wada, 1980). Estimation of the allophane content can be determined by calculating \( \frac{(Al_0 - Al_p)}{Si_0} \). Hence, \( \frac{(Al_0 - Al_p)}{Si_0} \) indicates the amount of the Al/Si ratio of allophane \( (2SiO_2.Al_2O_3.2.5H_2O) \) and imogolite \( (SiO_2.Al_2O_3.2.5H_2O) \) in soil (Egli et al., 2006). The Al/Si ratio decreases when the amount of allophane decreases (Parfitt et al., 1983).
Determination of Al and Si is conventionally done by extracting with acid-oxalate reagent and using subscript “o” (Al_o, Si_o). The Al_o represents the amount of Al dissolved from allophane, imogolite, and Al-humus complexes into soil solution. The Al_o also can be used for estimation of total translocated Al (Childs et al., 1983). Extraction with pyrophosphate reagent (using subscript “p” (Al_p)) represents the amount of organic-bound Al (Childs et al., 1983). As a result, Al_o minus Al_p indicates the amount of Al in allophane and imogolite. The Si_o indicates the amount of the Si in allophane and imogolite (Broquen et al., 2005; Drouza et al., 2007; Duncan & Franzmeier, 1999; Eger, 2007; Egli et al., 2006; Lilienfein et al., 2003; Parfitt & Kimble, 1989; Wada, 1980).

Iron weathers from primary minerals and can precipitate in several forms including goethite and as ferrihydrite (Fe_2O_3·4H_2O). The type formed will result from a combination of rainfall, drainage, temperature regimes, parent basaltic ash and pH dependent surface charge (Parfitt et al., 1988). These researchers found that the Akaka soil (Hawaii) contained high ferrihydrite (over 30%), where the rainfall was 3800 mm, and it dropped to 10% where the rainfall was 1000 mm (Parfitt et al., 1988). New Zealand Andisols contain ferrihydrite in the range 6-9% which can interfere with allophone/imogolite determination (Parfitt & Kimble, 1989). Some soil, formed from basic tephras in some countries, such as New Zealand, Oregon-USA, Fiji, Kenya and Canary Island contains Fe_o (acid-oxalate reagent) more than 3%, indicating the presence of ferrihydrite at more than 5% (Parfitt et al., 1988). Furthermore, this highlights that these soils have formed under high rainfall where Si and bases were leached from the soils. Parfitt et al. (1988) stated that under high rainfall ferrihydrite can form from basic tephras. In addition, the chronosequence of ferrihydrite concentrations at Mt. Shasta, California increased with increasing soil age (Lilienfein et al., 2003).

Ferrihydrite can be determined by using Fe_o alone (acid-oxalate reagent) (Parfitt et al., 1988). Other researchers have modified this to estimate ferrihydrite by multiplying by 1.7 and using (Fe_o-Fe_p) instead of Fe_o alone (Eger, 2007). The presence of ferrihydrite can be indicated by measuring Fe_o/Fe_d, where a high ratio of Fe_o/Fe_d means ferrihydrite occurs. In contrast, low Fe_o/Fe_d indicates low iron crystallinity through the influence of organic matter and acid soil environment with strong leaching (Eger, 2007).

The importance of metal oxides as weathering products is due to their specific adsorptive properties for anions and cations. In addition, metal oxides can occur as crystalline minerals or non-crystalline, as short-range order clays which are partly present as coatings on clay
minerals and/or humic substances, such as clay-metal and organic-metal complexes (Violante et al., 2002).

### 2.4 Nutrient availability during mining restoration

Reestablishment of vegetation that can thrive and sustain itself depends on the interaction between the nutrient supply from the growth medium and the plant physiology (Barber, 1995). In turn, the availability of nutrients in the growth medium depends on the quantity and nature of the nutrients (Barber, 1995).

In mining sites, nutrient deficiency can be a significant problem in the restoration processes. Plants require the supply and absorption of specific chemicals (macronutrients or micronutrients) that are essential for plant growth and reproduction. These are required as soon as possible to support plant growth in the early stage of re-vegetation (Barker & Pilbeam, 2007; Sengupta, 1993). Thus, maintaining plant nutrients in an adequate amount for the plant is necessary for successful re-vegetation. Since soil is the most favourable medium for growing plants, thus it is useful to model the remediation of overburden to the extent that it has similar chemical properties as soil for successful re-vegetation. To a large extent, the rating of elements in soil is listed in Table 2.4 (Hazelton & Murphy, 2007). Ratings for New Zealand soils and provisional targets for soil quality indicators are also available (Hill et al., 2003; Sparling et al., 2008).

<table>
<thead>
<tr>
<th>Rating</th>
<th>Organic Matter</th>
<th>Organic Carbon</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>CEC</th>
<th>Extractable P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>(g/100g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(mg P/kg soil)</td>
</tr>
<tr>
<td>Extremely low</td>
<td>&lt;0.7</td>
<td>&lt;0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Very low</td>
<td>0.70 – 1.0</td>
<td>0.4-0.6</td>
<td>0-0.1</td>
<td>0-0.2</td>
<td>0-2</td>
<td>0-0.3</td>
<td>1-6</td>
<td>&lt;6</td>
</tr>
<tr>
<td>Low</td>
<td>1.7-3</td>
<td>0.6-1</td>
<td>0.1-0.3</td>
<td>0.2-0.3</td>
<td>2-5</td>
<td>0.3-1.0</td>
<td>6-12</td>
<td>6-17</td>
</tr>
<tr>
<td>Moderate</td>
<td>1.7-3</td>
<td>1-1.8</td>
<td>0.3-0.7</td>
<td>0.3-0.7</td>
<td>5-10</td>
<td>1-3</td>
<td>12-25</td>
<td>10-17</td>
</tr>
<tr>
<td>High</td>
<td>3-5.15</td>
<td>1.8-3</td>
<td>0.7-2.0</td>
<td>0.7-2.0</td>
<td>10-20</td>
<td>3-8</td>
<td>25-40</td>
<td>17-25</td>
</tr>
<tr>
<td>Very high</td>
<td>&gt;5.15</td>
<td>&gt;3</td>
<td>&gt;2</td>
<td>&gt;2</td>
<td>&gt;20</td>
<td>&gt;8</td>
<td>&gt;40</td>
<td>&gt;25</td>
</tr>
</tbody>
</table>

Plants absorb nutrients mostly in the inorganic form; the organic form usually needs to be mineralized to the inorganic form before being able to be absorbed by plants (Barber, 1995). The inorganic ions are largely supplied to the plant by absorption through the root system. Nutrient concentration in plants that support plant growth and reproduction would vary with species and with varieties within species, and also vary among families (Barker & Bryson, 2007). For example, Wardle (1991) listed the nutrient content of green leaves from wild vegetation around New Zealand (Table 2.5). The reference for Red beech bioavailability used
in this study is taken from Wardle (1991). As no specific nutrient level for Wineberry (Makomako) was found, the podocarp/broad-leaved forest and Whitey wood (Mahoe) was used for Wineberry nutrient status. Wineberry and Whitey-wood have a similar performance in terms of leaf, fruit, and both plants are categorized as small tree, but they are different in terms of species classification. However, Wineberry is recommended to be used as a potential rehabilitation species in the West Coast forest (Davis & Langer, 1997a).

### Table 2.5 Nutrient content of green leaves (Wardle, 1991).

<table>
<thead>
<tr>
<th>Species</th>
<th>Miscellaneous</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>P</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asplenium bulbiferum</td>
<td>Understorey</td>
<td>0.5</td>
<td>37.0</td>
<td>11.0</td>
<td>5.3</td>
<td>3.0</td>
<td>27.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Coprosma grandifolia</td>
<td>Understorey</td>
<td>0.7</td>
<td>22.0</td>
<td>18.0</td>
<td>5.5</td>
<td>1.8</td>
<td>16.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Melicytus ramiflorus</td>
<td>Understorey</td>
<td>1.7</td>
<td>27.0</td>
<td>15.0</td>
<td>5.0</td>
<td>2.6</td>
<td>23.0</td>
<td>3.4</td>
</tr>
<tr>
<td>Weinmannia racemosa</td>
<td>Understorey</td>
<td>1.3</td>
<td>7.0</td>
<td>7.0</td>
<td>2.8</td>
<td>0.8</td>
<td>9.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Coprosma 6 spp.</td>
<td>Filiramulate</td>
<td>2.9</td>
<td>13.1</td>
<td>16.3</td>
<td>4.8</td>
<td>1.7</td>
<td>20.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Coprosma 3 spp.</td>
<td>Large-leaved</td>
<td>0.5</td>
<td>18.1</td>
<td>13.3</td>
<td>4.1</td>
<td>1.3</td>
<td>13.9</td>
<td>3.2</td>
</tr>
<tr>
<td>Podocarp/broad-leaved forest</td>
<td>Canopy</td>
<td>1.1</td>
<td>6.7</td>
<td>5.2</td>
<td>3.4</td>
<td>0.6</td>
<td>7.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Agathis australis</td>
<td>Current leaves</td>
<td>-</td>
<td>10.4</td>
<td>7.8</td>
<td>0.1</td>
<td>0.9</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td>Agathis australis</td>
<td>Older leaves</td>
<td>-</td>
<td>0.5</td>
<td>1.5</td>
<td>0.1</td>
<td>0.5</td>
<td>6.6</td>
<td>-</td>
</tr>
<tr>
<td>Nothofagus fusca</td>
<td>Recent soil</td>
<td>0.5</td>
<td>5.6</td>
<td>11.0</td>
<td>2.6</td>
<td>1.6</td>
<td>13.0</td>
<td>-</td>
</tr>
<tr>
<td>Nothofagus fusca</td>
<td>Yellow-brown earth</td>
<td>0.3</td>
<td>5.2</td>
<td>7.0</td>
<td>1.8</td>
<td>1.0</td>
<td>17.0</td>
<td>-</td>
</tr>
<tr>
<td>Nothifagus menziesii</td>
<td>Yellow-brown earth</td>
<td>0.5</td>
<td>4.2</td>
<td>3.0</td>
<td>1.0</td>
<td>1.1</td>
<td>15.0</td>
<td>-</td>
</tr>
<tr>
<td>Nothofagus truncata</td>
<td>Yellow-brown earth</td>
<td>0.7</td>
<td>5.6</td>
<td>8.0</td>
<td>1.5</td>
<td>0.6</td>
<td>11.0</td>
<td>-</td>
</tr>
<tr>
<td>Pinus contorta</td>
<td>1 yr needles</td>
<td>-</td>
<td>6.0</td>
<td>1.6</td>
<td>0.9</td>
<td>1.3</td>
<td>15.0</td>
<td>-</td>
</tr>
<tr>
<td>Pinus contorta</td>
<td>5 yr needles</td>
<td>-</td>
<td>5.0</td>
<td>6.5</td>
<td>0.5</td>
<td>1.0</td>
<td>15.0</td>
<td>-</td>
</tr>
<tr>
<td>Pinus radiata</td>
<td>1 yr needles</td>
<td>&lt; 0.1</td>
<td>8.3</td>
<td>2.7</td>
<td>1.3</td>
<td>1.7</td>
<td>15.0</td>
<td>-</td>
</tr>
<tr>
<td>Pinus radiata</td>
<td>3 yr needles</td>
<td>&lt; 0.1</td>
<td>7.3</td>
<td>3.2</td>
<td>1.4</td>
<td>1.5</td>
<td>10.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Among the nutrients, the largest quantity of nutrient that is required for plant production is N (Foth & Ellis, 1997; Marrs, 2002). On the other hand, N is also the most difficult nutrient to handle because of the complexity of chemical, physical, and biological transformation of N in soil and the loss of N through gas emission and leaching processes (Fowler et al., 2004). In uncultivated soils, where no N fertilizer has been applied, the source of N in soil comes from: (1) N in organic matter (including plant residues in the soil- mainly as NH₂ groups); (2) mineral N in the soil solution and on exchange sites (mainly as NH₄⁺ (ammonium) and NO₃⁻ (nitrate)), however NO₃⁻ is generally the principal form, since nitrification by microorganisms converts NH₄⁺ and NO₂⁻ to NO₃⁻; (3) ammonium fixed in clay minerals; and (4) gaseous N in the soil atmosphere (Barber, 1995; Foth & Ellis, 1997; Mengel & Kirkby, 2001). However, the availability of N will also be affected by the availability of other nutrients. Lack of other nutrients, growth-limiting temperatures or water supply can increase the concentration of total N and nitrate, along with suppression of yield (Barker & Bryson, 2007). Due to little N
contained in most raw mineral wastes, a N store must be built up during succession or restoration (Marrs, 2002). This can be solved through applying N fertilizer or planting N fixation species.

Plants roots readily absorb N from the soil solution in the form of NH₄⁺ or NO₃⁻. The rate of NH₄⁺ and NO₃⁻ uptake will depend on the pH of the solution (Barber, 1995; Mengel & Kirkby, 2001). The absorption of NH₄⁺ increases as pH increases, whereas the absorption of NO₃⁻ uptake tends to decrease with increasing pH (Barber, 1995). Mengel & Kirby (2001) suggested that the reduction of NO₃⁻ uptake at high pH was due to the effect of the OH⁻ ion that suppresses the NO₃⁻ uptake. N concentrations in plants will vary within species and with varieties within species, and will also vary among families (Barker & Bryson, 2007).

2.4.1 Organic sources

Even though inorganic fertilizers can be added in the form of fertilizer, this can be an expensive and labour-intensive technique for long-term processes, since it requires regular fertiliser applications. Hence the possibility of using other nutrient sources derived from organic sources, which can provide nutrients by slow release, over the long term.

**Biosolids:** According to the New Zealand Water and Wastes Association (2003), “biosolids are sewage sludge or sewage sludge mixed with other materials that have been treated and/or stabilized to the extent that they are able to be safely and beneficially applied to land”. Every year around 77 000 dry ton of municipal biosolids are produced in New Zealand and thus are a potential source of organic matter, suitable for beneficial use for land application (Magesan & Wang, 2003).

Biosolids have the potential for use as a soil amendment at most sites involving land reclamation, ranging from waste rock piles from underground extraction operations and surface metalliferous mines, waste material piles and tailing impoundments from processing mineral, as well as restoration of sites affected by mineral processing and forestry operations on reclaimed land (Phillips, 2005). Applying biosolid amendments to mine waste increases soil organic content, and thus helps to develop the physical nature of the rooting medium, particularly by increasing water and nutrient-holding capacity, and also decreasing bulk density of mine soils. In addition, it can provide nutrients (N and P) for vegetation in a slow-release (organic) form and increase microorganism activity (Abbott et al., 2001; Halofsky & McCormick, 2005; Tordoff et al., 2000) and consequently speed up plant establishment (Martinez et al., 2003). This is because biosolids contain high organic matter and adequate
levels of plant nutrients to sustain initial plant growth (Crush et al., 2003). In addition, biosolid application may increase the soils CEC, by the dissociation of H\(^+\) from the functional groups in organic matter (Adriano et al., 2004).

As well as being a potential material to remEDIATE degraded lands, biosolids may also contain significant amounts of undesirable materials, such as heavy metals that can cause contamination of the water pathway, flora and/or fauna and also in humans by entering the food chain (Calace et al., 2005). In New Zealand, guidelines for the safe application of biosolids to land uses the criteria grade “A” and grade “B” for microbiological contaminant and grade “a” and grade “b” for chemical contaminant (heavy metals). Grade “a” and “A” indicates that the concentration of all contaminants must be at, or below specific limitations (New Zealand Water and Waste Association, 2003). Abbott et al. (2001) found that biosolid amendment did not significantly contribute to down gradient groundwater nitrate and metal concentration. In addition, particularly in semi-arid ecosystems, the percentage of nutrients or toxic elements leaching to ground water was low (Martinez et al., 2003). To counter metal contaminant problems to land, materials can be applied to soil which are able to reduce the risk of contaminants entering the groundwater or surface water by being able to immobilise the mobile metal forms (by adsorption). This technique uses cement, lime, or organic polymers to bind the metals and transform them to more manageable forms and/or into a less toxic form by physically and/or chemically immobilizing the contaminants. This technique is more effective in terms of cost and can be applied in situ, and is thus more sustainable (Calace et al., 2005). Moreover, addition of biosolids to metal-contaminated soil may dilute the metal concentration in the mine soil, as the metal concentration of the biosolid may be less than the soil it is being added to.

**Wood waste:** Organic amendments can be in the form of wood waste; as either unprocessed or processed as sawdust. Clearing of trees or surface vegetation from the land is the first step that has to be done before mining exploration; this can lead to nutrient losses and erosion. Thus, trees will be removed to other sites and become essentially a “waste product”. Using tree materials that remain, such as leaves, branches and roots as nutrient sources is good for soil in order to return lost nutrients after land clearing. However, these materials also are easily broken down to release nutrients to soil and to be leached from the site before re-vegetation has started. In addition, burning these materials increases the nutrient loss, especially of more volatile components (West, 2006). Thus, there are two possible ways to manage the nutrient loss from the soil. These are firstly stripping the bark that contains a large amount of
nutrients (Douglas fir wood contains 48.8 % of C and high C/N ratio) (Arends & Donkersloot-Shouq, 1988) and leave it on the sites or secondly, burning the wood debris. Research has demonstrated that un-burnt bark and wood lowers the nutrient loss (N, P, Ca, Mg, and K) from sites compared to those sites that burn the wood only (bark taken). Taking the bark from the wood and burning the wood increased the nutrient loss from the site (West, 2006). In New Zealand, by 1980 the total weight of bark that had been produced was forecast to have risen to 653,000 ton. The tighter restrictions on air pollution will make it unfeasible to burn trees, however dumping this material increases the cost of transportation and makes this alternative less favourable (Reeve, 1974). As a result, wood waste as an organic amendment becomes a good solution to the issue of managing wood waste on site.

**Green manure:** Nowadays, much effort has been focused on using N fixing plants in order to increase organic matter for plant growth. Legumes are the plant species that are generally used as green manures due to their capability to deliver N into soil-plant system through symbiotic fixation of atmospheric N (N₂) (Hanly & Gregg, 2004). Green manure is a way of using plants as a fertilizer “within” the soil in order to improve soil quality (Astier et al., 2006). Green manure crops contribute to increasing cropping system sustainability by reducing soil erosion and ameliorating soil physical properties, increasing soil organic matter and fertility levels, increasing nutrient retention and helping control weeds (Cavigelli & Thien, 2003). Among the green manure crops, particularly in organic cropping systems, Lupin (*Lupinus angustifolius*) contributed an N concentration of 3.39 %, and produced a total N uptake of 162 kg N ha⁻¹ (Fowler et al., 2004). To increase the optimum benefit of lupin as green manure it is necessary to manage the growth stage of lupin incorporated with soil, the length of the fallow period following lupin soil incorporation, and any lupin residue effect (Hanly & Gregg, 2004). Furthermore, the importance of legumes in agriculture systems due to their ability to fix N can be seen in Table 2.6 (Foth & Ellis, 1997).

<table>
<thead>
<tr>
<th>System and organism</th>
<th>N₂ fixed, kg ha⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Legumes, bacteria</td>
<td></td>
</tr>
<tr>
<td>Alfalfa (<em>Medicago sativa</em>)</td>
<td>128-600</td>
</tr>
<tr>
<td>Lupins (<em>Lupinus sp</em>)</td>
<td>150-169</td>
</tr>
<tr>
<td>Clovers (<em>Trifolium sp</em>)</td>
<td>104-160</td>
</tr>
<tr>
<td>Soybeans (<em>Glycine max</em>)</td>
<td>57-94</td>
</tr>
<tr>
<td>Cowpeas (<em>Vigna unguiculata</em>)</td>
<td>84</td>
</tr>
<tr>
<td>Non legumes - nodulated, actinomycetes</td>
<td></td>
</tr>
<tr>
<td>Almus calder</td>
<td>40-300</td>
</tr>
<tr>
<td>Ceanothus</td>
<td>60</td>
</tr>
</tbody>
</table>
2.4.2 Inorganic sources

Since the availability of soil N and P is associated with organic matter, and the release of these nutrients from organic matter is slow and unpredictable, an inorganic source is required for supplying short-term N and phosphorus in soil.

In early re-vegetation programs, application of N to mine soils is always added as urea (CO(NH$_2$)$_2$), NH$_4^+$ or NO$_3^-$ (Lyle, 1987). Urea will convert to the NH$_4^+$ form after application to soil, then it will be held by soil or converted into the NO$_3^-$ form (Barker & Bryson, 2007), however a greater amount of N may be lost via volatilization (Lyle, 1987). Thus, any required fertilizer must be in the form of solid N fertilizer; otherwise N must be added frequently, for example every 2 months.

Certain plants also need a large amount of P, but the availability in soil is often low. Phosphate rocks, ammonium phosphate and other fertilizers which contain P are commonly used to overcome P deficiency in soils. However, in some situations, P sources can induce phytotoxicity (Sanchez, 2007). Thus, it is recommended that any potential for phytotoxicity must be considered when selecting P fertilizer (Sanchez, 2007).

2.5 Assessing successful restoration

There are many possible approaches that can be used for assessing successful restoration: for example, restoration success can be determined by the successful establishment of initial plantings that ensure a self sustaining, functioning natural system (Reay & Norton, 1999). A more specific approach is that outlined by The Society of Ecological Restoration International (SER) which provides a list of nine ecosystem attributes as a basis for measuring restoration success. It is recommended that a restored ecosystem should consist of the following attributes: (1) similar diversity and community structure in comparison with reference sites; (2) presence of indigenous species; (3) presence of natural functional groups necessary for long-term stability; (4) capacity of the physical environment to sustain reproducing population; (5) normal functioning; (6) integration with the landscape; (7) elimination of potential threats; (8) resilience to natural disturbances; and (9) self sustainability (Ruiz-Jene & Aide, 2005). However, in practice there are three main attributes that can be studied, (1) ecosystem diversity; (2) vegetation; and (3) ecological processes. Diversity can be measured by determining the richness and abundance of the organisms. Vegetation structure can be determined by measuring vegetation cover, plant density, biomass or vegetation cover. Nutrient cycling and biological interaction are important factors to be determined for ecological processes (Ruiz-Jene & Aide, 2005).
In addition, Ludwig et al. (2003) described that the biological system on mine sites is an important system for rehabilitation development; re-vegetating mine sites affects the water and nutrients that are retained on site (Figure 2.6). Moreover, biodiversity can actually be greater in revegetated, disturbed land compared to indigenous forest. It follows therefore that the curve in Figure 2.6 may not be a true representation of biodiversity. In the New Zealand context, biodiversity is considered a good marker of rehabilitation status (Smale et al., 2008). However, to some extent the knowledge of physical and chemical properties of waste minerals will place a constraint on the formulation of ecological goals for the restored areas. The potential indicator of a productive reclaimed soil will depend on the characteristics of the soil and/or spoil materials that affect the root zone, for example the chemical properties that effect plant growth. These properties are pH, cation exchange capacity, nutrient availability (Sengupta, 1993) and metal toxicity (Bech et al., 1997; Tordoff et al., 2000). It is expected that the spoil material has a capability as a growth medium to a similar extent as topsoil.

![Figure 2.6 Ecosystem development with time on mine sites (Ludwig et al., 2003).](image-url)
2.6 The use of topsoil and overburden as growth mediums in the restoration of the post mining landscape

The aim of this thesis is to determine initial parameters for a sustainable restoration method for managing the topsoil and/or any overburden or waste rock material remaining at gold mine sites, using the Globe Progress mine at Reefton as a study site. Several significant knowledge gaps have been identified in the review in this Chapter, and investigating these gaps will allow this issue to be addressed.

The first part of the review identified that current mine restoration practices incorporate a range of strategies, including re-contouring the land surface, topsoil stripping and storage, topsoil reuse; in combination with inorganic fertilisers and re-vegetation.

Yet the issue is that topsoil is limited in supply, compared to the spatial extent of the area of the post-mining landscape to be reclaimed. Overburden is in plentiful supply, but there is a significant gap in our knowledge concerning the parameters for its use as a growth medium. The issue with any growth medium to be used in mine site restoration is that there are often poor physical properties (high bulk density, low porosity and low water holding capacity), combined with nutrient deficiencies, low organic matter levels and possibly heavy metal toxicity. This knowledge gap (concerning the parameters for the use of overburden as a growth medium) is addressed in Objective 1 and 3 and Hypotheses 1 and 3 respectively.

However, there is also the need in this thesis to determine how inorganic and organic amendments influence topsoil nutrient status and plant response. Topsoil is currently an accepted growth medium and it is often mandatory for restoration. The effect of amendments on the topsoil will allow comparisons to be made with the use of overburden as a growth medium. This represents a knowledge gap for the response at the Reefton as part of study site; and is addressed in Objective 2 and Hypothesis 2. It is also addressed Objective 1 and 3 and Hypotheses 1 and 3, respectively.

The second part of the review demonstrated that these chemical and physical limitations of overburden can be overcome. Weathering of the overburden can release nutrients and the addition of organic matter can aid weathering process and also mitigate against the potential toxicity effects of heavy metals which may also be released during the weathering process. Again, there is a knowledge gap regarding the effect of organic and inorganic amendments on the weathering process and consequent nutrient release and heavy metal mobility. This knowledge gap is addressed in Objective 4 and Hypotheses 4.
Thus, a sustainable approach to restoration of the post mining landscape involves creating the conditions where a viable growth medium can be created with the minimal amount of additional fertiliser inputs over a period of time. This growth medium will be a combination of material, organic material, and biological components (similar to a soil). This combination will have the capacity to release nutrients over the long-term, from both organic and inorganic sources. When combined with re-vegetation appropriate to the biogeographic area, a self-sustaining ecosystem can be recreated. Ideally, this growth medium will be a combination of material, organic material, and biological components (similar to a soil).
Chapter 3
Materials and Methods

3.1 Introduction

This chapter covers the materials used and analysis of the growth mediums and plant samples used in this thesis. Unless stated otherwise, all methods of analysis were taken from Blakemore et al. (1987).

3.2 Substrate

Three different growth mediums were used in this thesis. Bulk samples of the growth mediums were collected from the OceanaGold-Globe Progress mine site near Reefton, New Zealand: topsoil, fresh waste rock (overburden) and 56 year old waste rock at the time of collection (mullock). The topsoil was collected from the current mine topsoil stock pile site (Figure 3.1). The overburden was collected from the site of current mining exploration (Figure 3.2), and the mullock from the site where waste rock from mining in 1950 was dumped (Figure 3.3). The inorganic characteristics of these materials are summarised in Table 3.1.

The topsoils in the Globe Progress mine include podzols (acid soils with low base saturation) and are closely associated to the podzolised yellow-brown earths of the NZ genetic soil classification (Gibbs, 1980; Hewitt, 1992). The overburden from Reefton is categorized as a metasedimentary rock, consisting of sandstone and mudstone. The sandstone contains quartz, rock fragments, muscovite, and plagioclase and biotite (K (Mg, Fe)₃AlSi₃O₁₀) that were altered to albite and chlorite, respectively, during metamorphism by hydrothermal processes. Furthermore, the sandstone has been metamorphosed to K-mica, carbonate (dolomite, ankerite, ferroan magnesite and magnesian siderite), chlorite, pyrite and arsenopyrite (Christie & Brathwaite, 2003).
Figure 3.1 Topsoil pile used as a growth medium in the experiment (main picture). Air dried and un-sieved topsoil material (inset).

Figure 3.2 Overburden pile used as a growth medium in the experiment (main picture). Air dried and un-sieved overburden material (inset).
Figure 3.3 Mullock pile (dumped in 1950) used as a growth medium in the experiment (main picture). The mullock pile remains substantially un-vegetated over 56 years after it was dumped. Air dried and un-sieved mullock material (inset).

Table 3.1 The characteristics of the topsoil, overburden and mullock from the OceanaGold-GlobeProgress mine site near Reefton, New Zealand.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Topsoil</th>
<th>Overburden</th>
<th>Mullock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractable NH$_4^+$-N (mg kg$^{-1}$)</td>
<td>8.07</td>
<td>6.93</td>
<td>5.08</td>
</tr>
<tr>
<td>Extractable NO$_3^-$-N (mg kg$^{-1}$)</td>
<td>0.88</td>
<td>0.73</td>
<td>1.32</td>
</tr>
<tr>
<td>Extractable P (mg kg$^{-1}$)</td>
<td>0.62</td>
<td>0.14</td>
<td>0.07</td>
</tr>
<tr>
<td>Extractable S (mg kg$^{-1}$)</td>
<td>8.18</td>
<td>18.77</td>
<td>14.24</td>
</tr>
<tr>
<td>Exchangeable Ca (cmol$_c$ kg$^{-1}$)</td>
<td>0.94</td>
<td>0.18</td>
<td>1.89</td>
</tr>
<tr>
<td>Exchangeable Mg (cmol$_c$ kg$^{-1}$)</td>
<td>0.19</td>
<td>0.25</td>
<td>1.44</td>
</tr>
<tr>
<td>Exchangeable Na (cmol$_c$ kg$^{-1}$)</td>
<td>0.15</td>
<td>0.07</td>
<td>0.21</td>
</tr>
<tr>
<td>Exchangeable K (cmol$_c$ kg$^{-1}$)</td>
<td>0.04</td>
<td>0.00</td>
<td>0.29</td>
</tr>
<tr>
<td>CEC (cmol$_c$ kg$^{-1}$)</td>
<td>7.43</td>
<td>5.58</td>
<td>-</td>
</tr>
<tr>
<td>Extractable metals (µg kg$^{-1}$): As, Al, Mn, Zn, Cu, Cr, Cd, Pb, Ni, Fe</td>
<td>&lt; 0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>pH</td>
<td>4.8</td>
<td>4.3</td>
<td>7.3</td>
</tr>
<tr>
<td>pH buffering capacity (mmol kg soil pH$^{-1}$)</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EC (µS cm$^{-1}$)</td>
<td>12.6</td>
<td>98.5</td>
<td>18.3</td>
</tr>
<tr>
<td>Particle size distribution (%):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>1.49</td>
<td>1.51</td>
<td>2.57</td>
</tr>
<tr>
<td>Silt</td>
<td>62.02</td>
<td>56.60</td>
<td>62.50</td>
</tr>
<tr>
<td>Sand</td>
<td>34.49</td>
<td>41.90</td>
<td>34.92</td>
</tr>
</tbody>
</table>
3.2.1 Substrate analysis

The bulk sample of the substrate in the plastic bag was manually mixed thoroughly and a subsample of each substrate (approximately 200 g) for soil analysis was collected from each bulk sample and placed in separate plastic bags. The substrate subsamples were air dried in a drying cabinet with the temperature at 25°C for 96 hours. After air-drying the subsamples, they were ground manually to pass through a 2 mm sieve.

For quality control of the true concentration of substrate elements measured, Standard Reference Materials (SRM) 2710 Montana Soil (U.S Environmental Protection Agency (EPA)) was used to determine pH, extractable N, P, S and metal concentration.

3.2.1.1 pH

Ten g of each substrate sample and 25 ml of deionised water (1:2.5 soil/water ratio) were used to measure the substrate pH. The solutions were stirred and left to stabilise overnight. Before measuring the pH of the substrate samples, the pH meter (Seven easy; Mettler Toledo, Switzerland) was calibrated by using buffer solutions at pH 4 and pH 7. The pH meter probe was then dipped into the supernatant to determine the pH (Blakemore et al., 1987).

3.2.1.2 Electrical conductivity

To measure the substrate electrical conductivity (EC), 20 g of each substrate sample was mixed with 100 ml of deionised water. The mixtures were centrifuged at 1500 rpm for 5 minutes. Before measuring the EC of substrates, the EC meter [Mettler Toledo conductivity meter (µS cm⁻¹), (Seven easy; Mettler Toledo, Switzerland) was calibrated using a conductivity standard of 1413 µS cm⁻¹. The EC meter probe was dipped into the supernatant to determine the EC (Blakemore et al., 1987).

3.2.1.3 Extractable $NH_4^+$ and $NO_3^-$

Potassium chloride (KCl) 2M was used as the extractant to measure the concentration of extractable $NH_4^+$-N and $NO_3^-$-N in the substrate. The extractant was made by dissolving 298 g KCl with 2 L of deionised water. A sample of substrate (10 g) was combined with 100 ml of 2M KCl and shaken for 1 hour, before centrifuging at 2000 rpm for 10 minutes. Then, the solution was filtered through Whatman No. 41 filter paper. Flow Injection Analysis (FIA) was used to determine the concentration of $NH_4^+$-N on the substrate. The FIA used an Alpkem FS3000 twin channel analyser produced by
Alpkem; Texas-USA. Ammonium-N in the extracts was determined by using a gas diffusion membrane. Sodium hydroxide was added to increase the pH of the sample stream, in order to convert any NH$_4^+$ present into NH$_3$(g). The gas diffused through the membrane and into the indicator stream. The indicator stream changed colour (red to blue) with an increase of absorbance at 590nm. The extent of the colour change was proportional to the concentration of ammonium ions present in the sample (Blakemore et al., 1987). Nitrate-N was analysed by the initial reduction of nitrate-N using a cadmium reduction coil (OTCR-Open Tubular Cadmium Reactor). It was followed by the reaction of nitrite-N with sulphanilamide/NDE to form an azo dye compound. The intensity of this compound was determined spectrophotometrically at 540nm (Blakemore et al., 1987).

To calculate the extractable NH$_4^+$-N and nitrate NO$_3^-$-N, the following calculations were performed: $\text{mg N kg}^{-1} = (\mu g \text{ N/ml} \times 100 \text{ ml}) / \text{weight of sample (g)} = \mu g \text{ N g (soil)}^{-1} = \mu g \text{ N g}^{-1}$

### 3.2.1.4 Exchangeable cations (Ca, Na, Mg and K)

The single extraction silver thiourea (AgTu) analysis was used for measuring exchangeable cations and the effective cation exchange capacity (CEC) of the soil. This method was used in preference to the ammonium acetate method, because the AgTu complex ion presents a very efficient exchanger of cations on the clay surface, and cation exchange takes place at low ionic strength, similar to that of many soil solutions (Blakemore et al., 1987). The silver thiourea (0.01M) was used as a reagent to measure the concentration of cations in the substrate solution. The 0.01M silver thiourea solution was made by dissolving 150 g thiourea into 3 L of deionised water and dissolving 16.99 g silver nitrate into 5 L of deionised water. The silver nitrate solution was added slowly to the thiourea solution and continually stirred with a magnetic stirrer until dissolved. The solution was then quantitatively made up to 10 L with deionised water.

Then 35 ml of the 0.01M silver thiourea solution was combined with 0.70 g of substrate sample. The sample was shaken for 16 hours, before centrifuging at 2000rpm for 10 minutes. Next the supernatant was filtered through Whatman No. 40 filter paper (Blakemore et al., 1987). Soil cation concentrations were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES; Varian 720, Varian Inc, Melbourne, Australia) with an SPS-3 auto sampler and ultrasonic nebuliser.
To calculate the concentration of exchangeable cations, the following calculations were performed:

\[
\begin{align*}
    \text{Ca} & = (\mu g/ml – \text{blank}) \times 0.175 / \text{weight of sample (g)} = \text{cmol c kg}^{-1} \\
    \text{Mg} & = (\mu g/ml – \text{blank}) \times 0.29 / \text{weight of sample (g)} = \text{cmol c kg}^{-1} \\
    \text{K} & = (\mu g/ml – \text{blank}) \times 0.09 / \text{weight of sample (g)} = \text{cmol c kg}^{-1} \\
    \text{Na} & = (\mu g/ml – \text{blank}) \times 0.15 / \text{weight of sample (g)} = \text{cmol c kg}^{-1} \\
    \text{CEC} & = (1- A_g) \times 50 = \text{cmol c kg}^{-1}
\end{align*}
\]

### 3.2.1.5 Extractable P, S and metals

Calcium chloride \((\text{CaCl}_2)\) 0.1M was used as the reagent to measure extractable P, S and heavy metals concentrations in the substrates. The reagent was made by dissolving 1.4702 g of calcium chloride into 1 L of deionised water. A 10 g sample was mixed with 30 ml of 0.01M CaCl\(_2\). The samples were shaken for 2 hours, and centrifuged at 15,000 rpm for 10 minutes, before being filtered through Whatman No.52 filter paper (Blakemore et al., 1987). Determination of extractable P, S and metals was done by ICP-OES.

To calculate the extractable P, S and metals the following calculations was performed:

\[
\text{Concentration of extractable element} = (\mu g/ml \times 30) : \text{weight of sample (g)} = \mu g \text{ soil}^{-1} = \text{mg kg}^{-1}
\]

### 3.3 Plant

Three different plants were used in this study. Red beech and Wineberry were used as the test species in Chapter 4, 5 and 6. These species have been recommended to be used for restoration planting in the Grey-Inangahua region (Norton, 1991). The plants were obtained from a nursery (Headford Propagators, Waimate, Canterbury) at approximately 6 months old. Plant roots were gently separated from the potting mixing before planting bare-rooted into the experimental substrates. In addition, lupin also used as the test species in Chapter 7.

At harvesting, each plant (roots and shoots) was carefully separated from the growth substrate and washed gently with tap water to remove any attached particles. The plants were further cleaned by the following sequential steps; rinsed in tap water with 2% decon (Decon Laboratory Limited, England); rinsed in tap water only and then rinsed twice in deionised water. The root and shoots were put in a paper bag (one bag per
plant) and oven dried at 60 °C over a period of 72 hours before each plant was weighed to provide total dry weight.

### 3.3.1 Plant analysis

Each plant was separated from the soil and washed carefully with tap water to remove any attached particles. Then each plant was cleaned by the sequential steps (Chapter 3.3.1) then oven dried. After the plant samples from the glass house experiments were oven-dried and the total dry matter weight determined, the roots and the shoots were then separated. The plant shoots were finely ground using a mortar and pestle until they were able to pass through a 2-mm sieve. Furthermore, the plant shoots were used for analysis of elemental concentration of shoot N, P, S, Ca, Mg, Na, K and metals (As, Cd, Cr, Cu, Ni, Pb, Al, Fe, Mn, Zn) in order to determine treatment effects.

For quality control of the true concentration of shoot elements measured, Standard Reference Materials (SRM) 1573a of tomato leaves (Department of Commerce, USA) was used to determine shoot macronutrients, micronutrients, and metal concentration.

#### 3.3.1.1 Dry matter weight

The total dry matter weight (g pot⁻¹) = roots + shoots weight

#### 3.3.1.2 Shoot N

The Kjeldahl method (Blakemore et al., 1987) was used to determine the N concentration of the shoot material. Sodium metabisulphite and 3% salicylic acid (C₆H₄(OH).COOH) solution were used as reagents. The 3% salicylic acid was made by dissolving 20 g salicylic acid in 600 ml concentrated H₂SO₄.

Each plant sample (0.1 g) was placed in individual digestion tubes. The reagents were added and the tubes placed in a digest block. When the temperature of the digest block reached 200 °C, 1 g of sodium sulphate (Na₂SO₄) was added as a catalyst. The digestion process finished when the samples turned a clear colour (after 380 minutes). If the sample colour was not clear, the digestion process was re-run for a further 380 minutes. The digest solution was quantitatively transferred to a 50 ml volumetric flask and deionised water was used to make the solution up to the 50 ml mark (Blakemore et al., 1987). Flow Injection Analysis (FIA) was used to determine the concentration of total N in each sample. The FIA instrument was an Alpkem FS3000 twin channel
analysed (Texas, USA). N concentration was determined by using a gas diffusion membrane. Analytical grade sodium hydroxide was added to increase the pH of the sample stream, and any ammonium ions present were converted into ammonia gas. The gas diffused through the membrane into an indicator stream. The indicator stream changed colour (red to blue) with an increase of absorbance at 590nm. The extent of colour change was proportional to the concentration of ammonium ions present in the sample (Blake et al., 1987).

To calculate the total N in the shoot material, the following calculation was performed:

\[
\text{Total N in shoots (\%) = (\mu g N/ml \times 50 ml): 0.1 g of sample} = \frac{\mu g N \text{ g plant}^{-1}}{10}
\]

### Shoot Macronutrients, Micronutrients and Metals

Concentrated nitric acid (HNO₃) was used to digest the plant material to analyse for the concentrations of P, S, Ca, Na, Mg, K, and heavy metals (As, Cd, Cr, Pb, Cu, Ni, Zn, Al, Fe and Mn) in shoots. Thus, 0.50 g of shoot sample and 10 ml of concentrate nitric acid was placed in digest tubes and then in the digest block. The temperature of the digest block was set to reach 140°C within 120 minutes and allowed to cool overnight. The sample was filtered using Whatman No. 52 paper into a 25 ml volumetric flask. Double deionised water was used to quantitatively transfer the solution into the volumetric flask and to make up the solution to the 25 ml mark (Blake et al., 1987). The concentration of elements in the solution was determined by ICP-OES with an SPS-3 auto sampler and ultrasonic nebuliser.

To calculate the total macronutrients, micronutrients and metals, the following calculation was performed:

\[
\text{Total elemental concentration in mg kg}^{-1} = (\mu g \text{ element/ml-blank sample}) \times 25 \text{ ml/weight of sample (g)}
\]


3.4 Statistical analysis

GenStat Release 10.1 (© 2007, Lawes Agricultural Trust, Rothamsted Experimental Station) was used for statistical analyses. Analysis of variance (ANOVA) was used to observe the effect (response variable) of amendment, substrate, plant and their interactions. It was assumed that the variables were taken from a normally distributed population. Least significant difference (LSD) at the 5% level was used to compare adjacent means within the treatment.
Chapter 4
Plant Growth and Nutrients Status of Amended Topsoil, Overburden and Mullock Materials

4.1 Introduction

After disturbance by mining, soil and any materials remaining on the site become a critical component of the early stages of reconstructing the original ecosystem that occurred on site before mining (Bradshaw, 1987; Younger, 2003). Topsoil is an ideal medium for growing plants. However, topsoil is a scarce resource and, as a result, mining waste remaining after mineral extraction may be the only available material to use as a growth substrate. However mining wastes often have a number of inherent physical and inorganic limitations. In the past, when environmental awareness may have been less, mining areas were often abandoned after mine-closure without any re-vegetation practices. As a result much historic overburden remains unrestored on historic mining site.

The difficulty of establishing plants on unmodified fresh and/or old overburden reflects the necessity for correct site preparation techniques to overcome such factors as poor drainage and substrate infertility (Langer et al., 1999). Whether fresh or historic, mine waste overburden is often a hostile growing environment for plants because of the presence of many growth limiting factors, e.g. high levels of heavy metals, macronutrient deficiencies and poor substrate structure (Bradshaw, 1997a; Tordoff et al., 2000). Therefore, mining wastes need to be manipulated during restoration in order to produce viable growing media for vegetation.

In the early stage of re-vegetation, application of N to mine soils is common, whether in the form of urea (CO(NH$_2$)$_2$), NH$_4^+$ or NO$_3^-$ (Lyle, 1987). This method is designed to meet the nutrient requirement of plants; however it must be added frequently, and it is costly (Lyle, 1987). Using organic amendments, such as biosolids is often recommended. The use of biosolids have been encouraged for use in land application,
due to them being a source of organic matter, a pool of slow release essential nutrients (including N and P), and of microorganisms (Abbott et al., 2001; Bradshaw, 2000; Magesan & Wang, 2003) and to improve the ability of soil to adsorb heavy metals, thus limiting their bioavailability (Bolan & Duraisamy, 2003). Biosolids can thus play an important role in fulfilling plant nutrition requirements (Maguire et al., 2000). However, some researchers are concerned that the sometimes heavy metal concentration in biosolids may hamper plant growth (Bradshaw, 1997a; Magesan & Wang, 2003; McLaren et al., 2007; Speir et al., 2003). It has been suggested that this problem can be alleviated through liming or by increasing the substrate pH (Bradshaw, 1997a; Speir et al., 2003).

Addition of either biosolids or other organic/inorganic amendments to the growth medium may improve the inorganic properties of the growth medium in former gold mine sites. However, different growth mediums have different characteristics and thus will have different responses to the organic and inorganic amendments. As a consequence the effect of organic and/or inorganic amendments could possibly worsen the inorganic properties of substrates. Therefore, it is necessary to investigate the effectiveness of organic amendments compared to inorganic amendments on the inorganic properties of soil and fresh and/or old overburden materials from mine sites for the proposed post-mining land uses. This essential information can then be used to help determine the most effective strategy for reconstructing the appropriate growth medium for mine sites (Parker, 1991).

The specific objective of this experiment was to characterise the nutrient status of growth medium and plants after the application of a range of soil amendments.

### 4.2 Materials and Methods

Three growth mediums were collected for characterisation from the OceanaGold Globe-Progress mine site near Reefton, New Zealand: topsoil, fresh waste rock (overburden) and old waste rock approximately 56 years old (mullock) (Chapter 3 section 3.2). The growth mediums were air dried. The overburden was crushed manually; all other substrates had a medium to fine tilth and did not require crushing. Each growth medium was passed through a 1.5 cm mesh sieve before placing in pots. The pot size used in this experiment had a diameter of 17 cm and 15.5 cm high. Inside the pot was covered by a
plastic bag and filled with the substrate. Each pot contained 2.5 kg of air-dry topsoil, 3.5 kg of air-dry overburden or 3.5 kg of air-dry mullock.

Red Beech and Wineberry were used as the test species for this experiment. The plants were obtained from a nursery (Headford Propagators, Waimate, Canterbury) at approximately 6 months old. Plant roots were gently separated from the potting mixing before planting bare-rooted into the experimental substrates.

Three different organic amendments were used in the experiment; biosolids, sawdust, and lupin as a green manure, and N fertiliser as an inorganic amendment. The biosolids were collected three days before use from the Christchurch City Council waste water treatment plant at Bromley, Christchurch and kept in sealed containers at 4°C until being applied to the pots. The biosolids were obtained from the belt-press at the end of the waste treatment process and contained approximately 25% solids. The biosolid characteristics are summarised in Table 4.1. The total metal concentrations were taken from McLaren et al. (2007); the biosolids used in this study were collected from the same location. Overall, the biosolids had a neutral pH, high EC, contained noticeable quantities of P, S, NH4+-N; metal concentrations were considerably less than the permissible limits (category B) in soils according to NZWWA (2003). The biosolids were applied at two rates: 20 t ha⁻¹ (45.4 g pot⁻¹) and 40 t ha⁻¹(90.8 g pot⁻¹), the water content was 80.33%. The sawdust was untreated sawdust from a commercial retail outlet (Parkhouse-Landscape supplies, Christchurch, New Zealand) with particle size <2 mm. The sawdust was applied at rates of 50 and 100 t ha⁻¹, and the amount of sawdust added was 113.5 g pot⁻¹ and 227 g pot⁻¹, respectively. The N source was analytical reagent grade ammonium nitrate (NH₄NO₃). N was applied at the rate of 150 kg N ha⁻¹ (1.0 g pot⁻¹); and 300 kg N ha⁻¹ (2.0 g pot⁻¹). Lupin plants for green manure were collected from Lincoln University experimental plots (Iversen fields) on the day of application to the pots. The roots were washed by tap water and the whole plant (shoots and roots) chopped into 1 cm lengths, the reason being that 1 cm lengths would fit in the pot size. Lupin as a green manure was added at a rate of 20 g pot⁻¹ (equivalent to 8.81 kg ha⁻¹). For each treatment, the amendments and the growing medium were thoroughly mixed before being placed in each pot (Refer to Appendix A for application rate calculations).
Table 4.1 The inorganic analyses on dry weight basis of the biosolid used in this experiment.

<table>
<thead>
<tr>
<th>Element</th>
<th>Biosolid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total C (%)</td>
<td>36</td>
</tr>
<tr>
<td>Extractable NH₄⁺-N (mg kg⁻¹)</td>
<td>4180</td>
</tr>
<tr>
<td>Extractable NO₃⁻-N (mg kg⁻¹)</td>
<td>5</td>
</tr>
<tr>
<td>Extractable P (mg kg⁻¹)</td>
<td>256</td>
</tr>
<tr>
<td>Extractable S (mg kg⁻¹)</td>
<td>1398</td>
</tr>
<tr>
<td>Exchangeable Ca (cmolₑ kg⁻¹)</td>
<td>17</td>
</tr>
<tr>
<td>Exchangeable Mg (cmolₑ kg⁻¹)</td>
<td>3</td>
</tr>
<tr>
<td>Exchangeable Na (cmolₑ kg⁻¹)</td>
<td>2</td>
</tr>
<tr>
<td>Exchangeable K (cmolₑ kg⁻¹)</td>
<td>2</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
</tr>
<tr>
<td>EC (µS cm⁻¹)</td>
<td>1633</td>
</tr>
<tr>
<td>CEC (cmolₑ kg⁻¹)</td>
<td>32</td>
</tr>
<tr>
<td>Total metals (mg kg⁻¹)*:</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>6195</td>
</tr>
<tr>
<td>As</td>
<td>4.33</td>
</tr>
<tr>
<td>Cd</td>
<td>1.836</td>
</tr>
<tr>
<td>Cr</td>
<td>370</td>
</tr>
<tr>
<td>Cu</td>
<td>263</td>
</tr>
<tr>
<td>Fe</td>
<td>15706</td>
</tr>
<tr>
<td>Mn</td>
<td>325</td>
</tr>
<tr>
<td>Ni</td>
<td>29</td>
</tr>
<tr>
<td>Zn</td>
<td>1282</td>
</tr>
<tr>
<td>Pb</td>
<td>50</td>
</tr>
</tbody>
</table>

*McLaren et al. (2007).

The pot trials were conducted in the glass houses of Lincoln University for 16 weeks (September 2006 to January 2007), with a temperature range of 14-27 °C. The experimental design of this experiment is summarised in Table 4.2. The trial was set up as a randomised block design (3 substrates x 2 plant species x 8 soil amendments = 48 pots) with four replicates of each treatment. Blocks were positioned across the glasshouse so that each replicate equalled a block (i.e. all replicate 1= block one, all replicate 2= block two, etc.). The treatments in each block were re-randomized every month. Plants were watered every 2-3 days.

Table 4.2 Experimental treatments

<table>
<thead>
<tr>
<th>Treatment group</th>
<th>Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant</td>
<td>Red beech (<em>Nothofagus fusca</em>)-tree species</td>
</tr>
<tr>
<td></td>
<td>Wineberry (<em>Aristotelia serrata</em>)- shrub species</td>
</tr>
<tr>
<td>Substrate</td>
<td>Topsoil</td>
</tr>
<tr>
<td></td>
<td>Overburden</td>
</tr>
<tr>
<td></td>
<td>Mullock (&gt; 50 year old overburden)</td>
</tr>
<tr>
<td>Soil Amendments</td>
<td>Control (C)</td>
</tr>
<tr>
<td></td>
<td>Biosolid (20 and 40 t ha⁻¹) (B1 and B2)</td>
</tr>
<tr>
<td></td>
<td>Sawdust (50 and 100 t ha⁻¹) (S1 and S2)</td>
</tr>
<tr>
<td></td>
<td>N (150 and 300 kg ha⁻¹) (N1 and N2)</td>
</tr>
<tr>
<td></td>
<td>Lupin; <em>Lupinus angustifolius</em> (8.81 kg ha⁻¹) (L)</td>
</tr>
</tbody>
</table>
The experiment was harvested after 120 days. Each plant was separated from the soil and washed carefully with tap water to remove any attached particles. Then each plant was cleaned by the sequential steps (Chapter 3.3.1). The substrate samples were collected after harvesting the plants. A sufficient amount of substrate (200 g) for soil analysis was collected from each pot and placed in plastic bags (Chapter 3.2.1).

4.3 Analyses

Two sets of analysis were carried out: substrate analysis (Chapter 3 section 3.2.1) and plant analysis (Chapter 3 section 3.3.1).

4.4 Results

In this section, results from the substrate analysis (topsoil, overburden and mullock) as well as plant shoot analysis are presented. The substrate and plant results are also presented in Appendix E.

4.4.1 Substrate

The result of analysis of variance (ANOVA) for the main effect of the amendments, plants, and substrate on soil characteristics and their interaction is presented in Table 4.3. To test the hypothesis, the results presented here are based on the interaction results between different amendments, plants and substrates (AxPxS). Thus, there was a significant interaction between amendment, plant and substrate on the values of EC, extractable NH$_4^+$-N, NO$_3^-$-N, P, S, exchangeable cations (Mg, Ca and K) and CEC.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>pH</th>
<th>EC</th>
<th>NH$_4^+$-N</th>
<th>NO$_3^-$-N</th>
<th>P</th>
<th>S</th>
<th>CEC</th>
<th>Ca</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>μS cm$^{-1}$</td>
<td>Extractable (mg kg$^{-1}$)</td>
<td>Exchangeable (cmol c kg$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amendment (A)</td>
<td>7</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>Plant (P)</td>
<td>1</td>
<td>ns</td>
<td>***</td>
<td>ns</td>
<td>ns</td>
<td>***</td>
<td>ns</td>
<td>ns</td>
<td>***</td>
<td>***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate (S)</td>
<td>2</td>
<td>***</td>
<td>***</td>
<td>*</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A x P</td>
<td>7</td>
<td>*</td>
<td>***</td>
<td>*</td>
<td>*</td>
<td>ns</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A x S</td>
<td>14</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P x S</td>
<td>2</td>
<td>*</td>
<td>***</td>
<td>ns</td>
<td>***</td>
<td>*</td>
<td>***</td>
<td>ns</td>
<td>***</td>
<td>***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A x P x S</td>
<td>13</td>
<td>ns</td>
<td>***</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>***</td>
<td>***</td>
<td>ns</td>
<td>***</td>
<td>***</td>
<td></td>
</tr>
</tbody>
</table>

Note: *** P< 0.001; ** 0.001 ≤ P < 0.01
* 0.01 ≤ P < 0.05 level; ns = non significant difference (P ≥ 0.05)
4.4.1.1 pH

There was no significant effect between amendment, plant and substrate on the pH level ($P>0.05$) (Table 4.3, Figure 4.1 and 4.2).

Figure 4.1 pH of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown ($n = 4$ for each treatment). There was no significant difference for the pH on the topsoil (a), overburden (b), and mullock (c) ($P>0.05$).
Figure 4.2 pH of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the pH on the topsoil (a), overburden (b), and mullock (c) (\(P>0.05\)).

4.4.1.2 **Electrical conductivity**

There was a significant effect (\(P<0.001\)) between amendment, plant and substrate on the EC level (Table 4.3). Organic amendments, particularly biosolid at both rates and N amendments at both rates increased the EC level compared to the control in all the substrates planted with either Red beech or Wineberry. In contrast, application of sawdust at both rates reduced the EC level the most compared to the control in all amendments (Figure 4.3 and 4.4). Notably in overburden which was planted with Red beech, both organic and inorganic amendments reduced the EC level compared to the control (Figure 4.6b).
In the topsoil, at the high application rate of N (300 kg ha\(^{-1}\)) both species had an affect on the EC, but to different degrees. At the same rate (300 kg ha\(^{-1}\)), the EC of substrates containing Red beech increased from below 50 to around 200 µS cm\(^{-1}\) (Figure 4.3a), while for Wineberry EC increased from below 50 to around 1100 µS cm\(^{-1}\) (Figure 4.4a).

All the amendments reduced the EC in the overburden planted with Red beech; application of sawdust at both rates reduced the EC the most. In contrast, in the Wineberry planted on the overburden, the level was quite similar.

Both species had a similar to effect on the EC level in the mullock (Figure 4.3c and 4.4c). Application of N at the high rate increased the EC level the most, followed by application of biosolid at the high rate. Application of sawdust at low rate reduced the EC level the most.

![Figure 4.3 Electrical conductivities of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).](image-url)
Figure 4.4 Electrical conductivities of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).

### 4.4.1.3 Extractable NH\(_4^+\)-N and NO\(_3^-\)-N

There was a significant effect between amendment, plant and substrate on the concentration of extractable NH\(_4^+\)-N \((P<0.01)\) and NO\(_3^-\)-N \((P<0.05)\) (Table 4.3). Among the amendments, applications of N at the high rate increased the amount of extractable NH\(_4^+\)-N in the topsoil (Figure 4.5a and 4.6a) and overburden (Figure 4.5b and 4.6b) the most, followed by application of biosolids. Both organic and inorganic amendments had little effect on the amount of extractable NH\(_4^+\)-N in the mullock (Figure 4.5c and 4.6c).

In the topsoil planted with Red beech, the high N treatment increased the amount of extractable NH\(_4^+\)-N from 6.8 to 48.4 mg kg\(^{-1}\) (Figure 4.5a; Appendix E, Table E1), whereas for the Wineberry treatments extractable NH\(_4^+\)-N increased from 8.7 to 73.9 mg kg\(^{-1}\) (Figure 4.6a; Appendix E, Table E2) compared to the control treatment. In the
overburden and mullock planted with Red beech (Figure 4.5) and Wineberry (figure 4.6), application of high N had similar result.

Among the different organic amendments, biosolid increased the amount of extractable $\text{NH}_4^+$-N in all substrates by different amounts. In topsoil planted with Red beech, the low rate of biosolids application resulted in increased extractable $\text{NH}_4^+$-N from 6.8 to 28.6 mg kg$^{-1}$ (Figure 4.5a, Appendix E, Table E1), whereas at the same application rate, topsoil planted with Wineberry had an increase in the amount of extractable $\text{NH}_4^+$-N from 8.7 to 11.2 mg kg$^{-1}$ compared to the control (Figure 4.6a; Appendix E, Table E2).

In the overburden planted with Red beech, the low rate of biosolid application resulted in an increase in the extractable $\text{NH}_4^+$-N from 9.1 to 51.3 mg kg$^{-1}$ (Figure 4.5b, Appendix E, Table E1), whereas for overburden planted with Wineberry the extractable
NH$_4^+$-N increased from 5.9 in the control to 13.7 mg kg$^{-1}$ in the low biosolid treatment (Figure 4.6b, Appendix E, Table E2).

Figure 4.6 Extractable NH$_4^+$-N of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment).

Among the amendments, applications of N at the high rate increased the amount of extractable NO$_3^-$-N in the topsoil (Figure 4.4a and 4.5a), overburden (Figure 4.7b and 4.8b) and mullock (Figure 4.7c and 4.8c) the most, followed by application of biosolid at both rates.

In the topsoil that was planted by Red beech, application of high N increased the amount of extractable NO$_3^-$-N from 1.3 to 175.5 mg kg$^{-1}$ (Figure 4.7a, Appendix E, Table E), whereas Wineberry effected an increase in the amount of extractable NO$_3^-$-N from 0.7 to 313.3 mg kg$^{-1}$ (Figure 4.8a). In the mullock that was planted by Red beech, application of high N increased the amount of extractable NO$_3^-$-N from 0.9 to 131.3 mg
-1 (Figure 4.7c), whereas at the same rate of N application the Wineberry effected an increase in the amount of extractable NO₃-N from 1.4 to around 235.2 mg kg⁻¹ (Figure 4.8c, Appendix E, Table E2).

Figure 4.7 Extractable NO₃-N of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (Nothofagus fusca). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05.
Figure 4.8 Extractable NO₃-N of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05.

### 4.4.1.4 Extractable P

There was a significant interaction (P<0.05) between amendment, plant and substrate on the concentration of extractable P (Table 4.3). The level of extractable P in the topsoil was higher than in the overburden or mullock, with concentrations of 0.59; 0.18; 0.04 mg kg⁻¹, respectively (control) (Figure 4.9 and 4.1; Appendix E, Table E1). The amendments had different effects in the different substrates; moreover plant species affected the level of extractable P in the substrate solution.

In the topsoil planted with Red beech or Wineberry, application of sawdust and biosolid at the high rate increased the extractable P (Figure 4.9a and 4.10b). However, application of sawdust at the high rate in Red beech increased the extractable P from 0.59 to 1.55 mg kg⁻¹ (Figure 4.9a; Appendix E, Table E1), whilst the Wineberry increased the extractable P from 0.65 to 1.08 mg kg⁻¹ (Figure 4.10a; Appendix E, Table
E2). This indicated that Red beech increased the amount of extractable P three times compared to the control; while the Wineberry doubled the extractable P, compared to the control.

![Figure 4.9 Extractable P of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P < 0.05\).

A similar trend to the observation in the topsoil occurred with the overburden. Application of biosolids at the high rate in the overburden planted with Red beech increased the amount of extractable P from 0.18 in the control to 1.40 mg kg\(^{-1}\) for the low biosolids rate (Figure 4.9b, Appendix E, Table E1), whilst in topsoil planted with Wineberry the extractable P increased from 0.16 to 1.00 mg kg\(^{-1}\) (Figure 4.103b, Appendix E, Table E2).

In the mullock planted with Red beech, application of biosolids at the low rate increased the extractable P the most of any amendment compared with the control (Figure 4.9c).
In contrast, with the Wineberry, application of biosolids at the high rate increased the extractable P the most of all the amendments tested (Figure 4.10c).

Figure 4.10 Extractable P of a pot trial containing (a) topsoil, (b) overburden, and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$.

### 4.4.1.5 Extractable S

There was a significant effect ($P<0.05$) between amendment, plant and substrate on the concentration of extractable S (Table 4.3). The amendments had different effect on the different substrates; moreover plant species affected the level of extractable S in the substrate solution.
In topsoil planted with Red beech, the application of biosolids at the low rate increased the extractable S the most of any amendment compared to the control (Figure 4.11a). Whilst, for the topsoil planted with Wineberry the application of biosolids at the high rate increased the extractable S the most of any amendment compared to the control (Figure 4.12a) with the concentration ranging from 10 to 100 mg kg$^{-1}$ (Appendix E, Table E1).

In the overburden planted with Red beech, the application of biosolids at the low rate increased the extractable S the most of any amendment compared with the control (Figure 4.11b). However, in the overburden planted with Wineberry, application of lupin increased the extractable S the most of any amendment compared with the control (Figure 4.12b).
In the mullock planted either with Red beech or wineberry, application of biosolids at the high rate increased the extractable S the most of any amendment compared to the control (Figure 4.11c and 4.12c).

Figure 4.12 Extractable S of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (\(n = 4\) for each treatment).

Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).

### 4.4.1.6 Exchangeable cations

There was a significant effect \((P<0.001)\) between amendment, plant and substrate on exchangeable Ca, Mg and K concentrations (Table 4.3)

**Exchangeable Ca:** Among the substrates, the mullock had a higher level of extractable Ca than topsoil and overburden, with concentrations of 2.28, 0.98 and 0.67 cmol\(_c\) kg\(^{-1}\), respectively (control) (Figure 4.13 and 4.14, Appendix E, Table E1). Among the amendments, organic amendments, particularly application of biosolids at the high rate (40 t ha\(^{-1}\)) increased the exchangeable Ca in the topsoil and overburden the most, regardless of whether it was planted with the Red beech (Figure 4.13a and 4.13b) or
Wineberry (Figure 4.14a and 4.14b). Whilst application of biosolids at the low rate (20 t ha⁻¹) increased the exchangeable Ca in the mullock (Figure 4.13c and 4.14c) the most, there was no effect of exchangeable Ca in the substrate solution between the two species.

The N amendment reduced the exchangeable Ca in the all substrates, and there was no difference between the plant species in enhancing the amount of exchangeable Ca from the substrates (Figure 4.13).

Figure 4.13 Exchangeable Ca of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05.
Figure 4.14 Exchangeable Ca of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P < 0.05\).
**Exchangeable Na:** There was no significant effect between amendment, plant and substrate on the exchangeable Na concentration (\(P>0.05\)) (Table 4.3) (Figure 4.15 and 4.16).

![Graph showing exchangeable Na concentrations](image_url)

Figure 4.15 Exchangeable Na of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (\(n = 4\) for each treatment). There was no significant difference for the extractable Na on the topsoil (a), overburden (b), and mullock (c) (\(P>0.05\)).
Exchangeable Na: The mullock had a higher level of extractable Mg than topsoil and overburden (Figure 4.17 and 4.18). In the topsoil, biosolids increased the exchangeable Mg. In the overburden, organic amendments had no effect on the exchangeable Mg. In the mullock, the high N application rate increased the amount of exchangeable Mg in the substrate (Figure 4.17c and 4.18c).
Figure 4.17 Exchangeable Mg of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).
Figure 4.18 Exchangeable Mg of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05.

**Exchangeable K**: Again, in a similar pattern to that observed with the exchangeable Ca and Mg, the mullock had a higher level of exchangeable K than both the topsoil and overburden, with concentrations of 0.31; 0.06; and 0.01 cmolc kg⁻¹ (Figure 4.19 and 4.20; Appendix E, Table E1). The amendments had different effects in the different substrates; moreover plant species affected the level of exchangeable K in the substrate solution.

In the topsoil planted with Red beech, the low rate of biosolids, N, and lupin increased the amount of exchangeable K in the solution. Application of sawdust at both rates reduced the exchangeable K (Figure 4.19a). In the topsoil planted with Wineberry, there was no amendments effect on extractable K for topsoil planted with Wineberry (Figure 4.20a).
Figure 4.19 Exchangeable K of a pot trial containing (a) topsoil, (b) overburden, and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$.

In the overburden planted with Red beech, application of lupin and sawdust at the high rate increased the exchangeable K. There was no effect of other amendments on the level of exchangeable K (Figure 4.19b). In the overburden planted with Wineberry, all organic amendments increased the amount of exchangeable K in solution, but there was no difference effect among them (Figure 4.20b).

In mullock planted with Red beech and Wineberry, there was no effect of any amendment on the amount of exchangeable K in the substrate (Figure 4.19c and 4.20c).
Figure 4.20 Exchangeable K of a pot trial containing (a) topsoil, (b) overburden, and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at *P* < 0.05.

### 4.4.1.7 Cation exchange capacity

There was a significant interaction (*P* < 0.001) between amendment, plant and substrate on the substrate CEC (Table 4.3). The CEC of the topsoil was higher than in the overburden and mullock. All substrates had a similar pattern in response to the amendments regardless of whether the substrate was planted with Red beech or Wineberry.

In the topsoil, application of sawdust at both rates increased the CEC the most, whilst application of N reduced the CEC of the substrate (Figure 4.21a and 4.22a). In the overburden, there was no effect of the amendments on the CEC level, but application of the high rate of N decreased the CEC of the substrate (Figure 4.21b and 4.22b). In the mullock, application of lupin, sawdust, and N increased the CEC the most, whilst the biosolid was no effect on the CEC level (Figure 4.21c and 4.22c).
Figure 4.21 CEC of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (Nothofagus fusca). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).
Figure 4.22 CEC of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. 
4.4.2 Plant

To test the hypothesis that plant biomass production and nutritional status will be improved by the addition of organic and inorganic amendments, the results presented here are based on the interaction results between the different amendments, plant and substrate (AxPxS). As a result, there was a significant interaction between the amendment, plant and substrate to change the concentration of shoot N, P, S, Ca, Mg and K, but there was no significant effect of amendments on the values of dry matter weight and shoot Na (Table 4.4).

Table 4.4 ANOVA main effects of amendment, plant and substrate on plant characteristics.

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<td>*** *** *** *** *** *** ***</td>
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<tr>
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<td>*** *** ns *** *** ***</td>
<td>*** *** *** *** *** *** ***</td>
</tr>
<tr>
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<td>*** *** * *** *** ***</td>
<td>*** *** *** *** *** *** ***</td>
</tr>
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<td>** ns *** *** *** ***</td>
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<td>* ns *** *** *** ***</td>
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<tr>
<td>A x P x S</td>
<td>13</td>
<td>ns * *** *** *** ns</td>
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</table>

Note: *** P< 0.001; ** 0.001≤P< 0.01; * 0.01≤P< 0.05 level; ns = non significant difference (P≥0.05)

4.4.2.1 Biomass

There was no significant effect between amendments, plant and substrate on the dry weight of the plant (P>0.05, Table 4.4). No Wineberry survived the high N application rate in the mullock (Figure 4.24c), therefore no shoot analysis results have been presented for this treatment.
Figure 4.23 Dry matter weight of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the total dry matter on the topsoil (a), overburden (b), and mullock (c) (P>0.05).
Figure 4.24 Dry matter weight of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g plant\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). All mullock plants in N2 treatment died and were not analysed. Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the total dry matter on the topsoil (a), overburden (b), and mullock (c) (P>0.05).

4.4.2.2 Shoot N

There was significant effect between amendments, plant and substrate on the shoot N concentration of the plant (P<0.05, Table 4.4). The amendments had a similar effect in all of the substrates; plant species affected the level of shoot N in the substrate solution, particularly in the overburden.

The concentration of N in shoots (control) from plants grown in the topsoil, overburden and mullock were all similar: being in the range of 0.5-1.0 % (Figure 4.25 and 4.26; Appendix E, Table E3 and E5). For both species tested in the topsoil and mullock, shoot N concentrations increased the most of all amendments by the application of N at high rate, followed by the application of biosolids at the high rate when compared with
the control (Figure 4.25 and 4.26). In comparison, the application of sawdust at both rates decreased the shoot N concentration for both species.

In the overburden, application of N at the high rate increased the shoot N of Red beech (wineberry died at the high N rate), followed by the application of biosolids at low rate (Figure 4.25b and 4.26b). In the same treatment (300 kg N ha⁻¹), the shoot N of Wineberry increased from 0.57 to 4.38% (Appendix E, Table E5), whereas shoot N of Red beech increased from 0.75 to 2.81% (Appendix E, Table E3).

Figure 4.25 Shoot N concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \( P<0.05 \).
Figure 4.26 Shoot N concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \( P<0.05 \). *All mullock plants in N2 treatment died and were not analysed.*

### 4.4.2.3 Shoot P

There was significant effect between amendments, plant and substrate on the shoot P concentration of the plant (\( P<0.01 \), Table 4.4).

In general, the treatment that reduced the shoot P concentration the most in both species and in all the substrates (topsoil, overburden and mullock) compared to the control was the N treatment (Figure 4.27 and 4.28). However the one exception to this was the concentration of P in Wineberry shoots grown in mullock amended with high and low amounts of sawdust. In both these sawdust treatments the concentration of shoot P was greater than in the control (Figure 4.27c).
Figure 4.27 Shoot P concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P < 0.05\).
There was significant effect between amendments, plant and substrate on the shoot S concentration of the plant \((P<0.001, \text{ Table 4.4})\). The shoot S concentration for Red Beech and Wineberry grown in unamended growth substrate was highest in the overburden compared to the topsoil and mullock (Figure 4.29 and 4.30).

The plant species had different effects on the concentration of shoot S (Figure 4.29 and 4.30). For example, application of biosolids at the high rate in the topsoil increased the shoot S concentration of Red beech from 357 to 756 mg kg\(^{-1}\) (Figure 4.29a; Appendix E, Table E3), whereas in the same substrate and for the same treatment, the shoot S concentration of Wineberry increased from 959 to 1809 mg kg\(^{-1}\) (Figure 4.30a; Appendix E, Table E5). The same pattern also can be seen for application of biosolids at...
the low rate in the overburden (Figure 4.29b and 4.30b), which resulted in an increase of shoot S for Wineberry that was higher than Red beech. In addition, the application of biosolids at the high rate in the mullock increased the shoot S of Red beech from 588 to 817 mg kg$^{-1}$ (Figure 4.29c; Appendix E, Table E3), whereas in the same substrate and the same treatment the shoot S of Wineberry increased from 1037 to 2449 mg kg$^{-1}$ (Figure 4.30c; Appendix E, Table E5).

Figure 4.29 Shoot S concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. 

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Figure 4.30 Shoot S concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. *All mullock plants in N2 treatment died and were not analysed.

### 4.4.2.5 Shoot Ca

There was significant effect between amendments, plant and substrate on the shoot Ca concentration of the plant ($P<0.01$, Table 4.4). Shoot Ca concentration was affected by the amendments applied to the different substrates and the plant species (Figure 4.31 and 4.32). In the topsoil, all amendments reduced the shoot Ca concentration of Red beech (Figure 4.31a). In contrast, application of all amendments increased the shoot Ca concentration of Wineberry (Figure 4.32a). A similar pattern occurred in the overburden, where application of all amendments reduced the shoot Ca of Red beech (Figure 4.31b), but increased the shoot Ca of Wineberry (Figure 4.32b).

In mullock the amendments showed a different pattern of effects on shoot Ca concentration. The highest increase in shoot Ca concentration compared to the control...
for plants grown on mullock was for Red beech grown in mullock amended with sawdust at the high rate (Figure 4.31c) and for Wineberry grown in mullock amended with N at the low rate (Figure 4.32c).

Figure 4.31 Shoot Ca concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. 
Shoot Ca concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\). *All mullock plants in N2 treatment died and were not analysed.*

**4.4.2.6 Shoot Mg**

There was significant effect between amendments, plant and substrate on the shoot Mg concentration of the plant (\(P<0.001\), Table 4.4).

Amendments applied to the different substrates and the plant species grown in the substrates affected the shoot Mg concentration (Figure 4.33 and 4.34). None of the amendments applied to the topsoil had an effect on the shoot Mg concentration of Red beech (Figure 4.33a), but a number of amendments had an effect on the shoot Mg concentration of Wineberry compared to the control (4.34a).

Of the organic amendments in the overburden, the application of biosolids at the low rate was the only treatment that increased the shoot Mg of Red beech (Figure 4.33b). In
addition, the N fertilizer also increased the shoot Mg concentration of Red beech, but there was no significant difference between these treatments. In comparison, Wineberry grown in overburden had greater concentrations of shoot Mg when compared to the same amendment treatments for Red beech. For example, application of N at the low rate increased the shoot Mg of Red beech from 16 to 18 mg kg\(^{-1}\) (Figure 4.33b; Appendix E, Table E3), whilst shoot Mg of Wineberry increased from 13 to 27 mg kg\(^{-1}\) (Figure 4.34b; Appendix E, Table E5).

![Figure 4.33 Shoot Mg concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).
Figure 4.34 Shoot Mg concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05.

*All mullock plants in N2 treatment died and were not analysed.*
4.4.2.7 **Shoot Na**

There was no significant effect between amendments, plant and substrate on the shoot Na concentration \((P>0.05)\) (Table 4.4) (Figure 4.35 and 4.36).

![Graphs showing Shoot Na concentration](image)

**Figure 4.35** Shoot Na concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown \((n = 4\) for each treatment). There was no significant difference for the shoot Na on the topsoil (a), overburden (b), and mullock (c) \((P>0.05)\).
Figure 4.36 Shoot Na concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (Aristotelia serrata). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. All mullock plants in N2 treatment died and were not analysed. Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the shoot Na on the topsoil (a), overburden (b), and mullock (c) (P>0.05).

4.4.2.8 Shoot K

There was a significant effect between amendments, plant and substrate on the shoot K concentration of the plant (P<0.001, Table 4.4).

In the control treatments, the concentration of K in Wineberry shoots was higher than in the Red beech shoots across all growth substrates (Figure 4.37 and 4.38). This indicates that plant species had an effect on the concentration of shoot K. In a similar manner to the shoot Ca and Mg results, amendments applied to the different substrates and the plant species grown in these substrates affected the concentration of shoot K (Figure 4.37 and 4.38).
All amendments applied to the topsoil, overburden and mullock reduced the concentration of shoot K of Wineberry compared to the control treatment (Figure 4.38). In comparison, the shoot K concentration in Red beech was increased by the sawdust amendment at the low rate in the topsoil (Figure 4.37a), by application of N at both rates in the overburden (Figure 4.37b), and by lupin in the mullock (Figure 4.37c).

Figure 4.37 Shoot K concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).
Figure 4.38 Shoot K concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments; (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. *All mullock plants in N2 treatment died and were not analysed.

### 4.4.2.9 Shoot heavy metals

To test the hypothesis that the nutritional status of plants would be improved by the addition of organic and inorganic amendments, the results presented here are based on the interaction results between the different amendments, plants and substrates (AxPxS) (Table 4.5). Thus, there was a significant interaction between amendment, plant and substrate resulting in a change in concentration of shoot concentrations of Cu, Cd, As, Ni, Pb, Mn, Zn and Fe (Table 4.5).
Table 4.5 ANOVA main effects of amendment, plant and substrate on shoot metal characteristics.

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<th>Cd</th>
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<th>Ni</th>
<th>Pb</th>
<th>Cr</th>
<th>Mn</th>
<th>Zn</th>
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<td>***</td>
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<tr>
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<td>***</td>
<td>ns</td>
<td>ns</td>
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<tr>
<td>Substrate (S)</td>
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<td>***</td>
<td>***</td>
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<tr>
<td>A x P</td>
<td>7</td>
<td>ns</td>
<td>ns</td>
<td>**</td>
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<td>***</td>
<td>ns</td>
<td>***</td>
</tr>
<tr>
<td>A x S</td>
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<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>**</td>
<td>ns</td>
<td>***</td>
<td>ns</td>
<td>***</td>
</tr>
<tr>
<td>P x S</td>
<td>2</td>
<td>ns</td>
<td>**</td>
<td>**</td>
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<td>***</td>
<td>ns</td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>A x P x S</td>
<td>13</td>
<td>*</td>
<td>**</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>*</td>
<td>***</td>
<td>ns</td>
<td>***</td>
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</tr>
</tbody>
</table>

Note: *** P< 0.001; ** 0.001≤P< 0.01
* 0.01≤P< 0.05 level; ns = non significant difference (P≥0.05)

**Copper:** There was significant effect between amendments, plant and substrate on the shoot Cu concentration of the plant (P<0.05, Table 4.5).

In the topsoil, all treatments increased the shoot Cu in Red Beech compared to the control (Figure 4.39a). In contrast, all treatments except for biosolid reduced shoot Cu in Wineberry (Figure 4.40a).

In the overburden, application of biosolids and N increased the shoot Cu concentration of Red Beech (Figure 4.39b) compared to the control treatment (Figure 4.40b). For wineberry, low rate biosolids and N increased shoot Cu (Figure 4.40c). Moreover, application of sawdust at high rate reduced the concentration of shoot Cu of Red beech in overburden (Figure 4.39b), shoot Cu of Wineberry in topsoil (Figure 4.40a), and overburden (Figure 4.40b) compared to the control.

In the mullock, there was no effect of the amendment treatments on the concentration of Cu in the shoots of Red Beech (Figure 4.39c). However, the low N rate, lupin and high biosolid all reduced the concentration of Cu in the shoots of Wineberry (Figure 4.40c) compared to the control.
Figure 4.39 Shoot Cu concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05.
Figure 4.40 Shoot Cu concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (Aristotelia serrata). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05. *All mullock plants in N2 treatment died and were not analysed.

Cadmium: There was significant effect between amendments, plant and substrate on the shoot Cd concentration of the plant (P<0.01, Table 4.5).

In the topsoil, application of biosolids and N at the high rate increased the shoot Cd in Red Beech compared to the control treatment (Figure 4.41a). The application of biosolids at the high rate also increased the shoot Cd in Wineberry, but the high application rate of N decreased the concentration of shoot Cd compared to the control (Figure 4.42a).

In the overburden, only N applied at the high rate increased the concentration of shoot Cd in Red Beech (Figure 4.41b). The application of biosolids and N at both rates increased the concentration of shoot Cd in Wineberry compared to the control (Figure...
4.42b). In contrast, the application of sawdust at both rates reduced the concentration of shoot Cd of Red Beech in overburden (Figure 4.41b).

Figure 4.41 Shoot Cd concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at *P*<0.05.
Figure 4.42 Shoot Cd concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\). All mullock plants in N2 treatment died and were not analysed.

**Arsenic:** There was significant effect between amendments, plant and substrate on the shoot As concentration of the plant (\(P<0.001\), Table 4.5).

For the topsoil, there was no difference effect between the control and amendments on the concentration of shoot As in Red beech (Figure 4.43a) or Wineberry (Figure 4.44a).

For the overburden, the low N treatment decreased shoot As in Red beech compared to the control (Figure 4.43b). In contrast, application of biosolid at high rate, lupin, and N at the high rate resulted in an increased of shoot As in Wineberry (Figure 4.44b).

In the mullock, there was no amendment effect on the concentration of As in the shoots Red beech (Figure 4.43c). In contrast, for Wineberry the only amendment treatment that had a shoot As concentration different to the control treatment was the low rate of N (Figure 4.44c).
Figure 4.43 Shoot As concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. 


Figure 4.44 Shoot As concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different.*

Aluminium: There was significant effect between amendments, plant and substrate on the shoot Al concentration of the plant (*P*<0.001, Table 4.5).

In all substrates, there was a significant effect of the plant species on the concentration of Al in the shoots (Table 4.5). For the topsoil, application of biosolid and N at both rates reduced the shoot Al of Red beech. In contrast for Wineberry, application of organic and inorganic amendments was not different to the control (Figure 4.46a).

In the overburden, application of sawdust at the low rate and N at the high rate increased the shoot Al of Red beech compared to the control (Figure 4.45b). In contrast, application of N was the only amendment which increased the shoot Al of Wineberry.

At the high N rate, the concentration of shoot Al of Red beech (compared to the control)
did not increase which was from 70 to 71 mg kg\(^{-1}\) (Appendix E, Table E4), while the concentration of shoot Al Wineberry increased (compared to the control) from 32 to 151 mg kg\(^{-1}\) (Appendix E, Table E6).

In the mullock, application of lupin, sawdust at the high rate and N at the high rate increased the shoot Al of Red beech, but there were no difference effect among these treatments compared to the others treatments (Figure 4.46c). Compared to the control, there was no difference effect between the organic and inorganic amendments in the concentration of shoot Al of Wineberry (Figure 4.46c).

![Figure 4.45 Shoot Al concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05.](image-url)
**Nickel:** There was significant effect between amendments, plant and substrate on the shoot Ni concentration of the plant (*P*<0.05, Table 4.5).

In the topsoil, all amendments increased the concentration of shoot Ni of Red beech, and application of biosolid at the low rate increased the most (Figure 4.47a). Application of N at the low rate increased the concentration of shoot Ni of Wineberry the most (Figure 4.48a). In contrast, application of N at the high rate reduced the concentration of shoot Ni of Wineberry.

In the overburden, amendments increased the concentration of shoot Ni of Red beech and Wineberry higher than in the topsoil and mullock. Application of high N increased the shoot Ni of Red beech and Wineberry the most, while application of sawdust...
reduced the concentration of shoot Ni in Wineberry (Figure 4.48b). For Red beech, low sawdust increased shoot Ni while high sawdust decreased shoot Ni, compared to the control (Figure 4.47b).

In the mullock, application of biosolid at both rates and N at the high rate increased the shoot Ni of Red beech (Figure 4.47c), but there was no significant difference between them. Only application of biosolid at both rates increased the shoot Ni of Wineberry, while other treatments were no different to the control (Figure 4.48c).

Figure 4.47 Shoot Ni concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha⁻¹; (B2) biosolid at 40 t ha⁻¹; (L) lupin at 20 g pot⁻¹; (S1) sawdust at 50 t ha⁻¹; (S2) sawdust at 100 t ha⁻¹; (N1) N at 150 kg ha⁻¹; (N2) N at 300 kg ha⁻¹. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. 
Figure 4.48 Shoot Ni concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P < 0.05\). All mullock plants in N2 treatment died and were not analysed.

**Lead:** There was a significant effect between amendments, plant and substrate on the shoot Pb concentration of the plant (\(P < 0.001\), Table 4.5).

In the topsoil, there was no significant difference between all these treatments to change the Red beech shoot Pb concentration (Figure 4.49a). Application of biosolids, lupin, low sawdust and low N all increased the shoot Pb of Wineberry (Figure 4.50a).

In the overburden, high biosolids, lupin and N amendments tended to reduce the concentration of shoot Pb of Red beech, with application of biosolid at high rate reduced the total shoot Pb the most, compared to the control (Figure 4.49b). In contrast, all amendments tended to increase the concentration of total shoot Pb of Wineberry except for sawdust, and application of N at high rate increased the most (Figure 4.50b).
In the mullock, there was no effect of the organic and inorganic amendments on the concentration of shoot Pb of Red beech (Figure 4.49c). In contrast, application of N and biosolid at the high rate increased the total shoot Pb in the Wineberry, but there was no difference between these treatments (Figure 4.50c).

Figure 4.49 Shoot Pb concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. 
Figure 4.50 Shoot Pb concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).

*All mullock plants in N2 treatment died and were not analysed.*
**Chromium:** There was no significant effect between amendments, plant and substrate on the shoot Cr concentration of the plant ($P>0.05$, Table 4.5) (Figure 4.51 and 4.52).

Figure 4.51 Shoot Cr concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha$^{-1}$; (B2) biosolid at 40 t ha$^{-1}$; (L) lupin at 20 g pot$^{-1}$; (S1) sawdust at 50 t ha$^{-1}$; (S2) sawdust at 100 t ha$^{-1}$; (N1) N at 150 kg ha$^{-1}$; (N2) N at 300 kg ha$^{-1}$. Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the shoot Cr on the topsoil (a), overburden (b), and mullock (c) ($P>0.05$).
Figure 4.52 Shoot Cr concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the shoot Cr on the topsoil (a), overburden (b), and mullock (c) (\(P>0.05\)).

**Manganese:** There was significant effect between amendments, plant and substrate on the shoot Mn concentration of the plant (\(P<0.001\), Table 4.5).

In the topsoil, all amendments increased the concentration of shoot Mn of the Red beech, and N at the high rate increased the most (Figure 4.53a). In contrast, there was no difference between the control and the amendments on the total shoot Mn of Wineberry (Figure 4.54a). Only application of lupin reduced the shoot Mn of Wineberry, compared to the control.

Furthermore, in the topsoil the species affected the uptake of this element. For example, at the high application rate of N the concentration of shoot Mn of Red beech increased from 423 to 838 mg kg\(^{-1}\) (Appendix E, Table E4), while at the same rate the
concentration of shoot Mn of Wineberry slightly increased from 229 to 263 mg kg\(^{-1}\) (Appendix E, Table E6).

Figure 4.53 Shoot Mn concentration of a pot trial containing (a) topsoil, (b) overburden, and (c) mullock substrates planted with Red beech (Nothofagus fusca). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).

In the overburden, there was no effect between the control and the amendments on the total shoot Mn of Red beech (Figure 4.53b). However, application of N at the high rate as well as biosolid and lupin all increased the shoot Mn of Wineberry (Figure 4.54b). As in the topsoil, the species affected the plant retention of this element. For example, at the high application rate of N the concentration of shoot Mn of Red beech slightly reduced from 935 to 928 mg kg\(^{-1}\) (Figure 4.53b; Appendix E, Table E4), while at the same rate the concentration of shoot Mn of Wineberry increased from 173 to 980 mg kg\(^{-1}\) (Figure 4.54b; Appendix E, Table E6).
In the mullock, there was no effect between the control and the amendments on the shoot Mn of both species (Figure 4.53c and 4.54c). Only low sawdust reduced the shoot Mn (Figure 4.53c). Again, the species affected the uptake of this element. For example, at the high application rate of biosolid the concentration of shoot Mn of Red beech increased from 125 to 273 mg kg\(^{-1}\) (Figure 4.53c; Appendix E, Table E4), while at the same rate the concentration of shoot Mn of Wineberry increased from 18 to 33 mg kg\(^{-1}\) (Figure 4.54c; Appendix E, Table E6).

![Graph showing Shoot Mn concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P < 0.05\). *All mullock plants in N2 treatment died and were not analysed.*

**Zinc:** There was significant effect between amendments, plant and substrate on the shoot Zn concentration of the plant (\(P < 0.001\), Table 4.5).
In the topsoil, application of high N increased the shoot Zn of Red beech the most, but application of sawdust at high rate reduced the amount of it (Figure 4.55a). In contrast, application of organic and inorganic amendments has no effect on the shoot Zn of Wineberry apart from high sawdust which reduced shoot Zn (Figure 4.56a). Again, the plant species affected the uptake of this element. For example, application of high biosolid increased the shoot Zn of Red beech from 68 to 105 mg kg\(^{-1}\) (Figure 4.55a) and slightly increased the shoot Zn of Wineberry from 173 to 179 mg kg\(^{-1}\) (Figure 4.56a).

In the overburden, application of biosolid and N increased the shoot Zn of Red beech and Wineberry the most, but application of sawdust and lupin both reduced shoot Zn concentration (Figure 4.55b and 4.56b). As in the case for the topsoil, the plant species affected the uptake of this element. For example, application of high N increased the shoot Zn of Red beech from 34 to 44 mg kg\(^{-1}\) and increased the shoot Zn of Wineberry from 46 to 112 mg kg\(^{-1}\).

Figure 4.55 Shoot Zn concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).
In contrast, for the mullock substrate, application of high N increased the shoot Zn of Red beech (Figure 4.55c). However, application of sawdust at low rate increased the shoot Zn of Wineberry (Figure 4.56c) the most. In contrast, application of biosolid at low rate reduced the shoot Zn of Red beech and biosolid at the high rate reduced the shoot Zn of Wineberry.

![Figure 4.56 Shoot Zn concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (Aristotelia serrata). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05. *All mullock plants in N2 treatment died and were not analysed.](image)

Iron: There was significant effect between amendments, plant and substrate on the shoot Fe concentration of the plant (P<0.001, Table 4.5).

In the topsoil, all amendments increased the shoot Fe of Red beech, and application of sawdust at high rate increased the most (Figure 4.57a). In contrast, application of biosolid, lupin and N reduced the shoot Fe of Wineberry, and application of lupin
reduced the most (Figure 4.58a). The species affected the uptake of this element, with the concentration in the Wineberry was higher than Red beech.

In the overburden, all amendments reduced shoot Fe, apart from application of sawdust at low rate which increased the shoot Fe of Red beech; application of lupin reduced the concentration of shoot Fe the most compared to the control (Figure 4.57b). In contrast, application of biosolid at the low rate, plus lupin and high N all increased the shoot Fe of Wineberry, while application of high biosolid, high sawdust and low N all reduced the shoot Fe (Figure 4.58b).

In the mullock, application of high sawdust and high N both increased the shoot Fe of Red beech (Figure 4.57c), while application of high biosolid, sawdust and low N all increased the shoot Fe of Wineberry (Figure 4.58c).

Figure 4.57 Shoot Fe concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Red beech (*Nothofagus fusca*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\).
Figure 4.58 Shoot Fe concentration of a pot trial containing (a) topsoil, (b) overburden and (c) mullock substrates planted with Wineberry (*Aristotelia serrata*). The substrates were treated with eight different amendments: (C) control; (B1) biosolid at 20 t ha\(^{-1}\); (B2) biosolid at 40 t ha\(^{-1}\); (L) lupin at 20 g pot\(^{-1}\); (S1) sawdust at 50 t ha\(^{-1}\); (S2) sawdust at 100 t ha\(^{-1}\); (N1) N at 150 kg ha\(^{-1}\); (N2) N at 300 kg ha\(^{-1}\). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at \(P<0.05\). *All mullock plants in N2 treatment died and were not analysed.

**Pearson’s correlations;** Pearson’s correlation between the mean values of plant relative growth and total shoot elements was calculated and is presented in Table 4.6. Three levels of significance were considered: \(P<0.01\), \(P<0.05\) and \(P<0.001\). A positive correlation is when the ability of one element to stimulate the absorption of other elements in plants occurs; and a negative correlation is when the ability of one element to inhibit the absorption of other elements in plants occurs.

The correlation demonstrated that Cu had a significantly positive correlation (\(P<0.001\)) with Al, Ni, Pb, Cr, Mn and Zn. Furthermore, the experiment also demonstrated where the Pb-Zn had antagonism affects. The experiment showed that Pb had a positive correlation with Zn. In addition, Cr was antagonistic with Mn and Cu; while the results showed an opposite pattern where Cr had a positive correlation with Mn and Cu.
The experiment supported the result that Mn had negative correlation with Fe. In addition, Fe-Zn have positive correlation. The Ni-Zn and Ni-Fe showed a negative correlation.

The interaction between the availability of macronutrient (Ca, Mg and P) in the plant as main antagonism element and the absorption and metabolism of several trace elements also has been discussed. This experiment demonstrated that Ca had negative correlation with Cu, Zn and Fe; P had negative correlation with Cu, Ni, Pb, Cr, Mn, Cd, Zn and Fe. Furthermore, Mg also had antagonistic effect with Cu, Al, Ni, Cr, Mn, Zn and Fe. This experiment supported that Na had negative correlation with Ca, but positive correlation with Mg.

This correlation supports the result that S had a positive correlation with P, but a negative correlation with K.
Table 4.6 Pearson’s correlation coefficients between total shoot elements and plant relative growth.

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DM: dry matter weight; all shoot elements was in total (digested by nitric acid)
4.5 Summary

This chapter was designed to investigate many parameters, and thus it generated many results. For clarity, the statistically significant results obtained from this study are summarised below and constitute the basic of the following discussion:

- Nutritional status of the growth medium. Application of biosolid and N fertilizer (both rates) increased the nutritional status of the topsoil, overburden and mullock. These amendments also increased the extractable $\text{NH}_4^{+}$-N and $\text{NO}_3^{-}$-N, of the growth medium, regardless of whether they were planted with Red beech or Wineberry.

- Extractable P, S, and Ca. Compared to the N fertilizer, application of biosolid increased these parameters in the topsoil, overburden, and mullock, regardless of whether they were planted with Red beech or Wineberry. N fertilizer had no effect on the extractable P, Ca, and also significantly reduced the extractable S.

- Electrical conductivity. Application of biosolid and N fertilizer at both rates increased the EC level of the topsoil and mullock. There was a plant species effect: the EC level was significantly higher when planted with Wineberry, compared to the Red beech.

- Red beech and Wineberry both demonstrated an increased shoot N, P, and Ca regardless of whether they were planted in the topsoil, overburden, and mullock.

- Heavy metal bioavailability. Both plant species had different responses to the organic and inorganic amendments and to the growth medium. Application of N increased the shoot Cd, Ni, and Mn of both plant species from optimum to toxic levels. Biosolid increased the shoot Cu, Cd, Pb, Zn of both plant species from deficient to optimum levels. These plant responses occurred in all growth mediums.

The following discussion will thus be based on these significant results.
4.6 Discussion

The availability of the nutrients in the substrate solution to assist sustainable restoration processes depends on the amount of the nutrients in the soil solution. This source can be from the natural occurrence in the substrate or supplemented by inorganic and organic amendments. It was hypothesised that the addition of these amendments to topsoil, overburden and mullock substrates would enhance the nutrient status in these substrates, thus enhancing biomass production. The results demonstrated that application of biosolid and N effectively increased the nutritional status of the growth mediums along with the biomass production, while other organic amendments (sawdust, lupin) had little effect on enhancing the nutritional status of the growth medium substrates.

The three different growth mediums from gold mine site Reefton have different characteristics. Pre-treatment analysis showed that the chemical and physical properties of the topsoil and overburden were similar, but the mullock had a higher cation content than both substrates (Chapter 3, Table 3.1). While this would suggest that the mullock could be used as a growth medium, it was only present in small amounts. The data in Table 3.1 suggested that the overburden, when used as a raw material, can potentially be used as a growth medium in much the same way as the topsoil is used. The significant difference for both these substrates was in the particle size; the topsoil includes fines, but the overburden is composed of coarse particle sizes and gravel. In contrast, since the mullock had a higher cation content than required for plant growth, it was expected that plants could grow in this substrate. However, observation at the mine site showed that the mullock pile had remained substantially un-vegetated for over 56 years after the last material was dumped at the site. This experiment demonstrated that the Red beech and Wineberry could growth in the mullock, but their performance was poor.

Application of N fertilizer to all the growth mediums (topsoil, overburden, and mullock) increased the concentration of extractable NH$_4^+$-N (Figure 4.5 and 4.6) and NO$_3^-$-N (Figure 4.7 and 4.8), but had no effect on pH (Figure 4.1 and 4.2), exchangeable Na (Figure 4.15 and 4.16), extractable P (Figure 4.9 and 4.10), CEC (Figure 4.21 and 4.22), and also reduced the extractable S (Figure 4.11 and 4.12) in the substrate solution. Other organic amendments like lupin green manure and sawdust had very little effect in enhancing the nutritional status of the growth medium. As a source of N it is clear that addition of N fertiliser would increase the amount of extractable NH$_4^+$-N and NO$_3^-$-N in the growth medium. This indicated that N fertilizer has a significant effect in enhancing nutritional status of the substrates themselves and would not be a sustainable and effective long-term amendment for use in mine
restoration. This is in agreement with Bradshaw (2000) who observed that even though N can be added to mine restoration sites, it is an expensive and ineffective practice, due to N being leached rapidly and must therefore be reapplied on an annual basis.

In contrast, compared to the N fertilizer effects, application of biosolid to all the growth mediums (topsoil, overburden and mullock) effectively increased the nutritional status of the substrate to a greater extent than N fertilizer. The biosolid increased the concentration of extractable NH$_4^+$-N (Figure 4.5 and 4.6) and NO$_3^-$-N (Figure 4.7 and 4.8), extractable P (Figure 4.9 and 4.10), extractable S (Figure 4.11 and 4.12), exchangeable Ca (Figure 4.13 and 4.14) on the substrate solution, but had no effect on pH (Figure 4.1 and 4.2), exchangeable Na (Figure 4.15 and 4.16), or CEC level (Figure 4.21 and 4.22). These results strongly indicate that biosolid may be a useful amendment material for mine restoration, by enhancing the nutritional status of the growth medium. Bearing in mind the concern about heavy metal contamination, this study demonstrated that all growth mediums had very low concentration of heavy metals, and application of biosolid resulted in heavy metal concentrations below the detection limit.

Previous experiments have demonstrated that application of biosolid significantly affected the availability of NH$_4^+$-N, NO$_3^-$-N in soil (Lavado et al., 2005; Martinez et al., 2003; Schroder et al., 2008). Due to mineralization processes, biosolid (with a high organic matter contents) can act as a source of N (Vaughan & Ord, 1985). However, the amount of N that will be available to plants in the short to medium term is still debatable; biosolid-N will be less readily mineralisable than N in other sources of organic waste. However, certainly in the long-term, the total N loading to soils from biosolids application will increase due to organic matter decomposition, and will also depend on the application rate (McLaren et al., 2007). Furthermore, research has found that biosolid also increased the P concentration in soil (Lavado et al., 2005; Martinez et al., 2003). Organic P compounds that were derived from biosolids need to be hydrolysed and mineralized by the microbial biomass. Assuming that biosolid contains high organic matter leading to high population of microorganisms, and an increase in the release of orthophosphate ions. This will be available to the plant, or will be transferred to the soil inorganic pool or less likely lost by leaching or runoff (Fuentes et al., 2008; Sanchez, 2007). The results presented in this Chapter demonstrated that all growth mediums from the Globe Progress gold mine at Reefton effectively responded to biosolid, particularly the overburden when the concentration of extractable P in the overburden was lower than topsoil (Table 4.1). The biosolid applied to the growth medium also contained high extractable S (Table 4.2), which may also contribute available sulphate to the growth medium.
However, the topsoil and overburden had low pH, and the amendments had no effect on pH. Since pH affects nutrient and heavy-metal availability it is necessary to increase the growth medium pH. Many researchers have also reported that application of biosolid to soil did not significantly change soil pH (Lavado et al., 2005; Martinez et al., 2003; Mullen et al., 2005; Schroder et al., 2008). However, occasionally soil pH slightly decreased after addition of sewage sludge, due to decomposition and the mineralization of the organic matter, which increased the CO₂ levels and decreased the pH of amended soils (Achiba et al., 2009). In contrast, organic amendments can increase soil pH, when original pH is relatively low, caused by the mineralization of carbon and subsequent production of OH⁻ ions by ligand exchange as well as the introduction of basic cations, such as K⁺, Ca²⁺, and Mg⁺ (Achiba et al., 2009).

Moreover, Teixeira et al. (2007) stated that water treatment sludge could increase soil pH, due to the use of hydrated lime in the water treatment processes. However, the biosolid from Bromley had high pH, due to ammonia content in the biosolid. As a result, biosolid may still increase the pH of the substrate for long-term use, and can thus be an effective amendment for mine restoration.

For the sustainable re-vegetation processes, optimizing the growth medium needs to be followed by optimizing plant growth. This study demonstrated that different plant species have different responses to the organic and inorganic amendments and to the growth medium. For example, application of biosolid and N in all substrates reduced the shoot Ca of Red beech (Figure 4.31abc), whilst the same amendments increased the shoot Ca of Wineberry (Figure 4.32abc). Furthermore, the experiment also demonstrated that application of biosolid and N fertilizer effectively increased the shoot N of Red beech (Figure 4.25) and Wineberry (Figure 4.26) in all substrates. In contrast, both amendments reduced the shoot P of Red beech (Figure 4.27ac) and Wineberry (4.28b). This effect is also related to the shoot heavy-metal concentrations; the plant species had different responses to the organic and inorganic amendments and to the growth medium. For example, application of N increased the shoot Cd (Figure 4.41b and 4.42b), Ni (Figure 4.47b and 4.48b), and Mn (Figure 4.54b) of both plant species from optimum which was adequate for maximum growth to toxic level which was deficient for maximum growth (Figure 4.41b and 4.42b). Whilst biosolid increased the shoot Cu (Figure 4.39 and 4.40), Cd (Figure 4.41 and 4.42), Pb (Figure 4.50), Zn (Figure 4.55 and 4.56) of both plant species, the concentration was in the range of deficient which was deficient for maximum growth to optimum which was adequate for maximum growth. This result indicated that both species have differed plant physiology for element uptake from solution and hence affecting biomass production.
The growth medium and shoot results indicated that biosolid was more effective than N fertilizer for enhancing the chemical properties of the growth medium; and that biosolid is a valuable material for use as an amendment for degraded sites. For the field application of amendments, this is in agreement with Bradshaw (2000) who observed that even though the availability of N can be improved through fertiliser application, it is an expensive and ineffective method for reclamation processes, due to the N being quickly leached and the need for regular reapplication. Application of biosolids is an alternative option for providing N, and it is more economical to use biosolid compared to inorganic fertilizer, since biosolid is a waste product, and is being effectively, recycled. However, applying biosolid to land faces the important issue that the biosolid may contain heavy metals and pathogenic micro-organisms which have the potential to damage plants and animals, and hence human health (NZWWA, 2003). To address these issues, there are strict protocols to cover the management of biosolids for land application purposes in New Zealand (NZWWA, 2003).

In order to cope with the EC level, it was found that application of sawdust effectively reduced the EC level in both the overburden (Figure 4.3b and 4.4b) and the mullock (Figure 4.3c and 4.4c). This result suggested that sawdust may be able to be used to overcome salinity problems for re-vegetation at this mining site. In addition, the sawdust also may act as a sink for N. Microbes will need to utilise any available N in order to breakdown the carbon source that is the sawdust. Other research has suggested that to minimize the environmental risk of using biosolid in agricultural soil it is recommended to incorporate the biosolid with pine bark (Hernandez-Apaolaza & Guerrero, 2008). However, the result of incorporation of the sawdust (in order to reduce the EC level) in conjunction with the biosolid (in order to increase the nutrients in growth medium) as a biosolid+sawdust mixed treatment was not tested in this experiment. From this, it can be suggested that incorporation of the sawdust and biosolid in growth medium from the Reefton gold mine site may be effective in increasing the substrate nutrient content, reduced soluble salts and reduce the environment impact.

Finally, the aim of restoration is to create soil conditions closely similar to pre-mining conditions (Norton, 1991; Ross & Mew, 1995). The pot trials in this chapter demonstrated that addition of biosolid to the topsoil, overburden and mullock improved those substrate as a growth medium, and thus the associated plant biomass production to a greater extent than pre-mining conditions.
4.7 Conclusions

- Application of biosolid effectively increased the nutritional status of all the growth mediums and increased available N. This was in contrast to the inorganic fertilizer source which only increased the available N -directly mineralised from the fertiliser N source. However, none of the amendments had any effect on the pH of growth mediums.

- Sawdust reduced the EC level of all the growth mediums. It may make an effective amendment, when mixed with the biosolid; as N would increase the growth medium nutrient content and decrease soluble salts and thus reduce environmental impacts.

- Red beech and Wineberry responded differently to all the amendments and to the growth mediums-as demonstrated by the biomass results and the shoot concentration of micro nutrients and heavy metals. It is likely that this is a particular plant physiological response.

- The overburden thus demonstrates potential as a growth medium substrate, when amended with biosolids and in conjunction with sawdust.

The results in this chapter have established some preliminary parameters: response to organic and inorganic amendments in both the growth medium substrates and plants. Organic amendments such as biosolids, when added to the overburden, can be an effective growth medium-as indicated by the biomass and nutrient responses of the two plant species.

However, topsoil is often the mandatory growth medium used for mine site restoration. As sustainable restoration methods for mine sites are likely to include using any stockpiled topsoil material, the following chapter will test plant growth responses to N, P and pH for topsoil. For sustainable restoration, rates of N, P and levels of pH must be optimised, especially for native plants.
Chapter 5
Effect of Nutrient and Lime Addition on Topsoil
Properties and Plant Growth

5.1 Introduction

During the restoration process, treating topsoil from stockpiled reserves for use as a growing medium is the first step for establishing plants in the post-mining landscape. The disturbance of topsoil reduces plant available N (Ollinger et al., 2002), due to the topsoil having been stockpiled and N has mineralised over time and volatilised. In addition, in soils from mine sites, P availability is often very low, due for example to the high fixation capacities of the exposed mine soil when it is composed of sandstone (Benfeld et al., 2001). Insoluble Fe and Al-phosphate compounds are formed in acid soils, and in alkaline soils insoluble calcium compounds are formed that hamper P availability (Lyle, 1987; Moody & Bolland, 1999). Moreover, in alkaline soils calcium carbonate (CaCO₃), along with Fe oxides are positively correlated with P sorption (Lyle, 1987; Moody & Bolland, 1999).

Often the topsoil from mining-sites has a pH which is outside the desirable range for plant growth, being either acid or alkaline (Kooijman et al., 2008; Ross & Mew, 1995; Sydnor & Redente, 2002). Soil reaction affects element availability and toxicity, microbial activity, and root growth thus affecting soil fertility (Foth & Ellis, 1997). For example, N mineralization is optimum between pH 6-8, thus at these pH values, N availability will be maximised for plant growth. Increasing the pH of acidic soils to between 6 and 7 generally improves plant-availability of macronutrients while reducing the heavy metal availability (Whalen et al., 2000). In addition, adding N fertilizer to acid topsoil can cause a further reduction in pH. Whereas, when topsoil from mining sites has a pH >8 and treatments containing ammonia or urea are added to soil it is likely that some of the N will volatilise into the atmosphere (Lyle, 1987).

Application of N, P and lime and their combination treatments in topsoil has been in use for many years and can prove as a useful technique to overcome N and P demand in topsoil. However, the fertilizer combination could result in side effects for the topsoil and vegetation such as changes in the bioavailability of other nutrients or heavy metals, thus further research
is required to evaluate the most effective combinations in order to enhance the soil restoration
technique on mine sites, and to ensure long-term sustainable soil remediation. In addition,
there is a little information on N, P and lime requirements of Red beech and other NZ native
plant species. So to optimise the mining restoration process it is important to have relevant
data on New Zealand native plants.

The specific objective of this experiment was to characterise the impact of N, P and lime
amendments on plant biomass and the nutrient status of the stockpiled topsoil.

5.2 Materials and Methods

Topsoil was collected from the current stock pile site at the Globe-Progress mine, Reefton,
New Zealand (Chapter 3 section 3.1). The soil was air dried, and passed through a 1.5 cm
mesh sieve. The pots used in the experiment had a diameter of 17 cm and were 15.5 cm high.
The inside of the pot was covered by a plastic bag and filled with 2.5 kg of the sieved air-dry
topsoil.

Red beech was used as the test species for this experiment. Plants were obtained from a
nursery (Headford Propagators, Waimate, New Zealand) with an approximate age of 6
months and planted bare-rooted into the substrate. N, P and lime were analytical reagent grade
NH₄NO₃ (ammonium nitrate), KH₂PO₄ (potassium dihydrogen orthophosphate) and CaCO₃
(calcium carbonate), respectively. N was applied at a rate of 150 kg ha⁻¹ (1.0 g pot⁻¹) and 300
kg ha⁻¹ (2.0 g pot⁻¹), P at the rate of 50 kg ha⁻¹ (0.5 g pot⁻¹) and 100 kg ha⁻¹ (1.0 g pot⁻¹), and
combinations of each N and P rate with lime at the rate of 37.5 t ha⁻¹ (212 g pot⁻¹) (Table 5.1,
Appendix B for application rate calculations). The N, P, and lime application rates were
based on the common application rate for agriculture in New Zealand. The lime application
rate was based on 15 t ha⁻¹ of lime to increase the pH by 1 unit. Since the topsoil pH was 3.5
and the desired pH was pH 6, this meant an increase by 2.5 pH units. The buffer capacity for
the topsoil was 4 mmol kg⁻¹ soil pH⁻¹ (Table 3.3) (Appendix G for pH buffering capacity
calculation). The pH buffering capacity for silt loams in New Zealand soils and this topsoil
are both similar (Table 3.3) (McLaren & Cameron, 2004). For each treatment, the amendment
and the topsoil were thoroughly mixed together before placing in the pot.

The pot trials were conducted in the glass houses of Lincoln University for 16 weeks
(September 2006 to January 2007), with a maximum temperature of 27 °C and minimum of
14°C. The trial was a randomised block design with 9 treatments and four replicates per
treatment. Each replicate was designated as a block placed next to each other in the green
house, and the treatments in each block were randomized once every 4 weeks. Watering the plants was conducted every 2-3 days. Soil and shoot biomass was determined at harvest.

Table 5.1 Experimental design.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Material</th>
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<tbody>
<tr>
<td>Substrate</td>
<td>Topsoil</td>
</tr>
<tr>
<td>Plant</td>
<td>Red beech</td>
</tr>
<tr>
<td>Treatment</td>
<td>Control</td>
</tr>
<tr>
<td></td>
<td>N 150 kg ha(^{-1}) (N-1)</td>
</tr>
<tr>
<td></td>
<td>N 300 kg ha(^{-1}) (N-2)</td>
</tr>
<tr>
<td></td>
<td>Phosphorus 50 kg ha(^{-1}) (P-1)</td>
</tr>
<tr>
<td></td>
<td>Phosphorus 100 kg ha(^{-1}) (P-2)</td>
</tr>
<tr>
<td></td>
<td>N 150 kg ha(^{-1}) + Lime 37.5 t ha(^{-1}) (N-1+L)</td>
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<tr>
<td></td>
<td>N 300 kg ha(^{-1}) + Lime 37.5 t ha(^{-1}) (N-2+L)</td>
</tr>
<tr>
<td></td>
<td>Phosphorus 50 kg ha(^{-1}) + Lime 37.5 t ha(^{-1}) (P-1+L)</td>
</tr>
<tr>
<td></td>
<td>Phosphorus 100 kg ha(^{-1}) + Lime 37.5 t ha(^{-1}) (P-2+L)</td>
</tr>
</tbody>
</table>

5.2.1 Analyses

Substrate was analysed for pH, EC, extractable N, P, S, exchangeable Ca, Na, Mg, K, and extractable heavy metals (As, Cd, Pb, Cr, Ni, and Cu) (Chapter 3 section 3.2.1). Plant was analysed for shoot N, P, S, Ca, Na, Mg, Na, K and heavy metals (Cd, Cr, Pb, As, Cu, Ni, Al, Fe, Zn, and Mn) (Chapter 3 section 3.3.1).

5.3 Results

In this section, results from the substrate analysis as well as plant shoot analysis are presented. The substrate and plant results are also presented in Appendix E.

5.3.1 Soil

The result of soil ANOVA for the main effect of the amendments showed that there were significant effects of amendments on the soil pH, EC, extractable \(\text{NH}_4^+\)-N, \(\text{NO}_3^-\)-N, P, exchangeable cations (Ca, Mg and K) and CEC, but there were no significant effects of amendments on the values of extractable S and Na (Table 5.2).
Table 5.2 ANOVA main effects of amendment on topsoil characteristics.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>pH</th>
<th>EC</th>
<th>NH\textsubscript{4}\textsuperscript{+}</th>
<th>NO\textsubscript{3}\textsuperscript{−}</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>CEC</th>
<th>Ca</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
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<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>µS cm\textsuperscript{−1}</td>
<td>Extractable (mg kg\textsuperscript{−1})</td>
<td></td>
<td></td>
<td></td>
<td>Exchangeable (cmol\textsubscript{c} kg\textsuperscript{−1})</td>
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<tr>
<td>Amendment</td>
<td>8</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>ns</td>
<td>*</td>
<td>***</td>
<td>ns</td>
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</table>

Note: *** P< 0.001; ** 0.001≤P< 0.01  * 0.01≤P< 0.05 level; ns = non significant difference (P≥0.05)

5.3.1.1 Soil pH

There was a significant effect of amendments on the soil pH (P<0.001) (Table 5.2). Compared to the control, the combination of N and lime at both application rates, as well as P and lime at both application rates, significantly increased the soil pH (Figure 5.1). Application of N at both rates reduced the soil pH compared to the control. This indicates that the treatments N-1+ lime, N-2+ lime, P-1+ lime and P-2+ lime reduced the acidity of stockpiled topsoil material.

![Figure 5.1](image-url)

Figure 5.1 The pH of the topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with nine treatments (N-1 = 150 kg N ha\textsuperscript{−1}; N-2 = 300 kg N ha\textsuperscript{−1}; P-1 = 50 kg P ha\textsuperscript{−1}; P-2 = 100 kg P ha\textsuperscript{−1}; lime = 37.5 t CaCO\textsubscript{3} ha\textsuperscript{−1}). Treatment means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P<0.05.
### 5.3.1.2 Soil extractable $\text{NH}_4^+$-N and $\text{NO}_3^-$-N

There was a significant amendment effect ($P<0.001$) on the extractable $\text{NH}_4^+$-N in the topsoil (Table 5.2). N at the high application rate (300 kg ha$^{-1}$) increased the amount of extractable $\text{NH}_4^+$-N in the topsoil compared to the control (Figure 5.2). There was no effect of other treatments (including lime) on $\text{NH}_4^+$-N in the topsoil compared to the control (Figure 5.2).

![Figure 5.2 The extractable $\text{NH}_4^+$-N in the topsoil collected from Oceana-Gold Globe Progress Mine Near Reefton, New Zealand and used in a pot trial with nine treatments (N-1 = 150 kg N ha$^{-1}$; N-2 = 300 kg N ha$^{-1}$; P-1 = 50 kg P ha$^{-1}$; P-2 = 100 kg P ha$^{-1}$; lime = 37.5 t CaCO$_3$ ha$^{-1}$). Means and standard errors are shown, and within a treatment means followed by the same lower case letter were not significantly different at $P<0.05$. n = 4 for each treatment.]

There was a significant amendment effect ($P<0.001$) on the extractable $\text{NO}_3^-$-N in the topsoil (Table 5.2). Application of N at the low and high rates, and the combination of N at both rates plus lime increased the amount extractable $\text{NO}_3^-$-N in the topsoil (Figure 5.3). Lime did not significantly increase the availability of $\text{NO}_3^-$-N when N was added relative to N fertilisation without lime. The combination of N at the high application rate plus lime had the greatest impact on the extractable $\text{NO}_3^-$-N in the soil.
Figure 5.3 The extractable NO$_3$-N in the topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with nine treatments (N-1 = 150 kg N ha$^{-1}$; N-2 = 300 kg N ha$^{-1}$; P-1 = 50 kg P ha$^{-1}$; P-2 = 100 kg P ha$^{-1}$; lime = 37.5 t CaCO$_3$ ha$^{-1}$). Means and standard errors are shown, and within a treatment means followed by the same lower case letter were not significantly different at $P<0.05$. $n = 4$ for each treatment.

5.3.1.3 Soil extractable P

There was a significant amendment effect ($P<0.001$) on the extractable P in the topsoil (Table 5.2). The combination of treatments (N and P) and lime reduced the extractable P in the topsoil (Figure 5.4). Application of P at the low and high rates increased the extractable P in the topsoil; however there was no difference effect between P-1 and the control. Application of N1 plus L and N2 plus L both reduced P.

Figure 5.4 The extractable P in the topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with nine treatments (N-1 = 150 kg N ha$^{-1}$; N-2 = 300 kg N ha$^{-1}$; P-1 = 50 kg P ha$^{-1}$; P-2 = 100 kg P ha$^{-1}$; lime = 37.5 t CaCO$_3$ ha$^{-1}$). Means and standard errors are shown, and within a treatment means followed by the same lower case letter were not significantly different at $P<0.05$. $n = 4$ for each treatment.
5.3.1.4 **Soil extractable S**

There was no significant amendment effect on the extractable S in the topsoil \( (P>0.05) \) (Table 5.2) (Figure 5.5).

![Figure 5.5 The extractable S in the topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with nine treatments (N-1 = 150 kg N ha\(^{-1}\); N-2 = 300 kg N ha\(^{-1}\); P-1 = 50 kg P ha\(^{-1}\); P-2 = 100 kg P ha\(^{-1}\); lime = 37.5 t CaCO\(_3\) ha\(^{-1}\)). Means and standard errors are shown. n = 4 for each treatment. There was no significant difference for the soil extractable S \( (P>0.05) \).](image)

5.3.1.5 **Soil exchangeable cations**

There were significant amendment effects \( (P<0.001) \) on the exchangeable Ca, Mg and K in the topsoil (Table 5.2). Both the low and high N with lime treatments had the greatest effect on the concentration of exchangeable Ca in the topsoil compared to the control treatment (Figure 5.6a). The next highest concentration of exchangeable Ca was the low P plus lime treatment. The control had the lowest exchangeable Ca of all treatments.

None of the fertiliser treatments tested had a significant effect \( (P>0.05) \) on the concentration of exchangeable Na in the topsoil (Figure 5.6b).

Both the N-1+lime and N-2+lime treatments, as well as the P-1+lime and P-2+lime reduced the amount of exchangeable Mg in the topsoil (Figure 5.6c). There was no difference between the control treatment and the single application of low and high N and high P.
The low and high P treatments had the largest effect of the treatments tested on exchangeable K in the topsoil compared to the control (Figure 5.6d). There was no effect between the control and N-1, N-2, N-2+lime, and P-1+lime treatments.

5.3.1.6 Cation exchange capacity

There was a significant effect ($P<0.01$) of the amendment treatments on the CEC of the topsoil (Table 5.2). Compared to the control, all the treatments reduced the CEC level of the topsoil, except the application of N-2 + lime and the P-2 + lime treatments (Figure 5.7).
Figure 5.7 The AgTu cation exchange capacity of topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with nine treatments (N-1 = 150 kg N ha\(^{-1}\); N-2 = 300 kg N ha\(^{-1}\); P-1 = 50 kg P ha\(^{-1}\); P-2 = 100 kg P ha\(^{-1}\); lime = 37.5 t CaCO\(_3\) ha\(^{-1}\)). Means and standard errors are shown and, within a treatment, means followed by the same lower case letter were not significantly different at \(P<0.05\). \(n = 4\) for each treatment.

5.3.1.7 Soil extractable heavy metals

There were significant amendment effects \((P<0.001)\) on the extractable As, Cd, Cr, Cu, Ni and Pb in the topsoil (Table 5.3). Compared to the control, the treatments reduced the amount of extractable As (Figure 5.8a), Cd (Figure 5.8b) and Cr in the topsoil (Figure 5.8d).

Table 5.3 ANOVA main effects of amendment on topsoil characteristics.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
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<td>Amendment</td>
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</tbody>
</table>

Note: *** \(P< 0.001\); ** \(0.001 \leq P < 0.01\) * \(0.01 \leq P < 0.05\) level; ns = non significant difference \((P \geq 0.05)\)

Application of N at the high rate was the only treatment that significantly increased the extractable Pb in the topsoil (Figure 5.8c); whilst other treatments reduced the extractable Pb in the topsoil compared to the control.
The combination of P at the low rate (50 kg ha\(^{-1}\)) plus lime increased the extractable Ni (Figure 5.8e) and extractable Cu (Figure 5.8f) in the topsoil compared to the control. In contrast, other treatments reduced the extractable Ni and Cu.

### Table

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Extractable Ni (mg kg(^{-1}))</th>
<th>Extractable Cd (mg kg(^{-1}))</th>
<th>Extractable Pb (mg kg(^{-1}))</th>
<th>Extractable As (mg kg(^{-1}))</th>
<th>Extractable Cu (mg kg(^{-1}))</th>
<th>Extractable Cr (mg kg(^{-1}))</th>
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<td>Control</td>
<td>0.00</td>
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<td>N-1</td>
<td>b</td>
<td>c</td>
<td>bc</td>
<td>c</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>N-2</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>b</td>
<td>ab</td>
</tr>
<tr>
<td>N-1 + Lime</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>d</td>
<td>c</td>
<td>b</td>
</tr>
<tr>
<td>N-2 + Lime</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>P-1</td>
<td>a</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
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</tr>
<tr>
<td>P-2</td>
<td>a</td>
<td>c</td>
<td>c</td>
<td>c</td>
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<tr>
<td>P-1 + Lime</td>
<td>c</td>
<td>b</td>
<td>c</td>
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<td>c</td>
</tr>
<tr>
<td>P-2 + Lime</td>
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<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
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</tr>
</tbody>
</table>

Figure 5.8 The extractable As (a), Cd (b), Pb (c), Cr (d), Ni (e), and Cu (f) in the topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with nine treatments (N-1 = 150 kg N ha\(^{-1}\); N-2 = 300 kg N ha\(^{-1}\); P-1 = 50 kg P ha\(^{-1}\); P-2 = 100 kg P ha\(^{-1}\); lime = 37.5 t CaCO\(_3\) ha\(^{-1}\)). Means and standard errors are shown, and within a treatment means followed by the same lower case letter were not significantly different at \(P<0.05\). \(n=4\) for each treatment. Note that the scale on the y-axis varies between metals.
5.3.2 Plant

The result of plant ANOVA for the main effect of the amendments on Red beech shoot showed that there was a significant effect of amendment on the dry matter yield of the Red beech as well as the shoot N, P, S, Ca, and K compared to the control (Table 5.4).

Table 5.4 ANOVA main effects of amendment on Red beech shoot characteristics.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>Shoot Concentration (%)</th>
<th>Shoot concentration (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DM</td>
<td>N</td>
</tr>
<tr>
<td>Amendment</td>
<td>8</td>
<td>***</td>
<td>***</td>
</tr>
</tbody>
</table>

Note: *** P < 0.001; ** 0.001 ≤ P < 0.01
* 0.01 ≤ P < 0.05 level; ns = non significant difference (P ≥ 0.05)

5.3.2.1 Biomass

There was a significant amendment effect (P < 0.001) on Red Beech dry matter weight (Table 5.4). N at the low application rate increased Red Beech dry matter weight the most of all treatments compared to the control, followed by N at the high application rate (Figure 5.9). The combination of low N with lime and low and high P with lime increased Red Beech dry weight compared to the control (Figure 5.9).

![Figure 5.9 Dry matter yield of Red Beech (Nothofagus fusca) seedlings grown in a pot trial using topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with nine treatments (N-1 = 150 kg N ha\(^{-1}\); N-2 = 300 kg N ha\(^{-1}\); P-1 = 50 kg P ha\(^{-1}\); P-2 = 100 kg P ha\(^{-1}\); lime = 37.5 t CaCO\(_3\) ha\(^{-1}\)). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at P < 0.05.](image)
5.3.2.2 **Shoot N**

There was a significant amendment effect ($P<0.001$) on the shoot N concentration of Red beech (Table 5.4). All treatments except the two P without lime treatments increased the N concentration in Red beech compared to the control (Figure 5.10). N at the high application rate increased the shoot N the most of all the treatments (Figure 5.10).

![Figure 5.10 Shoot N concentration in the Red Beech (*Nothofagus fusca*) seedlings grown in a pot trial using topsoil Collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with nine treatments (N-1 = 150 kg N ha$^{-1}$; N-2 = 300 kg N ha$^{-1}$; P-1= 50 kg P ha$^{-1}$; P-2 = 100 kg P ha$^{-1}$; lime = 37.5 t CaCO$_3$ ha$^{-1}$). Means and standard errors are shown, and within a treatment means followed by the same lower case letter were not significantly different at $P<0.05$. n = 4 for each treatment.]

5.3.2.3 **Shoot P**

There was a significant amendment effect ($P<0.001$) on the shoot P concentration of Red beech (Table 5.4). Most of the treatments reduced the shoot P in the Red beech compared to the control treatment, except the application of P at the high rate which was not significantly different to the control P shoot concentration (Figure 5.11).
5.3.2.4 Shoot S

There was a significant amendment effect ($P<0.001$) on the shoot S concentration of Red beech (Table 5.4). Application of N-2 + lime increased the shoot S the most (Figure 5.12). There were no difference effect between the P-1, P-2 and the control.
Figure 5.12 Shoot S concentration in the Red Beech (*Nothofagus fusca*) seedlings grown in a pot trial using topsoil Collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with nine treatments (N-1 = 150 kg N ha\(^{-1}\); N-2 = 300 kg N ha\(^{-1}\); P-1= 50 kg P ha\(^{-1}\); P-2 = 100 kg P ha\(^{-1}\); lime = 37.5 t CaCO\(_3\) ha\(^{-1}\)). Means and standard errors are shown, and within a treatment means followed by the same lower case letter were not significantly different at \(P<0.05\). \(n = 4\) for each treatment.

### 5.3.2.5 Shoot Ca, Na, Mg and K

There were significant amendment effects on the shoot Ca (\(P<0.001\)) and K (\(P<0.01\)) in the plants (Figure 5.13a and b) (Table 5.4). There were no significant effects of N, P or liming treatments on the concentration of Na and Mg (\(P>0.05\)) in the shoots of Red beech (Figure 5.13b and Figure 5.13c).

The combination of N at both rates plus lime increased the shoot Ca concentration in the Red beech the most of all treatments compared to the control (Figure 5.13a), followed by the low N rate with lime treatment. In contrast, N alone at both rates was the only treatments to reduce shoot Ca relative to the control (Figure 5.13a). There was no difference effect of N, P or lime treatments on the shoot Ca of P-1, P-2, P-1+lime and P-2+ lime treatments.

All treatments reduced the concentration of K in the shoots of Red beech relative to the control treatments (Figure 5.13b).
Figure 5.13 Shoot Ca (a), K (b), Mg (c) and Na (d) concentration in the Red Beech (*Nothofagus fusca*) seedlings grown in a pot trial using topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with nine treatments (N-1 = 150 kg N ha⁻¹; N-2 = 300 kg N ha⁻¹; P-1 = 50 kg P ha⁻¹; P-2 = 100 kg P ha⁻¹; lime = 37.5 t CaCO₃ ha⁻¹). Means and standard errors are shown, and within a treatment means followed by the same lower case letter were not significantly different at \( P < 0.05 \). \( n = 4 \) for each treatment. There were no significant different for the total Na (b) and Mg (c) (\( P > 0.05 \)).

### 5.3.2.6 Shoot heavy metals

There were significant amendment effects on the shoot heavy metal concentration in the topsoil, except for Cr concentration (Table 5.5).

#### Table 5.5 ANOVA main effects of amendment on Red beech shoot characteristics.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Al</th>
<th>Fe</th>
<th>Zn</th>
<th>Mn</th>
</tr>
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<tbody>
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<td></td>
<td></td>
</tr>
<tr>
<td>Amendment</td>
<td>8</td>
<td>*</td>
<td>***</td>
<td>***</td>
<td>ns</td>
<td>**</td>
<td>***</td>
<td>**</td>
<td>**</td>
<td>***</td>
<td>***</td>
</tr>
</tbody>
</table>

Note: *** \( P < 0.001 \); ** \( 0.001 \leq P < 0.01 \)

* \( 0.01 \leq P < 0.05 \) level; ns = non significant difference (\( P \geq 0.05 \))
Among the treatments, N at the low and high application rates, and P at the low rate increased the shoot Cd in the Red Beech (Figure 5.14a). Combination of P and lime reduced the shoot Cd, but there was no different effect compared to the control.

Figure 5.14 Shoot concentrations of Cd (a), Cr (b), Pb (c), As (d), Cu (e), and Ni (f) in the Red beech (*Nothofagus fusca*) seedlings grown in a pot trial using topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with nine treatments (N-1 = 150 kg N ha⁻¹; N-2 = 300 kg N ha⁻¹; P-1 = 50 kg P ha⁻¹; P-2 = 100 kg P ha⁻¹; lime = 37.5 t CaCO₃ ha⁻¹). Means and standard errors are shown, and within a treatment means followed by the same lower case letter were not significantly different at $P<0.05$. $n = 4$ for each treatment. There was no significant different for total Cr (d) ($P>0.05$).
Single application of N at both rates had no difference effect on the shoot Pb to the control (Figure 5.14c). Other treatments reduced the shoot Pb.

There was no different effect of amendments on the shoot As in the Red Beech (Figure 5.14d). There were similar patterns between the shoot Cu (Figure 5.14e) and Ni (Figure 5.14f) in that single N at the low and high application rate increased the shoot Cu and Ni.

Combination of N and lime at the both rates reduced the shoot Al (Figure 5.15a). The only treatments to increase shoot Fe concentration were the high P without lime and low P with lime treatments (Figure 5.15b). In comparison the combination of lime and N at both application rates reduced the shoot Fe in the Red Beech (Figure 5.15b). Shoot Zn (Figure 5.15c) and Mn (Figure 5.15d) showed a similar trend to that among the other treatments; N at the low and high application increased the shoot Zn and Mn the most. Furthermore, combination of the lime and N or P reduced the shoot Zn and Mn in the Red Beech.

Figure 5.15 Shoot concentrations of Al (a), Fe (b), Zn (c) and Mn (d) in Red Beech (Nothofagus fusca) seedlings grown in a pot trial using topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with nine treatments (N-1 = 150 kg N ha⁻¹; N-2 = 300 kg N ha⁻¹; P-1 = 50 kg P ha⁻¹; P-2 = 100 kg P ha⁻¹; lime = 37.5 t CaCO₃ ha⁻¹). Means and standard errors are shown, and within a treatment, means followed by the same lower case letter were not significantly different at P<0.05. n = 4 for each treatment.
5.4 Discussion

To ensure the establishment of vegetation and their continued viability in the post-mining landscape, it is necessary to treat the mine topsoil to optimise the availability of nutrients. At the same time, risks posed by changes leading to increases in the bioavailability of heavy metals must be minimised where possible. In general, the results presented in this Chapter demonstrated that application of N decreased the N deficiency in the topsoil, while the combination of P and lime was ineffective in increasing topsoil nutritional status. The following discussion will focus on the effect of the amendments on the topsoil, in order to address the hypothesis that un-amended topsoil would limit plant growth due to N and P deficiencies and acid soil.

5.4.1 Effect of amendments on reducing topsoil N deficiency

Application of high rates of inorganic N (300 kg ha⁻¹) resulted in increased amounts of extractable NH₄⁺-N and NO₃⁻-N in the topsoil. Extractable NH₄⁺-N increased from 6.8 to 48.4 mg kg⁻¹ (Figure 5.2), while extractable NO₃⁻-N increased from 1.4 to 180.8 mg kg⁻¹. The combination of high N and lime also increased the extractable NO₃⁻-N, while application of single P in combination with lime had no effect on extractable NO₃⁻-N (Figure 5.3). The availability of nitrate (NO₃⁻) and ammonium (NH₄⁺) ions in soils are affected by both inorganic fertilisers and soil organic matter (Strong & Mason, 2005; Whitehead, 1995); the latter representing pools of organic-N which can be microbial mineralised to produce NH₄⁺-N and NO₃⁻-N. Since the topsoil contained a high organic matter content (6.3%) (Table 3.1) and ammonium nitrate (NH₄NO₃) was added as a fertiliser, this helps to explain the relationship between N amendment and extractable NH₄⁺-N and NO₃⁻-N.

Shoot N concentrations increased with the high N application rate to the topsoil, increasing from 0.7 to 2.0 % (Figure 5.10). However, shoot N concentrations were at toxic levels, as Red beech requires 1.3 -1.7 % of N in the green leaves for optimum growth (Strong & Mason, 2005; Wardle, 1991). N toxicity can be detected in many ways, such as yield suppression by 5 or 10 % when N concentration reaches the critical level (Barker & Bryson, 2007). Yield suppression was expressed here by a reduction in the dry matter weight for the high N amendment (12.76 g plant⁻¹) compared to the dry matter weight at the low N rate (16.76 g plant⁻¹) (Figure 5.9). Application of N at the low rate was sufficient to increase both the plant dry matter weight and the shoot N concentration (1.4%) to optimum levels. Furthermore, the low application rate of N (150 kg ha⁻¹) resulted in 64.5 mg kg⁻¹ of extractable NO₃⁻-N. This addressed the N deficiency problem in the topsoil with sufficient N to be taken up by the root,
resulting in an increase in dry matter. In comparison, the high application rate resulted in 180.8 mg kg\(^{-1}\) of NO\(_3\)\(^{-}\)-N, but reduced the Red beech yield.

### 5.4.2 Effect of amendments on reducing topsoil P deficiency

The high application rate of P did not reduce the topsoil P deficiency, or the shoot deficiency. While P applied at the high rate (100 kg ha\(^{-1}\)) resulted in an increase in the extractable P from 2.93 to 5.14 mg kg\(^{-1}\) (Figure 5.4), the concentration was still very low (<5 mg P kg\(^{-1}\)) (Hazelton & Murphy, 2007; Moody & Bolland, 1999).

The high application rate of P lead to a slightly increased shoot P concentration from 0.14 to 0.18% (Figure 5.11), and the dry matter weight from 5.94 to 6.38 g plant\(^{-1}\) (Figure 5.9). Red beech requires 0.1-0.6% of P in the green leaves for optimum growth (Wardle, 1991). While the low application rate of P lead to a shoot P concentration less than the control shoot N, this low P application rate was still sufficient enough to support Red beech growth in the topsoil (Figure 5.9). However, there are implications for the growth of more established plants on mine sites. More available P is necessary in the soil for growing plants, since roots will require a high rate of phosphate to be absorbed from the soil solution (Foth & Ellis, 1997; Mengel, 2007). Once the mobility of phosphate in the soil solution is low, then inorganic P uptake from fertiliser sources will depend on root growth and the root morphology of plants (Mengel, 2007). Alternatively, native pioneer species may be adapted to growing on P deficient soils. However, application of P at 100 kg ha\(^{-1}\) did not allow optimum plant growth. Furthermore, the combination of P and lime did not reduce the P deficiency in this soil (Figure 5.4). A more effective way to boost plant yield in these soils may be to substitute the amount of P fertilizer required with lime; as lime will increase the solubility of organic and inorganic soil P due to reduction of Al and Mn toxicity (Bolan et al., 2008a).

### 5.4.3 Effect of amendments on reducing topsoil acidity

Both of the N rates (at 150 and 300 kg N ha\(^{-1}\)) plus lime as well as P (at 50 and 100 kg N ha\(^{-1}\)) plus lime increased the topsoil pH from 4.7 to above 7.5. The lime effect was higher than was expected (increased the topsoil pH to 6). There was a possibility that over liming occurred. It was most likely to have been caused by the low topsoil buffer capacity (4 mmol kg\(^{-1}\) soil pH\(^{-1}\)) (Table 3.3) and it would require only 250 kg CaCO\(_3\) ha\(^{-1}\) (Appendix G). However, the over liming had contributed to the positive results for the biomass production and the concentration of heavy metals in the topsoil.
Raising the topsoil pH increased the Red beech biomass from 6 gram plant$^{-1}$ to the range of 7.3-9.8 gram plant$^{-1}$ (Figure 5.9). Raising topsoil pH to $>$ 7.5 increased exchangeable NO$_3^-$-N, Ca and K and reduced the concentration of many heavy metals. Plant uptake of soil nutrients is optimum in pH neutral soils (Comerford, 2005; Mengel & Kirkby, 2001), so increasing the pH from acid to neutral will generally increase plant growth. In addition to an increase in pH, it was expected that the combination of these fertilizers and lime also would increase nutrient availability and bioavailability and thus indirectly, the plant yield. However, the results demonstrated that while increasing the pH did not increase the availability of P, NH$_4^+$-N, S, Na, Mg and CEC in the topsoil, it did increase the exchangeable Ca, K, and extractable NO$_3^-$-N.

The levels of extractable As, Cd, Cr, Pb, Ni and Cu in the topsoil were low. The pot experiment demonstrated that by increasing pH, the levels of extractable As, Cd, Cr, Pb, Ni and Cu were further reduced in the topsoil (Figure 5.8). It is widely accepted that pH is key to determining the solubility and bioavailability of most heavy metals in soils. A high pH contributes to a decrease in heavy metal mobility by the formation of precipitates and by increasing the number of soil adsorption sites. Decreasing the competition of H$^+$ for adsorption and by increasing the metal stability with humic substances will also reduce heavy metal bioavailability (Bolan & Duraisamy, 2003; Busenelli et al., 2009; Naidu et al., 1994; Von Uexkull, 1989; Zaccheo et al., 2006).

As soil acidity increases, the bioavailability of metals increases leading to potential toxicity problems for plant growth (Maiti, 2007). Thus, it was expected that raising the pH would reduce the bioavailability and uptake of metals in the Red beech. The pot experiment demonstrated that increasing the pH did reduce the concentration of shoot Cd, Pb, Cu, Ni, and Al, but the level was in the low range (Kabata-Pendias & Pendias, 2001). Shoot Zn and Fe concentrations were still at optimum concentrations, and only shoot Mn reduced from toxic to optimum level. While the presence of certain metals (Co, Cu, Cr, Mn, and Zn) in soil are essential plant micro elements at low concentrations (Bolan & Duraisamy, 2003), it is necessary to manage heavy metal concentration in topsoil by manipulating pH levels, to keep their concentration at a low level.
5.5 Conclusions

- Application of N at the low rate was sufficient to increase the soil extractable NO$_3^-$-N, the plant dry matter weight as well as the shoot N concentration to optimum levels. This provided adequate N within the topsoil to produce optimum yield for Red beech plant growth.

- Application of P at the high rate was not effective in reducing P deficiency in the topsoil; barely and raising shoot P concentration into the optimum range. However, adequate shoot P concentration was achieved in the control, when no P was added to the topsoil.

- Even though over liming (37.5 t ha$^{-1}$) was likely to have occurred, but it was an effective approach to reducing soil acidity. It also reduced both heavy metal mobility in soil and also the bioavailability of heavy metals, as reflected in the shoot concentrations.

The implications of these conclusions for mine restoration involving Red beech and topsoil is that low N (150 kg N ha$^{-1}$) and lime (37.5 t ha$^{-1}$) will reduce N and P deficiency, and reduce topsoil acidity to near neutral pH levels. This will also allow a reduction in soil heavy metal mobility and bioavailability. However, unless there is P in the substrate, liming will not increase the available P content of the medium. In this experiment, the addition of lime decreased the available P in both the presence and absence of P application. It was clear that the addition of N to the growth medium was still needed to support plant growth in the early stage of re-vegetation processes. Further pot experiments are required to determine the optimum N rate for re-vegetation plant species (Red beech and Wineberry) that will allow the optimization of the N requirement for mine restoration.
Chapter 6

Effect of Nitrogen fertiliser Addition on Plant Growth in Topsoil and Overburden Materials

6.1 Introduction

The topsoil and overburden material remaining after gold mining tend to have different characteristics, either from nutrient and organic matter content or weathering processes, and thus their ability to supply nutrients would differ widely. Excavating the forest floor during mining and exposing the parent material beneath often results in a rapid loss of organic matter and N content (Davis & Langer, 1997b). Since N accumulation and its efficient recycling are important factors in soil ecosystem (Foth & Ellis, 1997) N fertiliser is commonly added to mine sites in order to alleviate potential N deficiencies. The topsoil and overburden would respond differently in order to provide N in solution, to thus maximise growth where vegetation is to be established. However, plant species also have different responses to N, due to inherent differences between species, including growth rates, and efficiency of nutrient use in the growth processes (Cobb et al., 2008). Application of low levels of N may be effective for some species, whereas application of high N levels can cause toxicity in more sensitive species. The N uptake by plant either it is in low or high concentration is directly related to stand productivity (Cobb et al., 2008). By understanding the demand of N in different plant species and different growth medium will lead to better management of site fertility for sustainable restoration.

The objective of this experiment was to determine the N rate for optimal plant growth of Red beech and Wineberry in topsoil and overburden material from the OceanaGold-Globe Progress mine site near Reefton, New Zealand.

6.2 Materials and Methods

Two growth mediums were collected for this experiment from the OceanaGold Globe-Progress mine site near Reefton, New Zealand: topsoil and overburden (Chapter 3 section 3.1). The topsoil and overburden were air dried, and passed 1.5 cm mesh sieve before putting in the pot. The pot size used in this experiment had a diameter of 13.2 cm and a height of 14 cm. The inside of each pot was covered by a plastic bag and filled with the substrate. Pots
were filled with 1.4 kg of air-dry topsoil or 1.7 kg of air-dry overburden. Both growth mediums was moderately acid, had low or very low levels of total carbon (C), N, CEC, exchangeable cations, and had similar particle size distribution (Table 6.1). The overburden had a noticeably smaller percentage of organic matter, C and N than the topsoil (Table 6.1).

Table 6.1 Selected chemical and physical characteristics of topsoil and overburden used in a N rate trial

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Topsoil</th>
<th>Overburden</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (1:5, soil:water)</td>
<td>4.8</td>
<td>4.5</td>
</tr>
<tr>
<td>OM (%)</td>
<td>6.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Total C (%)</td>
<td>3.7</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Total N (%)</td>
<td>0.14</td>
<td>0.05</td>
</tr>
<tr>
<td>C/N ratio</td>
<td>25.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Exchangeable Ca (cmolc kg⁻¹)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Exchangeable Na (cmolc kg⁻¹)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Exchangeable Mg (cmolc kg⁻¹)</td>
<td>0.15</td>
<td>0.31</td>
</tr>
<tr>
<td>Exchangeable K (cmolc kg⁻¹)</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>CEC (cmolc kg⁻¹)</td>
<td>11</td>
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</tr>
<tr>
<td>Clay (%)</td>
<td>36.49</td>
<td>41.90</td>
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<tr>
<td>Silt (%)</td>
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<tr>
<td>Sand (%)</td>
<td>1.49</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Red beech and Wineberry were used as the test species. The plants were obtained from a nursery (Headford Propagators-Waimate, Canterbury, New Zealand) with an approximate age of 6 months. Plants were gently separated from the potting mix provided so as to minimise disturbing the roots and planted bare-rooted into the substrates, one plant per pot.

The N source was analytical reagent grade ammonium nitrate (NH₄NO₃). N was supplied at rates of 0 kg N ha⁻¹ (0 g pot⁻¹), 50 kg N ha⁻¹ (0.2 g pot⁻¹), 100 kg N ha⁻¹ (0.4 g pot⁻¹), 200 kg N ha⁻¹ (0.8 g pot⁻¹) and 400 kg N ha⁻¹ (1.6 g pot⁻¹), respectively (Appendix C for calculation of application rates).

The pot trial was conducted in the glass houses of Lincoln University for 24 weeks (May to September 2007), with the maximum temperature at 21°C and minimum 13°C. Throughout the experiment, plants were watered to 90% field capacity. Every 2-3 days tap water was added to the plant, by putting every pot on a balance and added the water. The amount of water added was dependent on the amount of water lost during the 2-3 days by comparing with the original weigh of the pot treatment (Appendix F for field capacity calculation).

The trial was set up as a randomised block design (2 substrates x 2 plants x 5 N rates = 20 treatments) with four replicates of each treatment (Table 6.2). Blocks were positioned across the glasshouse so that each replicate equalled a block (i.e. all replicate 1= block one, all replicate 2= block two, etc.). The treatments in each block were re-randomized every month.
Table 6.2 Experimental design

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Topsoil</td>
</tr>
<tr>
<td></td>
<td>Overburden</td>
</tr>
<tr>
<td>Plant</td>
<td>Red beech (<em>Nothofagus fusca</em>, tree spp.)</td>
</tr>
<tr>
<td></td>
<td>Wineberry (<em>Aristotelia serrata</em>, shrub spp.)</td>
</tr>
<tr>
<td>N rate</td>
<td>0 kg N ha(^{-1})</td>
</tr>
<tr>
<td></td>
<td>50 kg N ha(^{-1})</td>
</tr>
<tr>
<td></td>
<td>100 kg N ha(^{-1})</td>
</tr>
<tr>
<td></td>
<td>200 kg N ha(^{-1})</td>
</tr>
<tr>
<td></td>
<td>400 kg N ha(^{-1})</td>
</tr>
</tbody>
</table>

6.2.1 Plant analysis

The total biomass (root + shoots) and the shoot N concentration (Chapter 3 section 3.3.1) were measured at the end of experiment in order to determine treatment effects.

6.3 Results

In this section, results from plant shoot analysis are presented. The plant results are also presented in Appendix E.

To address the hypothesis, the results presented here are based on the interaction results between the N rate, plant and substrate. As a result, there was a significant interaction between amendment, plant and substrate on the values of dry matter weight and shoot N (Table 6.3).

Table 6.3 ANOVA main effects of amendment, plant and substrate on plant characteristics.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>DM (g plant(^{-1}))</th>
<th>Shoot N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N rate</td>
<td>4</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Plant</td>
<td>1</td>
<td>***</td>
<td>*</td>
</tr>
<tr>
<td>Substrate</td>
<td>1</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>N rate x plant</td>
<td>4</td>
<td>**</td>
<td>***</td>
</tr>
<tr>
<td>N rate x substrate</td>
<td>4</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Plant x substrate</td>
<td>1</td>
<td>ns</td>
<td>***</td>
</tr>
<tr>
<td>N rate x plant x substrate</td>
<td>4</td>
<td>***</td>
<td>***</td>
</tr>
</tbody>
</table>

Note: *** P< 0.001; ** 0.001 ≤ P< 0.01
* 0.01 ≤ P< 0.05 level; ns = non significant difference (P≥ 0.05)

6.3.1 Dry matter

Application of N to the topsoil increased the dry weight of Red beech and Wineberry (Figure 6.1, Table 6.3). Both species showed a similar pattern: from 0 to 50 kg N ha\(^{-1}\) the dry weight increased, at higher N rates the dry matter weight reached a plateau. In the overburden, both species showed a different pattern of dry matter gain (Figure 6.2, Table 6.3). By increasing
the N application rate from 0 to 400 kg ha\(^{-1}\), the Red beech dry weight gradually increased. In contrast, the Wineberry dry matter weight gradually decreased.

In the topsoil, at the highest application rate (400 kg N ha\(^{-1}\)) the plants showed a different response to the highest N rate; the Red beech dry matter weight decreased, whilst the Wineberry dry matter weight increased (Figure 6.1).

However, in the overburden, both species showed a similar effect to the highest N rate addition; the Red beech dry matter weight decreased and for the Wineberry all plants in the highest N rate died during the experiment and therefore no dry matter weights were determined for this treatment (Figure 6.2).

![Figure 6.1: Dry matter yield of Red Beech (Nothofagus fusca) and Wineberry (Aristotelia serrata) seedlings grown in a pot trial using topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with 5 different N rates. Means and standard errors are shown (n = 4 for each treatment).](image-url)
6.3.2 Shoot N

Increasing the N application rates from 0 to 400 kg ha$^{-1}$ increased the shoot N concentration in the Red beech and Wineberry in the topsoil (Figure 6.3) and overburden (Figure 6.4).

In the topsoil, compared to the 200 kg N ha$^{-1}$ at the highest N rate (400 kg N ha$^{-1}$) both species showed contrasting effects. The Red beech shoot N concentration increased, whereas for Wineberry there was no difference in shoot N concentration between the 200 and 400 kg ha$^{-1}$ (Figure 6.3). For Wineberry, at the highest N rate all of the Wineberry plants died, thus no shoot N concentration were determined for this particular treatment (Figure 6.4).
Figure 6.3 Shoot N concentration of Red Beech (*Nothofagus fusca*) and Wineberry (*Aristotelia serrata*) seedlings grown in a pot trial using topsoil collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with 5 different N rates. Means and standard errors are shown (n = 4 for each treatment).

Figure 6.4 Shoot N concentration of Red Beech (*Nothofagus fusca*) and Wineberry (*Aristotelia serrata*) seedlings grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and amended with 5 different N rates. Means and standard errors are shown (n = 4 for each treatment).
6.4 Discussion

Plant response to N fertiliser depends on soil conditions, plant species and especially depends on the amount of available N in the soil solution and the amount of N which will become available during the growth period (Mengel & Kirkby, 2001). Thus to ensure that the topsoil or overburden could provide sufficient N to support the vegetation in a re-vegetation scenario, it was necessary to supply the growth medium with suitable rate of N application. The following discussion will focus on the effect of a high N application rate on the growth medium, in order to address the hypothesis that the application of high N rate will hamper the plant growth; it may due to N toxicity in both plant species. In addition, the internal N requirement of both plant species will be discussed.

6.4.1 Differences in response to N for Red beech & Wineberry grown in topsoil and overburden

The rate of N application for optimal dry-matter production in topsoil was 200 kg ha\(^{-1}\) for Red beech and 400 kg ha\(^{-1}\) for Wineberry (Figure 6.1). Both plants had adequate growth at 200 kg ha\(^{-1}\) and so it is suggested that this would be a suitable overall rate for N application the topsoil for restoration purposes. In comparison, the N application rate resulting in optimal dry-matter yield in overburden was 50 kg ha\(^{-1}\) for Red beech and 0 kg ha\(^{-1}\) Wineberry (Figure 6.2). The differences in N requirement between substrates can probably be explained by differences in the characteristics of the substrates (Mengel & Kirkby, 2001). Analysis of the shoot N concentration in the substrates showed that the reduced N requirement in overburden was not due to the presence of adequate N in this substrate as there was approximately one third the N in the un-amended overburden compared to the un-amended topsoil (Table 6.1) and the previous measurements of extractable N in the un-amended overburden was similar to that in un-amended topsoil (Figures 4.5, 4.6, 4.7 and 4.8). In addition, the concentrations of N in the plants were roughly comparable for the same N application rate across substrates (Figure 6.3 and 6.4). This suggests that the lack of response to N application of plants grown in the overburden was probably due to other factors limiting growth (possibly micronutrients), and thus, response to N. To achieve optimal growth of plants growing in the overburden it is therefore necessary to investigate what the limiting factors might be and to ameliorate the limiting factor(s). Once ameliorated it is likely that both species would show a greater response to N in the overburden. A number of potentially limiting factors are investigated in other chapters of this thesis (Chapter 4 and 7). The results presented in this Chapter suggest
that the lack of N response in Wineberry compared with Red beech in section 4.4.2 was not due to a lower internal N requirement in Wineberry for optimal growth.

### 6.4.2 Internal plant requirement for N

The concentration of N in the shoot of Red beech and Wineberry was 1.53 and 1.96 % respectively at the optimal rate of N application in topsoil which resulted in the targeted optimal yield (Section 6.4.1; 200 kg N ha$^{-1}$) the concentration of N in the shoots of Red beech and Wineberry was 1.53 and 1.96 % respectively (Figure 6.3). These results suggest that Wineberry has a greater internal N requirement and therefore requires a greater concentration of N in the shoot than Red beech for optimal growth. This is not what would be intuitively expected as Wineberry is a pioneer species, whereas Red beech is a later successional species (Norton, 1991). Pioneer species regularly encounter growth substrates that are relatively low in N (Begon et al., 2006) and thus need to be efficient at absorbing N from the growth substrate or have other means of obtaining N such as N-fixation by the legume-rhizobium symbiosis (Hanly & Gregg, 2004). However, Wineberry is a fast growing species, thus the species could require more N to ensure rapid growth as compared to the relatively slow growing Red beech. It could also be that the true optimal N rate lies between 200 and 400 kg ha$^{-1}$ for both species and this there might be little difference in N requirement for optimal yield of the two species. Thus the results presented here suggest that the lack of N response in Wineberry compared with Red beech in section 3.4 was not due to a lower internal N requirement in Wineberry for optimal growth.

For plants grown in overburden, the shoot N concentrations of the treatment giving optimal growth were 1.22 and 0.65 % respectively for Red beech and Wineberry (Figure 6.4). These concentrations are lower than those considered adequate for Red beech and other similar species (Wardle, 1991). At the highest rate of N application neither species had reached N tissue concentrations that would generally be considered toxic (Figure 6.4 and Wardle, 1991) despite significant decreases in biomass production (Figure 6.2). As further N was added to the overburden the shoot N concentrations continued to increase (Figure 6.4). This gives further credence to the suggestion in section 6.4.1 that Red beech and Wineberry grown in overburden were limited by another factor besides N supply.
6.5 Conclusions

- The optimal rate of N in the topsoil was 200 kg N ha\(^{-1}\), and 400 kg N ha\(^{-1}\) for Red beech and Wineberry respectively, with a general recommendation of 200 kg N ha\(^{-1}\) for post-mining reclamation at the OceanaGold Globe-Progress Gold Mine.
- Plants grown in overburden appeared to be limited by other unidentified factors more than by N. It is therefore recommended that limiting factors are identified and removed so that plants grown in overburden can respond to N applications.
- The results suggest that the decrease in plant growth was not due to N toxicity in Red beech and Wineberry.
- The results also suggest that the lack of N response in Wineberry compared with Red beech was not due to a lower internal N requirement in Wineberry for optimal growth.
- The results presented suggest that the overburden tested is limiting plant growth and unless these factors can be identified and ameliorated it is suggested that restoration processes include a topsoil layer fertilised at 200 kg N ha\(^{-1}\).

This result suggested that overburden has the potential to be used as a growth medium, even though plants grown in the overburden appeared to be limited by nutrient availability. In contrast, the overburden also demonstrated potential as a source of soil nutrients, but these are contained in the primary minerals. As a result, further experimentation is required on the effects of short-term weathering processes on the overburden material. Altering the water regime status and adding organic and inorganic amendments may well accelerate weathering processes. Weathering will break down the primary minerals, and release cations, which will contribute to the nutrient status of the overburden and thus support re-vegetation processes.
Chapter 7
Short-term Weathering of Mine Overburden Material

7.1 Introduction

On mining sites, excavation breaks up overburden materials thus exposing the fresh material to weathering. Weathering of mining wastes is an important process because it may increase the availability of nutrients or heavy metals to plants; elements present in the mineral are released from the crystal lattice as weathering progresses (Bradshaw, 1997).

There are two forms of weathering: physical and chemical. Physical weathering is the disintegration of rock without changing the chemical composition (Bland & Rolls, 1988). Chemical weathering is the changes of chemical and/or mineralogical composition of the original rock and minerals (Carol, 1970). The connection between chemical weathering and the physical weathering processes can be close; for example, chemical alteration may reduce the strength of a rock to a level at which the stresses of mechanical weathering are adequate to cause break down and increase the rock surface area (Bland & Rolls, 1988).

Water and gasses dissolved in rocks and minerals are the main cause of chemical weathering reactions. As water percolates through soil or rocks it often reacts with the constituent minerals or organic matter, thus changing the chemical composition of the water (Nahon, 1991). Chemical weathering will decompose the chemical and/or mineralogical composition of the original rock and mineral. Aluminium and iron are the two key elements in weathering and pedogenic processes (Van Hees et al., 2006), and the common reaction products of chemical weathering are the clay minerals and hydrous oxides of Al and Fe (Birkeland, 1999). Description of these products is important because of their impact on soil properties; they reflect the long-term effect of the chemical and leaching environment of the soil, and they influence many soil properties (such as surface exchange properties, cation and phosphorous retention) (Birkeland, 1999). Weathering will result in the breakdown the crystal lattice of the primary minerals in the overburden. There will be two main effects; the release of nutrients (cations) and the release of heavy metals from within the crystal lattice.
Nutrient deficiencies and heavy metal toxicities can be major issues in the restoration of mining areas (Sengupta, 1993). Nutrient reactions with the soil surface are affected by the chemical and physical properties of the soil surface which in turn is related to the nature of the inorganic and organic materials from soil particle. The character of soil particles will depend on the physical, chemical and biological weathering of substrates (Barber, 1995). During weathering processes, organic matter penetrates into the system by means of oxidation (consumption of O₂) and its mineralization (production of CO₂) (Nahon, 1991). Furthermore, the nature of overburden may change due to the application of organic amendments and water regimes through weathering period that could speed up nutrient release and help to overcome other chemical and physical limitations to plant growth by means of a pot trial.

The objective of this chapter was to investigate the effects of short-term weathering regimes in combination with amendments (both organic and inorganic) on the overburden and hence, the production of a viable growing medium. This was investigated by means of pot trial.

7.2 Materials and Methods

The overburden was used as the growth medium substrate (Chapter 3 section 3.1.1). The overburden was air dried, crushed manually, and passed a 1.5 cm mesh sieve before placing in pots. The pot size used in this experiment had a diameter of 15 cm and 11.5 cm high. The inside of the pot was covered by a plastic bag and filled with the substrate. Each pot contained 3.5 kg of air-dry overburden.

Four different amendments were used in the experiment; biosolids, lupin as a green manure, N fertiliser, and lime. The biosolids were collected three days before use from the Christchurch City Council waste water treatment plant at Bromley, Christchurch and kept in sealed containers at 4°C until being applied to the pots. The biosolids were obtained from the belt-press at the end of the waste treatment process and contained approximately 25 ± 5% solid (Table 3.2 for characterization of the biosolids). The N source was analytical reagent grade ammonium nitrate (NH₄NO₃). Lupin plants for green manure were collected from Lincoln University experimental plots (Iversen fields) on the day of application to the pots. Lupin roots were washed with tap water, then the whole plant (shoots and roots) was chopped into 1 cm lengths. The lime source was analytical reagent grade CaCO₃ (calcium
carbonate). Biosolids, N and lupins were applied at the rate of 200 kg N ha$^{-1}$ which was equivalent to 1 g N pot$^{-1}$, fresh weight biosolid (water content 80.33%) was 31.5 g pot$^{-1}$, lupin was 56.43 g pot$^{-1}$, and lime was 86 g pot$^{-1}$ (Appendix D for application rate calculations).

The pot trial was conducted in the glass houses of Lincoln University for 24 weeks (May 2007 to January 2008), with a maximum temperature of 25$^\circ$C and minimum of 14$^\circ$C. The trials were set up as a randomised block design (1 substrate x 5 soil amendments x 4 water treatments x 1 plant = 20 treatments) with four replicates of each treatment (Table 7.1). Blocks were positioned across the glasshouse so that each replicate equalled a block (i.e. all replicate 1= block one, all replicate 2= block two, etc.). The treatments in each block were re-randomized every month.

**Table 7.1 Experimental design of this experiment.**

<table>
<thead>
<tr>
<th>Growth medium</th>
<th>Amendment</th>
<th>Weathering treatment (Phase 1; T$_{1}$)</th>
<th>Plant (Phase 2; T$_{2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overburden</td>
<td>• Control</td>
<td>• Continuous air dry</td>
<td>• Lupin</td>
</tr>
<tr>
<td></td>
<td>• N fertilizer (200 kg N ha$^{-1}$)</td>
<td>• Wet and dry (2 weeks 90 % field capacity alternating with 2 weeks of drying)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Biosolid (200 kg N ha$^{-1}$)</td>
<td>• Aerobic (90 % field capacity continuously)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Lupin (200 kg N ha$^{-1}$)</td>
<td>• Anaerobic (saturated continuously)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Lime (24.9 t ha$^{-1}$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The experiment was divided into 2 phases. In the first phase, the overburden was determined for 90% field capacity (Appendix F for overburden field capacity calculations) then incorporated with amendments and then subjected to four different short-term weathering regimes for 24 weeks:

- Continuous air dry: the treatment was maintained dry (no water added) during the weathering period.
- Wet and dry: the treatment was maintained at 90% field capacity for two weeks and dry for 2 weeks. During the wet stage, every 2-3 days the treatment was added by putting every treatment pot on a balance and adding tap water. The amount of water added was dependent on the amount of water lost during the dry stage by comparing with the original weight of the pot treatment.
• Aerobic: the treatment was always maintained to 90% field capacity during the weathering period. Every 2-3 days the treatment was added by putting every treatment pot on a balance and added with tap water. The amount of water added was dependent on the amount of water lost during the 2-3 days by comparing with the original weight of the pot treatment.

• Anaerobic: the treatment was maintained in a saturated stage during the weathering period. The water added up to a 1 cm mark above the substrate surface. Every 2-3 days the treatment was added by tap water up to the mark.

To provide baseline data, 200 g pot$^{-1}$ of material plus the soil amendment was sampled (having been mixed thoroughly) prior to the incubation period; this is referred to as T$_o$ in the results section. At the end of the 24 week period, sampling at this time point is referred to in the results section as T$_i$. A sufficient amount of substrate (approximately 200 g) sample for soil analysis was collected from the pot trial and placed in plastic bags. The substrates were air dried in the drying cabinet at 25°C for 4 days, and then used for soil analysis.

The second phase of the experiment commenced at the end of the T$_i$. In the second phase, Lupin (*Lupinus angustifolius*) was planted (5 seeds per pot, thinned to 3 plants after 21 days) in the treated substrates and grown for 60 days to measure plant responses to the weathering regimes instigated in the first phase (Figure 7.1). Lupin (as opposed to Red beech or Wineberry) was selected as the test plant due to its rapid growth response to allow harvest within 60 days. Sampling at this time point is referred to in the results section as T$_h$. In phase 2, the water status of all substrates was maintained at 90% field capacity to provide ideal growing conditions for the plants. The Lupin plants were harvested after 60 days. Each plant was carefully separated and washed from the growth medium according to the procedure determined in Chapter 3 section 3.3.
7.2.1 Analyses

Two sets of analysis were carried out: substrate analysis (pH, EC, exchangeable cation) (Chapter 3 section 3.2.1) and plant analysis (total dry matter weight, shoot N, P, S, Ca, Na, Mg, Na, K and heavy metals concentration) (Chapter 3 section 3.3.1). In addition, substrate also was analysed to determine the extractable Al, Fe, Si and particle size distribution.

7.2.1.1 Extractable Al, Fe, and Si

Selective dissolution techniques were used to determine the pools of Si, Al and Fe in substrate solution.

- Dithionite-citrate-bicarbonate (DCB) extraction

The tri-sodium citrate (0.3M) and sodium hydrogen carbonate (1.0M) were used as the reagent for Al, Fe, and Si in the substrates. The tri-sodium citrate (0.3M) was made by dissolving 88.23 g of tri-sodium citrate into 1 L of deionised water. The sodium hydrogen carbonate (1.0M) was made by dissolving 84.01 g of sodium hydrogen carbonate into 1 L of deionised water.

A sample of 1.0 g of substrate with 40 ml of tri-sodium citrate solution and 10 ml of sodium hydrogen bicarbonate solution placed in the tube was brought to 75-80°C in water bath. Then 1 g sodium dithionite was added to the sample (added in approximately three equal amounts to minimize frothing). The samples were left in the water bath for a further
15 minutes after the last addition of sodium dithionite. Then, the samples were centrifuged at 2000 rpm for 10 minutes and filtered through Whatman No. 52 (Blakemore et al., 1987). Determination of dithionite-citrate-bicarbonate (DCB) extractable Al, Fe, and Si was done by ICP-OES. To calculate the DCB extractable Si, Al and Fe, the following calculation was performed: Si/Al/Fe (%) = (µg/ml-blank) x 50 /weight of sample (g) x 10^-4

- **Acid oxalate extraction**

Acid oxalate reagent was made by dissolving 81.0 g of ammonium oxalate \((\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O})\) and 54.0 g of oxalic acid \((\text{COOH})_2\cdot\text{H}_2\text{O})\) into 5 L of deionised water. The reagent was measured at pH \(3 \pm 0.05\), if necessary adding 2-5 drops of 0.2M oxalic acid to adjust the pH. The 0.2M oxalic acid was made by dissolving 12.60 g of oxalic acid into 500 ml of deionised water.

For each sample, 2.0 g of substrate (air dry, < 2mm) was combined with 50 ml of acid oxalate reagent, shaken for 4 hours, with the extraction carried out in the dark. Then, the samples were centrifuged at 2000 rpm for 10 minutes, and filtered through Whatman No. 42 (Blakemore et al., 1987). Determination of Al, Fe, Si was done by ICP-OES.

To calculate the oxalate extractable Fe, Al and Si, the following calculation was performed: Si/Al/Fe (%) = (µg/ml – blank) x 0.025

- **Pyrophosphate extraction**

The sodium pyrophosphate \((\text{Na}_4\text{P}_2\text{O}_7\cdot10\text{H}_2\text{O})\) (0.1M) and 0.2% superfloc solution were used as a reagent to extract Al and Fe from the substrate. The 0.1M sodium pyrophosphate was made by dissolving 223 g of sodium pyrophosphate into 5 L of deionised water. The superfloc was made by dissolving 0.2 g of superfloc into 100 ml of deionised water.

For each sample, 0.35 g of substrate (air dry, < 2mm) and 35 ml of sodium-pyrophosphate were shaken for 16 hours. After that, five drops of 0.2% superfloc was added and shaken vigorously. Then the samples were centrifuged at 20 000 rpm for 30 minutes, and filtered through Whatman No. 42 (Blakemore et al., 1987). Determination of Al, Fe, Si was done by ICP-OES.

To calculate the pyrophosphate extractable Fe, Al and Si, the following calculation was performed: Si/Al/Fe (%) = (µg/ml – blank) x 0.05
Processing and calculation of the extraction results

Throughout this thesis, the oxalate extractable Si, Al and Fe will be written with the subscript o (i.e. Si_o, Al_o, Fe_o); for DCB extraction with the subscript d (i.e. Si_d, Al_d, Fe_d), and for pyrophosphate extraction with the subscript p (i.e. Si_p, Al_p, Fe_p).

In order to estimate the amount of the short-range order clay minerals (SRO’s), the allophane content, and the amount of amorphous bound Fe (ferrihydrite) in the substrate, the following calculations were performed:

- The calculation of oxalate extractable Al, Fe and Si indicated the amount of Fe and Al organic and in-organic forms of the non-crystalline clay components and also poorly crystalline (allophone/imogolite) forms in the substrate (Broquen et al., 2005; Drouza et al., 2007; Duncan & Franzmeier, 1999; Eger, 2007; Lilienfein et al., 2003; Parfitt & Kimble, 1989; Parfitt et al., 1988; Wada, 1980).

- The calculation of Al and Fe from pyrophosphate extractions indicated the amount of non-crystalline, organically bound Al and Fe (Broquen et al., 2005; Drouza et al., 2007; Duncan & Franzmeier, 1999; Eger, 2007; Lilienfein et al., 2003; Parfitt & Kimble, 1989; Parfitt et al., 1988; Wada, 1980).

- The method for estimating the allophane (Al_2Si_2O_5.nH_2O) content (the Al/Si ratio) was based on the ratio of (Al_o – Al_p)/Si_o. If the ratio is close to 1, this indicates allophane and allophane-like minerals; if close to 2, this indicates imogolite-like minerals (Broquen et al., 2005; Drouza et al., 2007; Duncan & Franzmeier, 1999; Eger, 2007; Lilienfein et al., 2003; Parfitt & Kimble, 1989; Parfitt et al., 1988; Wada, 1980).

- Fe_o/Fe_d indicates the activity ratio of ferrihydrite, the degree of ageing and crystallinity of the free iron oxides. A high Fe_o/Fe_d ratio is interpreted as an indication of low iron crystallinity (Schwertmann et al., 1993).

- To estimate the amount of ferrihydrite (HFe_5O_8.4H_2O) percentage, the following calculation was used: ferrihydrite (%) = 1.7*Fe_o (Birkeland, 1999; Eger, 2007; Parfitt et al., 1988).
7.2.1.2 **Particle size distribution**

To determine the particle size distribution at times T₀ and T₁, 5 g of air-dried sieved overburden was put in a 50 ml beaker glass. In the fume cupboard, a sufficient volume of 10% hydrogen peroxide (H₂O₂) was added to the sample until the solution covered the sample. The mixture was left overnight and then a further 5 ml of H₂O₂ was added to the sample and heated gently on a hotplate. If the sample frothed, 1-2 drops of amyl alcohol was added to reduce the frothing. A small volume of distilled water was used to rinse down the beaker to remove particles adhering to walls. The sample was heated until the volume had reduced to approximately 5 ml of slurry and then left to cool. Then, 10 ml of 10% calgon was added and the sample left overnight. The samples were then placed in an ultrasonic bath for 5 minutes before the particle size distribution was determined with a Malvern Mastersizer 2000 version 5.22 (Malvern, UK).

7.3 Results

In this section, results from the soil analysis (overburden) and plant analysis are presented. The substrate and plant results are also presented in Appendix E.

7.3.1 Soil properties

Analysis of variance (ANOVA) for the main effect of the amendments, time (before (T₀) and after weathering (T₁)), and weathering regime on overburden characteristics was calculated (Table 7.2). To test the hypothesis, the results presented here are based on the interaction results between different incubation time and weathering regime status (TₓW); and incubation time and amendment (TₓA). The statistical analysis showed that during the incubation time, the amendments significantly affected the pH, EC, cations (Ca, Mg and K), and clay percentage. The weathering regime status significantly affected the pH, Ca, and Na level.
Table 7.2 The ANOVA of selected elements composition of the overburden.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>pH (µS cm⁻¹)</th>
<th>EC (µS cm⁻¹)</th>
<th>Ca (cmol_c kg⁻¹)</th>
<th>Mg (cmol_c kg⁻¹)</th>
<th>Na (cmol_c kg⁻¹)</th>
<th>K (cmol_c kg⁻¹)</th>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amendment (A)</td>
<td>4</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>ns</td>
<td>***</td>
<td>*</td>
<td>ns</td>
<td>***</td>
</tr>
<tr>
<td>Weathering regime (W)</td>
<td>3</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>ns</td>
<td>***</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Time (T)</td>
<td>1</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>ns</td>
<td>***</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>A x W</td>
<td>12</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
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<tr>
<td>T x A</td>
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<tr>
<td>T x W</td>
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<tr>
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</tbody>
</table>

Note: *** P< 0.001; ** 0.001 ≤ P< 0.01
* 0.01 ≤ P< 0.05 level; ns = non significant difference (P≥0.05)

7.3.1.1 pH

Weathering regime effect on pH over time

There was a significant effect between incubation time and weathering regime status (P< 0.001) on the pH level (Table 7.2). After 24 weeks incubation, the an-aerobic regime resulted in values up to 0.1 pH unit higher than the other water regimes (Figure 7.2). Comparing the pH before weathering (T₀) with after weathering (T₁) showed the substrate in the aerobic weathering regime had a slightly reduced pH. Both wet-dry cycles and the anaerobic regimes resulted in an increase of the substrate pH, while the continuously air dry regime had no significant change of pH after incubation.

![Figure 7.2 Substrate pH level, before (T₀) and after (T₁) weathering of overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four weathering regimes (air-dry, aerobic, wet-dry and an-aerobic). Means and standard errors are shown (n = 4 for each treatment). Treatments means followed by the same lower case letter were not significantly different (P>0.05).](image-url)
**Amendment effect on pH over time**

There was a significant effect of incubation time and amendment \((P< 0.001)\) on the pH level (Table 7.2). Before \((T_o)\) and after \((T_i)\) weathering, the N and lime increased the pH of the material, but there was no significant effect of biosolid and lupin treatment on pH \((P<0.05)\) between \(T_o\) and \(T_i\) (Figure 7.3).

![pH graph](image)

Figure 7.3 The pH level, before \((T_o)\) and after \((T_i)\) weathering in the overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four amendments (biosolid, N, lupin and lime). Means and standard errors are shown \((n = 4\) for each treatment). Treatments means followed by the same lower case letter were not significantly different at \(P>0.05\).

**7.3.1.2 Electrical conductivity**

**Weathering regime effect on EC over time**

The ANOVA (Table 7.2) showed that there was no significant effect between incubation time and weathering regime status on the EC level \((P<0.05)\).
Amendment effect on EC over time

There was a significant effect between incubation time and amendment ($P < 0.001$) on the EC level (Table 7.2). At $T_t$, biosolid and lupin as organic amendments increased the EC. In contrast, N and lime as in-organic amendments reduced the EC level. In a similar way to the organic amendments, after weathering ($T_i$), the EC level of the control also increased but the level was lower for the than other amendments.
Figure 7.5 The substrate EC, before (To) and after (Ti) weathering of overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four amendments (biosolid, N, lupin and lime). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different (P>0.05)

### 7.3.1.3 Particle size distribution

Preliminary observations on the overburden material indicated that the material broke apart easily with moderate blows of a geological hammer. The nature of the weakly argillic rock would suggest that a lack of cohesion, combined with desiccation would contribute to the rock breaking apart along natural planes of weakness.

**Weathering regime effect on particle size distribution with time**

There was no significant effect between incubation time and weathering regime status at T₀ and Tᵢ on the clay, silt and sand distribution (P>0.05) (Figure 7.6).
Figure 7.6 The clay, silt and sand concentration, before (T₀) and after (T₁) weathering in the overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four weathering regimes status (air-dry, aerobic, wet-dry and an-aerobic). Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the overburden clay (a), silt (b) and sand percentage (c) (P>0.05).

Amendments effect on particle size distribution over time

There was no significant effect between incubation time and amendment on the silt and sand percentage at T₀ and T₁ (P>0.05) (Figure 7.7). The treatments affected clay percentage only (P< 0.05) and liming increased the clay percentage more than the other amendments trialled due to a flocculation effect (Figure 7.7a).
Figure 7.7 The clay, silt and sand concentration, before (T₀) and after (T₁) weathering in the overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four amendments (biosolid, N, lupin and lime). Means and standard errors are shown (n = 4 for each treatment). Treatments means followed by the same lower case letter were not significantly different at \( P < 0.05 \). There was no significant difference for the overburden silt (b) and sand percentage (c) \( P > 0.05 \).

### 7.3.1.4 Exchangeable cations

Weathering regime effect on soil cations over time

There was a significant effect between incubation time and weathering regime status \( (P<0.001) \) on the exchangeable Ca and Na \( (P<0.001) \), but not on Mg and K (Table 7.2). After weathering \( (T₁) \), air-dry and wet-dry weathering regime status reduced the exchangeable Ca on the substrate; whilst aerobic and an-aerobic status increased the Ca. Wet-dry weathering regime status reduced exchangeable Ca from 9 to 1 cmolc kg\(^{-1}\). For Na, after weathering \( (T₁) \), weathering regime status increased the exchangeable Na, with an-aerobic weathering regime status increasing the most, followed by the continually aerobic weathering regime status (Figure 7.8).
Figure 7.8 The AgTu exchangeable Ca, Mg, Na and K concentration, before (T₀) and after (T₁) weathering in the overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four weathering regimes status (air-dry, aerobic, wet-dry and an aerobic). Means and standard errors are shown (n = 4 for each treatment). Treatments means followed by the same lower case letter were not significantly different at \( P < 0.05 \). There was no significant difference for the overburden exchangeable Mg (b) and K (d) (\( P > 0.05 \)).

Amendments effect on soil cations over time

There was a significant effect between incubation time and amendment (\( P < 0.001 \) level) on the exchangeable Ca, Mg and K (\( P < 0.001 \)), but not on Na (Table 7.2).

Lime increased exchangeable Ca higher than other amendments, however the exchangeable Ca before (T₀) and after (T₁) weathering did not change significantly, except for lime amendment (Figure 7.9a). The biosolid treatment increased the exchangeable Ca on the overburden.

After weathering (T₁), both the biosolid and N amendments increased exchangeable Mg relative to the lupin amendment; the lime amendment reduced exchangeable Mg. This was a similar pattern to that demonstrated by the control. Exchangeable K was increased by the addition of lupin at both T₀ and T₁, compared to the control.
Figure 7.9 Exchangeable Ca, Mg, Na and K concentration, before (To) and after (Ti) weathering in the overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four amendments (biosolids, N, lupin green manure and lime). Means and standard errors are shown (n = 4 for each treatment). Treatments means followed by the same lower case letter were not significantly different at \( P<0.05 \). There was no significant difference for the overburden exchangeable Na (c) \( (P>0.05) \).

7.3.2 Geochemistry

7.3.2.1 Estimation of short-range order (SRO) clays values

The result of analysis of variance (ANOVA) for the main effect of the amendments, time, and water regimes status and their interaction with extractable Si, Al, and Fe is presented in Table 7.3. The results presented here are based on the interaction results between different time and weathering regime (TxW); and time and amendment (TxA).
Table 7.3 The ANOVA for selected extractable Al, Fe, Si and short-range order clays mineral of the overburden.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>Si&lt;sub&gt;p&lt;/sub&gt;</th>
<th>Al&lt;sub&gt;p&lt;/sub&gt;</th>
<th>Fe&lt;sub&gt;p&lt;/sub&gt;</th>
<th>Al&lt;sub&gt;p&lt;/sub&gt; (%)</th>
<th>Fe&lt;sub&gt;p&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amendment (A)</td>
<td>4</td>
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<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Weathering regime (W)</td>
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</tr>
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<td>***</td>
<td>***</td>
<td>**</td>
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<tr>
<td>T x A</td>
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<td>ns</td>
<td>ns</td>
<td>***</td>
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<tr>
<td>T x W</td>
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<td>ns</td>
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<td>***</td>
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<tr>
<td>T x A x W</td>
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<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
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</tr>
</tbody>
</table>

Note: *** P< 0.001; ** 0.001 ≤ P< 0.01
* 0.01 ≤ P< 0.05 level; ns = non significant difference (P≥0.05)

Weathering regime effect on oxalate extractable Si, Al and Fe over time

There was no significant effect between incubation time and weathering regime status on the oxalate extractable Si, Al and Fe at T<sub>0</sub> and T<sub>1</sub> (P>0.05) (Figure 7.10).

Figure 7.10 The oxalate extractable Si, Al and Fe concentration, before (T<sub>0</sub>) and after (T<sub>1</sub>) weathering in the overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four weathering regimes status (air-dry, aerobic, wet-dry and an-aerobic). Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the overburden extractable Si (a), Al (b) and Fe (c) (P>0.05).
Amendments effect on oxalate extractable Si, Al and Fe over time

There was no significant effect between incubation time and amendment on the oxalate extractable Si, Al and Fe at T₀ and T₁ (P>0.05) (Figure 7.11).

Figure 7.11 The oxalate extractable Si, Al and Fe concentration, before (T₀) and after (T₁) weathering in the overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand and used in a pot trial with four amendments (biosolid, N, lupin and lime). Means and standard errors are shown (n = 4 for each treatment). There was no significant difference for the overburden extractable Si (a), Al (b), and Fe (c) (P>0.05).
Weathering regime effect on pyrophosphate extractable Al and Fe over time

There was a significant effect between incubation time and weathering regime status on the pyrophosphate extractable Fe at $T_o$ and $T_i$ ($P>0.05$) (Figure 7.12).

Amendments effect on pyrophosphate extractable Al and Fe over time

There was significant effect between incubation time and amendment on the pyrophosphate extractable Fe at $T_o$ and $T_i$ ($P>0.05$) (Figure 7.13).
7.3.2.2  *Estimation of Allophane values*

There were no significant effects between incubation time and weathering regime status and/or amendments on percentage allophane \( \left( \frac{\text{Al}_{\text{o}} - \text{Al}_{\text{p}}}{\text{Si}_{\text{o}}} \right) \) \((P>0.05)\) (Table 7.4).

7.3.2.3  *Estimation of Ferrihydrite values*

There were no significant effects between time, weathering regime status and/or amendments on the activity ratio \( \left( \frac{\text{Fe}_{\text{o}}}{\text{Fe}_{\text{d}}} \right) \) and estimation of percentage ferrihydrite \((1.7* (\text{Fe}_{\text{o}} - \text{Fe}_{\text{p}}))) \((P>0.05)\) (Table 7.5).
Table 7.4 Calculation of estimation allophane ratios ($Al_o$-$Al_p$)/$Si_o$ from five different amendments and four different weathering regimes status.

<table>
<thead>
<tr>
<th>Amendment</th>
<th>Water Treatment</th>
<th>$Al_o$</th>
<th>$Al_p$</th>
<th>$Si_o$</th>
<th>$Al_o$/$Si_o$</th>
<th>$Al_o$-$Al_p$</th>
<th>$(Al_o$-$Al_p$)/$Si_o$</th>
<th>$Al_o$</th>
<th>$Al_p$</th>
<th>$Si_o$</th>
<th>$Al_o$/$Si_o$</th>
<th>$Al_o$-$Al_p$</th>
<th>$(Al_o$-$Al_p$)/$Si_o$</th>
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<td>Control</td>
<td>Air dry</td>
<td>0.76</td>
<td>0.23</td>
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<td>12.12</td>
<td>0.54</td>
<td>8.54</td>
<td>0.91</td>
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<td>0.11</td>
<td>8.16</td>
<td>0.67</td>
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<td>0.05</td>
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<td>7.29</td>
<td>0.88</td>
<td>0.17</td>
<td>0.12</td>
<td>7.62</td>
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<tr>
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<td>0.04</td>
<td>14.85</td>
<td>0.38</td>
<td>9.88</td>
<td>0.87</td>
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<tr>
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<td>4.97</td>
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<tr>
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<td>0.25</td>
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Table 7.5 Calculation of activity ratio $(Fe_o/Fe_d)$ and ferricydrite $(1.7*Fe_o)$ from five different amendments and four different weathering regimes status.

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<thead>
<tr>
<th>Amendment</th>
<th>Water Treatment</th>
<th>$Fe_o$</th>
<th>$Fe_p$</th>
<th>$Fe_d$</th>
<th>$Fe_o/Fe_d$</th>
<th>$1.7*Fe_o$</th>
<th>$Fe_o$</th>
<th>$Fe_p$</th>
<th>$Fe_d$</th>
<th>$Fe_o/Fe_d$</th>
<th>$1.7*Fe_o$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% (before weathering: $T_o$)</td>
<td></td>
<td></td>
<td></td>
<td>% (after weathering: $T_i$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>Air dry</td>
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<td>5.95</td>
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<td>1.05</td>
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<td>1.17</td>
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<td>3.57</td>
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<td>0.85</td>
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<td>1.52</td>
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<td>4.08</td>
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<td>1.21</td>
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<td>4.28</td>
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<td>1.17</td>
<td>3.85</td>
<td>7.68</td>
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</tbody>
</table>
7.3.3 Plant

The summary of ANOVA results for dry matter and element concentration in shoot lupin is presented in Table 7.6. The results presented here are based on the amendment effect (A); and the weathering regime status (W). The table showed that the amendments significantly affected element concentrations in the shoot lupin and the yield. Weathering regime status significantly affected the shoot Ca, Na, P, and S concentration in the plant, but there was no significant effect on dry matter, shoot N, Mg and K concentration.

Table 7.6 The ANOVA of selected element composition from shoot lupin.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Dry matter (g plant(^{-1}))</th>
<th>N (µg gram(^{-1}))</th>
<th>Ca (mg kg(^{-1}))</th>
<th>Mg (mg kg(^{-1}))</th>
<th>Na (mg kg(^{-1}))</th>
<th>K (mg kg(^{-1}))</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amendment (A)</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Weathering regime (W)</td>
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<td>ns</td>
<td>***</td>
<td>ns</td>
<td>**</td>
<td>ns</td>
<td>*</td>
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<td>A x W</td>
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<td>***</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>***</td>
</tr>
</tbody>
</table>

Note: *** P< 0.001; ** 0.001 ≤ P< 0.01
* 0.01≤P< 0.05 level; ns = non significant difference (P ≥ 0.05)

7.3.3.1 Dry matter weight

The experiment demonstrated that there was a significant difference (P<0.001) among the amendments to increase lupin dry matter. Lupin as an organic amendment (applied as a green manure) increased the dry matter the most, followed by biosolid (Figure 7.14b). Compared with the control, liming significantly reduced the lupin dry matter (P<0.05).

Figure 7.14 Dry matter yield of lupin (shoots + roots) (Lupinus angustifolius) seedling grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand, treated with four weathering regimes status (a) and four amendments (biosolid, N, lupin and lime) (b). Means and standard errors are shown (n = 4 for each treatment). Treatments means followed by the same lower case letter were not significantly different at P<0.05. There was no significant difference for the weathering regimes status (a) (P>0.05).
7.3.3.2 **Shoot N**

The result showed that there was no significant difference ($P>0.05$) between aerobic and other weathering regimes status to increase N concentration in shoot lupin (Figure 7.15a).

However, there was a significant difference among the amendments ($P<0.001$) (Table 7.6). Application of N increased the shoot N of lupin the most (Figure 7.15b).

![Shoot N concentration](image)

**Figure 7.15** Shoot N concentration in the lupin (*Lupinus angustifolius*) seedling grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand, treated with four weathering regimes status (a) and four amendments (biosolid, N, lupin and lime) (b). Means and standard errors are shown (n = 4 for each treatment). Treatments means followed by the same lower case letter were not significantly different at $P<0.05$. There was no significant difference for the weathering regimes status (a) ($P>0.05$).

7.3.3.3 **Shoot P**

The results showed that there was a significant difference ($P<0.05$) among the weathering regime status to change the P concentration in shoot lupin (Table 7.6). The air-dry weathering regime status contributed P to a greater extent than the aerobic weathering regime status (Figure 7.16a). All the weathering regimes decreased the shoot P uptake by lupin (compared to the air-dry weathering regime).

The pot experiment found that there was a significant difference among the amendments ($P<0.001$) on the shoot P of lupin (Table 7.6). The addition of biosolid increased the shoot P concentration of lupin higher than the other amendments (Figure 7.16b). Compared with the control, the shoot P of lupin was higher than lime, lupin and N, respectively.
7.3.3.4 Shoot S

There was a significant difference ($P<0.05$) among the weathering regime status to change the S concentration in shoot lupin (Table 7.6). The results showed that the air-dry weathering regime status increased the shoot S of lupin higher than any of the other weathering regimes status (Figure 7.17a). Furthermore, the aerobic weathering regime status contributed to shoot S lower than the an-aerobic and wet-dry status.

The experiment found that there was a significant difference among the amendments ($P<0.001$) on the shoot S of lupin (Table 7.6). Biosolid increased the shoot S higher than other amendments (Figure 7.17b). In addition, lupin and N contribution to S availability in shoot lupin was lower than the control.
7.3.3.5 Shoot Ca, Mg, Na and K

Weathering regime effect on shoot Ca, Mg, Na and K concentration

There was a significant effect of weathering regime status on the Ca ($P<0.001$) and Na ($P<0.01$) shoot concentration (Table 7.6). The Ca concentration in shoot lupin was higher than Mg, K and Na (Figure 7.18). There was no difference effect between aerobic, wet-dry and an-aerobic weathering regime status. The Na result showed a similar trend to that of Ca. There was no significant effect of weathering regimes status on shoot Mg and K concentrations.

Amendment effect on shoot Ca, Mg, Na, and K concentration

There were a significant effect of amendment status on shoot Ca, Na, Mg and K concentration ($P<0.001$) (Table 7.6). As the main source of Ca, lime as CaCO$_3$ increased the concentration of shoot Ca of lupin, and the concentration of shoot Ca in lupin was higher than Mg, K and Na concentration.
Figure 7.18 Shoot Ca (a), Mg (b), Na (c), and K (d) concentration in the lupin (*Lupinus angustifolius*) seedling grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand, treated with four weathering regimes status (a) and four amendments (biosolid, N, lupin and lime) (b). Means and standard errors are shown (n = 4 for each treatment). Treatments means followed by the same lower case letter were not significantly different at $P<0.05$. There was no significant difference for the Mg (b) and K (d) ($P>0.05$).

Figure 7.19 Shoot Ca (a), Mg (b), Na (c), and K (d) concentration in the lupin (*Lupinus angustifolius*) seedling grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand, treated with four weathering regimes status (a) and four amendments (biosolid, N, lupin and lime) (b). Means and standard errors are shown (n = 4 for each treatment). Treatments mean followed by the same lower case letter were not significantly different at $P<0.05$. 

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7.3.3.6 **Shoot heavy metals**

The summary of ANOVA results for metal concentration in shoot lupin is presented in Table 7.7. The results presented here are based on the amendment effect (A); and the weathering regime status (W). The table showed that amendments significantly affected the heavy metal bioavailability of lupin, except for the shoot Cr and Al. The weathering regimes status significantly affected the shoot As ($P<0.05$), Cr ($P<0.05$), Cu ($P<0.01$), Mn ($P<0.001$), and Ni ($P<0.05$) concentration of the plant, but there was no significant effect for the shoot Cd, Fe, Al, Pb and Zn.

Table 7.7 The ANOVA of selected metals composition from shoot lupin.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe ($\text{mg gram}^{-1}$)</th>
<th>Mn</th>
<th>Ni</th>
<th>Al</th>
<th>Pb</th>
<th>Zn</th>
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</thead>
<tbody>
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<td>***</td>
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<td>***</td>
<td>*</td>
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<td>***</td>
</tr>
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<td>*</td>
<td>**</td>
<td>ns</td>
<td>***</td>
<td>*</td>
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<td>*</td>
</tr>
<tr>
<td>A x W</td>
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<td>*</td>
<td>ns</td>
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</tbody>
</table>

Note: *** $P<0.001$; ** $0.001 \leq P < 0.01$

* $0.01 \leq P < 0.05$ level; ns = non significant difference ($P \geq 0.05$)

**Weathering regime effect on shoot heavy metals concentration**

The results reported here show that the weathering regime status affected the As, Cu, Mn and Ni concentration in the plant (Table 7.7). The concentration of shoot As (Figure 7.20a) and Cr of lupin increased the most under an-aerobic weathering regime status (Figure 7.20c), whilst the concentration of shoot Cu (Figure 7.20e) under air dry weathering regime status was higher than either the aerobic, wet-dry or the an-aerobic status. The concentration of shoot Cr (Figure 7.20c) in air dry weathering regime status was close to the Cr concentration in an-aerobic status.

**Amendment effect on shoot heavy metals concentration**

Amendments affected the concentration of shoot As, Cd, Cu, Mn, Ni, Pb and Zn of lupin (Table 7.7). Compared with the control treatment, the amendments reduced the concentration of shoot Cd, Cu, Mn, and Ni of lupin (Figure 7.21 and 7.22). However, some amendments (lupin, N and biosolid) increased the heavy metal bioavailability; lupin as a green manure increased the concentration of shoot As (Figure 7.21a). In no case did N increase uptake. However, liming noticeably reduced the concentration of shoot Pb (Figure 7.21d), Ni (Figure 7.22a), and Mn (Figure 7.22e) of lupin close to 0 mg kg$^{-1}$. 
Figure 7.20 Shoot As (a), Cd (b), Cr (c), Pb (d), and Cu (e) concentration in the lupin (Lupinus angustifolius) seedling grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand, treated with four weathering regimes status. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. There was no significant difference for the Cd (b), and Pb (d) ($P>0.05$).
Figure 7.21 Shoot Ni (a), Zn (b), Al (c), Fe (d), and Mn (e) concentration in the lupin (*Lupinus angustifolius*) seedling grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand, treated with four weathering regimes status. Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. There was no significant difference for the Zn (b), Al (c), and Fe (d) ($P>0.05$).
Figure 7.22 Shoot As (a), Cd (b), Cr (c), Pb (d), and Cu (e) concentration in the lupin (*Lupinus angustifolius*) seedling grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand, treated with four amendments (biosolid, N, lupin and lime) (b). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. There was no significant difference for the Cr (c) ($P>0.05$).
Figure 7.23 Shoot Ni (a), Zn (b), Al (c), Fe (d), and Mn (e) concentration in the lupin (*Lupinus angustifolius*) seedling grown in a pot trial using overburden collected from Oceana-Gold Globe Progress Mine near Reefton, New Zealand, treated with four amendments (biosolid, N, lupin and lime) (b). Means and standard errors are shown (n = 4 for each treatment). Treatment means followed by the same lower case letter were not significantly different at $P<0.05$. There was no significant difference for the Al (c) ($P>0.05$).
7.4 Discussion

This incubation pot trial was designed to simulate the early stages of weathering at the mine site. During sample collection at Reefton, the following was observed: after a short period of exposure at the surface the overburden rock was noticeably friable and the rock readily broke down into small fragments. It is reasonable to assume that this rapid physical weathering and increase in the surface area would lead to an increase in infiltration and the water holding capacity. The input and internal movement of air and water would facilitate chemical weathering processes such as hydration and hydrolysis; thus leading to a change in the geochemistry of the overburden. The addition of amendments may increase the rock alteration and breakdown of the overburden by a variety of physical and chemical mechanisms, thus enhancing nutrient release for successful re-vegetation and reconstruction of a viable growth medium (Brown & Grant, 2000). The biosolid and lupin amendments in particular would have been a potential source for the generation of organic acids and carbon dioxide, which would have further aided weathering processes. Weathering could also result in the release of heavy metals if present in the overburden. These may have potentially toxic effects on plants, dependant on their bioavailability.

The hypothesis tested in this chapter was that weathering, in collaboration with amendments, would improve the nutritional status of the overburden and hence improve plant biomass production. The results are thus discussed in the following sections: the weathering regime effect on the nutritional status of the overburden; the amendment effect on the nutritional status of the overburden; the weathering regime effect on the geochemistry. Finally, the overall implications of the weathering regime effect on restoration processes are considered.

7.4.1 Weathering regime effect on nutritional status of the overburden

**pH:** After 24 weeks of simulated weathering (Ti), the aerobic weathering regime status (90% of field capacity) slightly reduced the overburden pH, whilst the an-aerobic weathering regime status increased the pH from 5.4 to 6.1 (Figure 7.2). Similar results are presented by Seoane & Leiros (1997) who noted that after a 1 year incubation of lignite mine spoil (in open air and at laboratory temperature of 20°C) the mine spoil pH was in a slightly reduced state under field capacity and the drop in pH was lower than under the wetting-drying status. Soil pH decreases as soil becomes more weathered and H⁺ gradually replaces exchangeable basic cations. The results presented in this chapter suggest that under aerobic status (field capacity),
the overburden releases H⁺ ions into the overburden solution, reducing pH. In contrast, under an-aerobic status, where no oxygen is present, the weathering processes will be slower and any acidity generated stimulates the weathering of primary minerals where the weathering consumes H⁺ and produces more OH⁻, resulting in an increase in pH (Foth & Ellis, 1997).

The wet-dry and an-aerobic status increased the pH level from 5.79 (T₀) to 5.94 (T₁) and from 5.8 (T₀) to 6.1 (T₁) (Figure 7.2), respectively. Van Breemen et al. (1983) stated that in well drained acid soil with excess drainage, H⁺ neutralization primarily occurs through weathering reactions; due to the dissociation of CO₂ and organic acids in acidic soil contribute little to the total flux of H⁺. A similar experiment, but in lignite spoil demonstrated that the field capacity and wetting-drying status slightly decreased the pH (Seoane & Leiros, 1997). They suggested that at field capacity, lignite released more acid into the medium; whereas under forced percolation, the continuous washing reduced the formation of labile acid. The results presented here suggest that the wet-dry status would be the most appropriate for the overburden to allow a gradual increase in pH. In the field situation, this would be achievable throughout the winter-summer season.

**Cations:** The weathering regime affected the concentration of exchangeable Ca and Na in the overburden. Compared to before weathering (T₀), after weathering (T₁) reduced the concentration of exchangeable Ca under all weathering regimes (Figure 7.8a). Chemical weathering of parent rock consisting of primary minerals will produce secondary minerals. Destruction of the primary minerals in the parent rock by water (hydrolysis) releases mobile ions like Ca, Mg, Na and K into the substrate solution (Chamley, 1989). An increase in hydrolysis intensity effectively reduces ion concentration in the primary mineral weathering complex. This will result in secondary minerals that are more depleted in cations, especially the more mobile ones (Chamley, 1989). Furthermore, acid deposition is known to decrease Ca²⁺ concentration in soils. Pilbeam & Morley (2007) attributed this increased loss partly to increased water flows, and also through the breakdown of plant material which would enhance the turnover of the N cycle and the consequent generation of H⁺ ions, resulting in a release of cations from the soil cation-exchange sites.

In contrast, after weathering (T₁), the concentration of exchangeable Na increased under both aerobic and an-aerobic status (Figure 7.8c). It is possible that the weathering regime enhanced base cation release from the overburden. The results suggested that in order to enhance this base cation release from the overburden, constant water presence is required (aerobic). However, in the field, this status is hard to achieve due to the coarse particle size of the
overburden, with a consequential low water holding capacity. Thus, breaking the overburden into the smaller particle sizes by physical weathering processes will help water to be retained longer within the overburden.

**Nutrient bioavailability:** The weathering regime affected shoot Ca and Na concentration; as such, this result demonstrated a similar trend to that seen in the substrate results. Under aerobic weathering status, the shoot Ca concentration increased the most, from 253.85 to 392.38 mg kg\(^{-1}\) (Figure 7.18a), when compared to the air dry status. *Lupinus angustifolius* requires 2.2 % (22,000 mg kg\(^{-1}\)) of Ca for optimum growth level (Reuter et al., 1997). So this result demonstrated that the shoot Ca concentration was at a deficient level. For shoot Na, aerobic status increased the concentration of shoot Na the most: from 15.87 to 21.72 mg kg\(^{-1}\), when compared to the air dry status (Figure 7.18c). Lupin requires 0.02-0.35% of shoot Na for optimum growth level (Reuter et al., 1997). The result demonstrated that the Na concentration was at a deficient level.

In addition, at Ti, the weathering regime affected the concentration of shoot P (Figure 7.16a) and S (Figure 7.17a) of lupin. The air-dry status increased the shoot P and S higher than for the other weathering regimes, and the concentration was 1625 and 2873 mg kg\(^{-1}\), respectively. Lupin requires 2400-5000 mg kg\(^{-1}\) of P and 6200 mg kg\(^{-1}\) of S in the plant for optimum growth (Reuter et al., 1997). Even though the concentration was still below the required level the air-dry status was able to provide more available P and S to be up taken by lupin, compared to the other weathering regimes. P availability in the soil solution is affected by precipitation and adsorption onto soil surfaces as well as biological processes. It follows that water availability through precipitation may increase the P concentration in soil solution and thus uptake by the plant. Furthermore, S is more available in soil solution when the soil is well-aerated, thus aerobic status will provide more S in soil solution (Foth & Ellis, 1997). It is possible that after 24 weeks of air-dry status, followed by field capacity, precipitation as well as biological processes in this treatment were higher than in the other weathering regimes, thus enhancing the shoot P and S of lupin.

**Heavy metal bioavailability:** For the shoot heavy metal concentration the results demonstrated that the weathering regime affects the shoot As, Cr, Cu, Mn, and Ni concentrations (Figure 7.20 and 7.21). The an-aerobic status increased the concentration of shoot As, Cr, and Mn, whilst the air-dry status increased the concentration of shoot Cu. As well as being affected by the pH or presence of organic and inorganic materials, the mobility and availability of metals in soil is also affected by the redox potential (Achiba et al., 2009;
Vega et al., 2004). This means that the absence or presence of water and air will affect the availability of heavy metals in the soil solution (according to the redox potential of the heavy metals) and thus their bioavailability.

7.4.2 Amendment effect on the nutritional status of the overburden

**pH:** It was expected that after weathering ($T_i$), the addition of lime would increase the pH. However, the increase was less than anticipated (pH 8.2) (Figure 7.3). The rate of lime added was expected to increase the overburden pH up to 6.5. Calculation of the net acid generating potential and also the pH buffering capacity would have allowed an estimation of the change in pH for these substrates and the use of a more appropriate amount of lime. CaCO$_3$ was used as a liming source, and the CaCO$_3$ was applied in as a fine particle size which rapidly reduced the time for the lime to dissolve and neutralize acid. There was a possibility that over liming occurred, as the liming reduced the dry matter yield of lupin from 0.85 (control) to 0.65 g plant$^{-1}$ (Figure 7.14b). Jessop et al. (1990) found that liming reduced the lupin biomass; lupin grew poorly where the CaCO$_3$ presence in the soil was higher than 5-10%. The shoot Ca of lupin was increased by application of lime from 172.5 (control) to 788.9 mg kg$^{-1}$.

The organic amendments (biosolid and lupin as green manure) slightly increased the overburden pH (Figure 7.3). A possible mechanism whereby organic amendments could increase soil pH (when the original pH is relatively low) could be the mineralization of carbon and subsequent production of OH$^{-}$ ions by ligand exchange as well as the introduction of basic cations, such as K$^{+}$, Ca$^{2+}$, and Mg$^{2+}$ (Achiba et al., 2009). This experiment agreed with the results in section 6.3.3; where application of lupin green manure and biosolid increased the dry matter yield of lupin (Figure 7.12b). In contrast, the inorganic amendment (N) reduced the pH.

**Cations:** During weathering, application of lupin green manure effectively increased the release of exchangeable Ca, Mg and K from the overburden (Figure 7.9). Both organic matter and organisms play a major role in weathering. During the weathering processes, organic acid (formed from the CO$_2$ released during the decay of organic matter) in combination with organic chelates form complexes with the mobilised cations which will allow the movement and subsequent release of ions to solution. This process also occurs when the primary mineral is attacked by simple organic chelates, excreted by microorganisms (Kabata-Pendias & Pendias, 2001). The lupin green manure possibly contributed to the cation level in solution by the plant material enhancing the consequent generation of H$^+$ ions, thereby releasing cations...
from the cation-exchange sites of the soil (Pilbeam & Morley, 2007). The results strongly suggest that the lupin green manure may contain more organic acid and organic chelates than the biosolid; thus resulting in a release of cations from the overburden primary minerals through weathering. Alternatively, since biomass mineralisation consumes H⁺, it is possible that the constituent cations of the lupin were released into the soil and soil solution as the plant material was decomposed.

Ca, Mg, Na and K in plants are required in small amounts, but play a important function in building cell walls (Ca), as constituents of the chlorophyll molecules (Mg), involved in plant regeneration (Na) and as a cofactor for more than 40 enzymes (K) (Taiz & Zeiger, 2002). Application of lupin green manure increased the exchangeable Ca, Mg and K in the substrate, along with the shoot Ca and K only (Figure 7.19a and 7.19d).

**EC:** After the weathering period (Tᵢ), the organic amendments (biosolid and lupin green manure) increased the EC level, but the concentration was still categorized as non saline (Hazelton & Murphy, 2007) (Figure 7.5). The biosolid used in this experiment contained high salt levels (1633 µS cm⁻¹); suggesting the salts were derived from the biosolid. The lupin green manure possibly contributed to EC level by decomposition of lupin material enhancing the generation of H⁺, thus releasing cations from the cation-exchange sites, particularly releasing Na⁺ more than other base cation as a source of salinity. In contrast, the inorganic amendments (N and lime) reduced the EC level (Figure 7.5). In contrast, Wei et al. (2007) reported that chemical fertilizer could increase soil salinity, due to the chemical fertilizer containing inorganic compounds that could affect the level of osmotic pressure of soils.

**Heavy metal bioavailability:** The results demonstrated that during the weathering processes, the amendments affected the lupin shoot concentration (As, Cu, Mn, Ni, Cd, Pb, Zn and Fe) (Figure 7.22 and 7.23). Application of lupin as a green manure increased the concentration of shoot As and Fe, whilst application of the organic and inorganic amendments reduced the concentration of shoot Cd, Cu, Ni and Mn.

In their study of soil metal immobilitation, Nwachukwu & Pulford (2009) demonstrated that chemical amendments can reduce the solubility of heavy metals by precipitation, while organic amendments reduces the solubility of heavy metals by sorption and chelation of the heavy metals. While these findings agree with the results reported here, organic amendments are also able to promote metal mobility if the metal complexes are formed with amendments are more soluble than the initial status of the metal. Furthermore, it is well known that liming
is able to control metal solubility by raising pH, which causes the precipitation of many heavy metals (Nwachukwu & Pulford, 2009). In the results reported here, the pH level of the overburden increased by the application of lime (Figure 7.3); thus reducing the heavy metal concentration in the lupin shoot.

### 7.4.3 Weathering effect on geochemistry of the overburden

**Sort Range Order (SRO) clays:** Fractionation of Si, Al and Fe by acid oxalate extraction aims to quantify the presence of organic and inorganic forms of the non-crystalline and poorly crystalline clays (allophane/imogolite) in the substrate (Broquen et al., 2005; Drouza et al., 2007; Duncan & Franzmeier, 1999; Eger, 2007; Lilienfein et al., 2003; Parfitt & Kimble, 1989; Parfitt et al., 1988; Wada, 1980). SRO clay minerals have a high cation exchange capacity and hence a major influence on the exchange chemistry of the weathered overburden material. Examination of the ANOVA result (Table 7.3) showed a non significant effect between time, weathering and water regimes status and/or amendments on Si, Al, and Fe (P>0.05), but did show that the value of Si, Al, and Fe at T1 was higher than that at T0.

In a contrasting study, Drouza et al. (2007) found that the values of Si, Al, and Fe at T1 were higher (between 0.08-0.13%, 0.66-0.91%, and 3.2-4.69%, respectively) than the values of Si, Al, and Fe for soils derived from volcanic rocks of Nisyros-Greece which were 0.022, 0.09, and 0.35 %, respectively. Despite the volcanic rock parent material of the soils, this study by Drouza et al. (2007) highlights that after the short-period of weathering (24 weeks), there was a tendency for the overburden in this study to have a higher non-crystalline component than the volcanic rocks of Drouza et al., (2007). These researchers further stated that the presence of high organic matter content and high non-crystalline minerals lead to an increased high water retention capacity, variable charge, high P-retention, and low values of bulk density. In addition, the Si value can indicate a rate of weathering (Broquen et al., 2005). In this study, the overburden had very low levels of Si (Table 7.4). After the period of weathering (T1), the treatments doubled the Si values in the range of 0.05-0.06% to 0.08-0.13%, but the level was still very low compared to the findings of Broquen et al. (2005) who found that an Andisol from Argentina contained low Si around 0.3-1.6%; indicating a soil possibly in an early stage of development.

The pyrophosphate extractions give an estimation of Al and Fe present in humus-complexes (Parfitt et al., 1988). After weathering (T1), the values of Alp (Table 7.5) and Fe (Table 7.4) were lower than T0. The amount was in the range 0.05-0.24% for Alp, and 0.05-0.68% for...
Fe\textsubscript{p}, respectively. In contrast, Drouza et al. (2007) reported values of Al\textsubscript{p} and Fe\textsubscript{p} from volcanic rocks of Nisyros-Greece ranged from 0.00 to 0.02%. This was attributed to the low organic matter content of the samples as well as to the low solubility of Fe and Al at pH values greater than 5.5. For the results reported here, after weathering (T\textsubscript{i}), the an-aerobic status increased the value of Fe\textsubscript{p} (Figure 7.12b); most probably due to the Fe\textsuperscript{2+} produced under reducing conditions being more soluble and mobile and thus able to form Fe-humus complexes.

After weathering (T\textsubscript{i}), the organic amendments (biosolid and lupin green manure) promoted the value of Fe\textsubscript{p} higher than the inorganic amendments (N and lime) (Figure 7.13b), with lupin increasing the Fe\textsubscript{p} value the most. Egli et al. (2006) stated that there were similarities between the behaviour of Fe, Al and trends for organic matter. The high percentage of organically-bound Fe in the overburden indicates that the overburden contained high amounts Fe-humus complexes. A combination of low pH of the overburden and high concentration of Fe-humus complexes resulted in the high solubility of Fe which may speed up weathering processes. It is possible that lupin as a green manure, contains organic acid and organic chelates may also increase the incidence of Fe-humus complexes.

The dithionite extraction gives an estimation of the entire pool of free iron oxides (both crystalline and non-crystalline) (Eger, 2007; Parfitt et al., 1988). The value of Fe\textsubscript{d} reduced after 24 weeks of weathering (T\textsubscript{i}) (Table 7.5). A reduction in the crystallinity of the free iron oxides in the overburden means that there is more free iron oxide being released into solution ready to react with humus complexes, and thus an indication of an increase in the weathering processes.

**Allophane estimation:**

Parfitt & Kimble (1989) and Parfitt et al. (1988) estimated allophane (Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}.nH\textsubscript{2}O) contents of soil clays when the value of (Al\textsubscript{o}-Al\textsubscript{p}/Si\textsubscript{o}) is close to 2 (corresponding to allophane with Al/Si=2). A value of between 1 and 2 is indicative of allophane, with silica-rich allophane close to 1 and aluminium-rich allophane (proto-imogolite allophane) close to 2. The formation of non-crystalline minerals (allophane, imogolite, ferrihydrite) is determined by the rate of weathering and the resistance of the primary minerals to chemical weathering (Drouza et al., 2007). The values of (Al\textsubscript{o}-Al\textsubscript{p}/Si\textsubscript{o}) in most samples were greater than 2 (Table 7.4). The result demonstrated that compared to before weathering (T\textsubscript{o}), the values of (Al\textsubscript{o}-Al\textsubscript{p}/Si\textsubscript{o}) after weathering (T\textsubscript{i}) were lower than T\textsubscript{o}, with the amount being in the range of 4.68% -7.22%. The high values of (Al\textsubscript{o}-Al\textsubscript{p}/Si\textsubscript{o}) may have been caused by the amount of
organic matter in the overburden being insufficient to account for the movement of Al in the substrate as organic complexes (Childs et al., 1983). It has been reported that the formation of allophane and imogolite in volcanic ash soil and podzolised soils is affected by soil acidity, which occurs at pH 5.0 to 7.0 (Drouza et al., 2007; Parfitt & Kimble, 1989; Wada, 1980). The availability of high organic matter in soils with pH below 5.0 will work against the allophane formation, due to the sorption of Al by humus-complexes (Drouza et al., 2007; Schwertmann et al., 1993). This agrees with the pyrophosphate extractable results reported above, where values for Al increased after weathering (Ti) to 0.05% -0.24% (Table 7.4). In addition, the overburden contained low amounts of organic matter and low pH (4.8) which would further inhibit the formation of allophane and imogolite.

**Ferrihydrite estimation:**

The values of the ferrihydrite activity ratio (Feₐ/Fe₄) from these samples were above 2.85%. This result is in contrast to other experiments which found that the values of Feₐ/Fe₄ were below 1 (Eger, 2007). In general, a high Feₐ/Fe₄ ratio is interpreted as an indication of low iron crystallinity through the influence of organic matter and an acid soil environment with strong leaching (Schwertmann et al., 1993). Furthermore, the experiment demonstrated that the ferrihydrite (Fe₃HO₈.4H₂O) percentage was higher at Ti than To, and the values were in the range of 3.57% -6.21% to 5.46%-8.25% (Table 7.5). Eger et al. (2007) found that the value of ferrihydrite from the study of part of the Canterbury High Country in New Zealand was below 2%. In contrast, The Akaka soil of Hawaii contains large amounts of ferrihydrite, in the order of around 24% (Parfitt et al., 1988). The presence of ferrihydrite in soil is important due to its influence on soil properties; high values of ferrihydrite indicate that the soils have a large surface area and reactive surface groups for cation exchange. The combination of rainfall, drainage and temperature regime for the Akaka soil in Hawaii, along with the parent basaltic ash (which contains more Fe than the more silicic volcanic ashes), caused the Fe to weather out of the primary minerals and precipitate as ferrihydrite (Parfitt et al., 1988). Nevertheless, 1% of allophane or ferrihydrite contributes 85% of the total soil mineral surface area. It can be said that even though allophane or ferrihydrite may be minor in the sense of mass or volume, it has a very high significant contribution in terms of contributing to the reactive surface area in soils (Schwertmann et al., 1993).

**7.4.4 Implication of weathering effects on restoration processes**

Overburden as a raw material has the potential to be used as a growth medium in much the same way as the topsoil is currently used in mine restoration (Chapter 3 section 3.1.1). The
discussion above highlights that the weathering regime and the type of amendments added to the overburden did affect the weathering processes of the overburden and hence the nutritional status of the overburden. The discussion in this section will now consider the implications of this for restoration processes.

Weathering will be intense and rapid in the zone where the availability of water and air is balanced and continuous. This study found that the aerobic status had a dominant affect on reducing the ion concentration in the primary mineral weathering complex of the overburden, increasing the mobile ions (Ca, Mg, Na and K) in the overburden solution, along with an increase in nutrient bioavailability (Section 7.4.1.). The aerobic status affected the heavy metal bioavailability by redox potential processes. However, this ideal condition is unlikely to be achieved under field conditions, especially at Reefton, where aerobic status driven by rainfall is unpredictable. Thus manipulating the overburden weathering stages with organic matter (biosolid and lupin) in order to enhance the release of plant nutrients is a more realistic strategy. It should also be noted that organic matter will increase the water holding capacity and improve the aeration status and porosity of the overburden-derived growth medium, as well as providing long-term nutrient release from organic pools of N, P and S.

Apart from the presence of water, the presence of carbonic acid, formed from the CO₂ released during decay of organic matter and organic chelates is also an important factor in weathering processes (Kabata-Pendias & Pendias, 2001; Wardle, 1991). This study found that inorganic amendments were less effective than organic amendments for augmenting weathering processes. Among the organic amendments used, application of lupin as a green manure was the most effective organic amendment for reducing ion concentration in the primary mineral weathering complex of the overburden (implying a breakdown of the primary crystal lattice structure). It is possible that the lupin green manure may contain more organic acid and organic chelates than biosolid; thus resulting in the release of cations from the overburden primary minerals, and an increase in the nutrient bioavailability (Section 7.4.2). Furthermore, lupin does not contribute to heavy metal contamination. As organic matter, lupin can also retain water for longer to be absorbed by overburden during the pot trial, the lupin treatment required less water addition than other treatments.

The results discussed in this section are supported by the geochemistry results in section 7.4.3; that lupin as a green manure increased the quantity of non-crystalline Fe from humus-complexes in the overburden (Feₚ) to a greater extent than the biosolid (Section 7.4.3). So, the addition of lupin increased the release of Fe from these organic complexes in the overburden.
which readily reacted with organic acids from the lupin green manure, thus increasing the rate of weathering processes. Alternatively, the shoot Fe concentration increased under the lupin treatment, possibly as a result of the release of the constituent Fe in the lupin plant material during decomposition. In addition, after the weathering period ($T_i$) the values of ferrihydrite ($1.7^{*}Fe_d$; Table 7.5) increased on application of lupin. The presence of ferrihydrite in soils is an indication that the soil has a large surface area and reactive surface groups. An increase in the surface area and reactive surface groups would lead to an increase in overburden exchange capacity and the progression of pedogenesis.

### 7.5 Conclusions

- The aerobic weathering regime status had a dominant effect; reducing ion concentration in the primary mineral weathering complex of the overburden, increasing the mobile ions (Ca, Mg, Na and K) in the overburden solution, along with an increase in nutrient bioavailability (Ca, Na, K, P and S). However, the practical application of maintaining such a weathering regime in the field situation (at Reefton especially) may be challenging.
- Among the amendments, the application of lupin as a green manure effectively improved the nutritional status of the overburden by increasing the pH, EC level and cation concentration. Adding organic matter would also increase water holding capacity, permeability and improve physical structure. The application of lupin also increased the Fe present in humus-complexes.
- The weathering period increased the presence of $Si_o$, $Al_o$ and $Fe_o$; organic and inorganic forms of non-crystalline and poorly crystalline clays in the overburden substrate.
- The weathering period increased the presence of Fe in humus-complexes ($Fe_p$). The weathering period increased the amount of ferrihydrite present in the overburden substrate.
- No allophane occurred in the overburden after the weathering period, due to the overburden having a low pH and low organic matter. Any remaining organic matter formed complexes with Al, as there was an increase in Al-humus complexes ($Al_p$) at $T_i$. 

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Chapter 8
General Discussion, Conclusions, and Recommendations for Future Research

8.1 General discussion and conclusion

This study aims to determine a sustainable restoration method for managing the topsoil and/or any overburden or waste rock material remaining at gold mine sites, by determining the effect of both amendments (organic and inorganic) and short-term weathering processes on the substrate nutrient availability, plant bioavailability, and plant growth of selected species. The study site was the OceanaGold Globe-Progress mine site, Reefton.

The following sections will synthesise the discussions from Chapters 4, 5, 6 and 7 which have each addressed in turn the objectives and hypotheses. Recommendations for future work will be outlined.

Topsoil and overburden were the major materials remaining from OceanaGold Globe-Progress Mine near Reefton, following the commencement of open cast extractive operations in 2005. Both of these growth medium substrates lacked nutrients (Chapter 3 table 3.1) and thus required a supply of nutrients to support re-vegetation processes. The effects of inorganic and organic amendments were examined first for the topsoil, as this is the required material for many restoration protocols.

Among the amendments tested, application of N fertilizer and biosolid affected the nutritional status of the growth medium substrates the most. This study demonstrated that biosolid contributed to the enhancement of the topsoil nutrient status to a greater extent than N fertilizer; and would thus be an effective method for mine restoration of topsoil for the OceanaGold Globe-Progress Mine (Chapter 4 section 4.4.1). In addition, the biosolid effectively increased the concentration of extractable NH$_4^+$-N, NO$_3^-$-N, Ca, Mg, P, and S of topsoil, along with the bioavailability of the Red beech. For the overburden, there was a similar response as to that seen with the topsoil. The biosolid enhanced the nutritional status of the overburden to greater extent than inorganic (N fertilizer), and there was an associated increase in the biomass production (Chapter 4 section 4.4.2). Application of biosolid to the overburden effectively increased the concentration of extractable NH$_4^+$-N and NO$_3^-$-N, extractable P, extractable S, exchangeable Ca in the substrate solution, but had no effect on pH, exchangeable Na, or the CEC. Whilst the application of N fertilizer to the overburden
only increased the concentration of extractable \( \text{NH}_4^{+} \) and \( \text{NO}_3^{-} \), it had no effect on pH, exchangeable Na, CEC, extractable P, and even reduced the extractable S in the substrate solution. Biosolid thus increased the nutritional status of the growth medium substrates more than N fertilizer alone, due to the biosolids high nutrient content (Chapter 4 table 4.1) contributing to enhancing the growth medium nutrient status. These nutrients are most likely to be organically-bound; as organic matter decays over time the nutrients are released, and will represent a steady supply in a plant available form. These results suggested that addition of biosolid to overburden was able to create a viable growth medium substrate as effective as the topsoil, and able to support re-vegetation processes.

In mine restoration, increasing the nutritional status of growth medium substrate is not the only issue that needs to be addressed. Heavy metal availability is a concern, as heavy metal contamination is an issue in mine sites. Application of sawdust reduced the shoot Cu, Cd, and Zn of Wineberry grown in the overburden (Chapter 4 section 4.4.2.9). This result indicated that sawdust may contain organic chelates such as lignin and polyphenols which can form complexes with the heavy metals in solution and so reduce the heavy metal bioavailability. Furthermore, biosolids can contribute to enhancing heavy metal contamination when they contain high concentrations of heavy metals. The biosolids used in this study were within the guideline concentrations for heavy metals (NZWWA, 2003). This study demonstrated that applying biosolid to the topsoil and overburden had no effect on the heavy metal availability, with concentration below the detection limits. Land application guidelines for biosolids in New Zealand specify low heavy metal concentrations; and are set at different thresholds depending on the land use (Magesan & Wang, 2003; NZWWA, 2003).

Thus, biosolids demonstrated an effective approach to enhancing the nutritional status of the topsoil and overburden and had no effect on increasing heavy metal availability and bioavailability. However, the field application of biosolids to mine sites may be impractical at the Oceana-Gold Globe Progress Mine site in Reefton, on a cost basis. Applying biosolid to a large area such as a mine site will involve costs related to transport and application. These operational costs must be considered, particularly as transporting this product by truck to remote terrain areas where many mine sites are located is the only viable option.

Kelly (2008) conducted a series of experiments on a reshaped overburden at Narama Mine, NSW, Australia. Kelly demonstrated that even though biosolid was a waste product that would cost nothing to buy ($0), spreading the product over large area was costly (c. $1350 ha\(^{-1}\)). In comparison, a N in-organic fertiliser, had a higher purchase cost (c. $350 ha\(^{-1}\)), but a
lower land application cost (c. $340 ha$^{-1}$). The total annual cost for the biosolid treatment is $1350, compared to the N fertiliser cost of $690. However, if it was assumed that the biosolid application is a one off cost, but that the N fertiliser needs re-applying every year, then the biosolid is the cheaper treatment after 2 years. This cost benefit based on one application of biosolid is supported by Bradshaw (2000), who stated that one application of biosolid can provide sufficient N to compare to the total capital of N in a normal soil. Furthermore, there are other legislative issues to consider. The Globe-Progress mine and other parts of the Reefton Gold field are surrounded by the Department of Conservation-administered Victoria Conservation Park; so there may be further issues to address surrounding land application of biosolids.

So, instead of covering the overburden with the topsoil, the results presented here demonstrate that the overburden alone was able to be used as growth medium, and to be more effective than the topsoil for mine restoration (Chapter 4 and Chapter 7). While biosolids can provide nutritional input, the operational costs of land application and the potential as a source of heavy metal contamination, their use is still a concern. It is necessary to consider using other amendments as a nutrient source for the overburden.

The results presented here demonstrate that lupin as green manure contributed to enhancing the nutritional status of the overburden. Even though the application of lupin as a green manure had little effect on nutrient availability of the overburden itself, it did increase the bioavailability of the Red beech (shoot N, K, Cd, Ni) and the Wineberry (shoot N, S, Ca, Mg, As, Al, Ni, Pb and Mn) (Chapter 4 section 4.4.2).

In contrast, during the 24 week incubation period used to simulate the early stages of weathering (Chapter 7), lupin green manure slightly increased the overburden pH and effectively increased the release of exchangeable Ca, Mg and K from the overburden. Lupin green manure also increased the lupin shoot Ca and K and the dry matter yield of lupin. Lupin as a green manure affected the heavy metal bioavailability of lupin (As, Cu, Mn, Ni, Cd, Pb, Zn and Fe), and the effect could decrease or increase the heavy metals. The lupin green manure thus had similar results to the biosolid on the overburden, and both the organic amendments (biosolid and lupin green manure) enhanced the nutritional status of the overburden to greater extent than inorganic amendments (N and lime). But lupin contributed more than biosolid in releasing nutrients from the overburden. The presence of organic acid (formed from the CO$_2$ released during decay of organic matter) together with organic chelates is an important factor in weathering processes (Kabata-Pendias & Pendias, 2001; Wardle,
These results indicated that using the lupin as a green manure required an initial weathering period to release these organic compounds and complexes contained in the lupin and to react with the overburden to release the nutrients into solution. Alternatively, the observed effects may simply be due to the release of the constituent Ca, Mg and K from the lupin plant material as it decomposed in the soil.

Furthermore, among the organic amendments used, application of lupin as a green manure was the most effective organic amendment for reducing the cation concentration in the primary mineral weathering complex of the overburden (implying a breakdown of the primary crystal lattice structure: Chapter 7 section 7.4.4). It is possible that the lupin as a green manure may contain more organic acid and organic chelates than the biosolid; thus resulting in the release of cations from the overburden primary minerals, and an increase in the nutrient bioavailability. Furthermore, lupin does not contribute to heavy metal contamination, and as organic matter, lupin incorporated into the overburden can also help retain water for longer and to be absorbed by overburden. During the pot trial, the lupin green manure treatment required less water addition than the other treatments.

In addition, during the incubation period, application of lupin green manure promoted the formation of Fe humus-complexes. The presence of oxalate extractable Si, Al and Fe indicated the presence of non-crystalline and poorly crystalline clays (short-range order clays, such as allophane, imogolite, ferrihydrite and aluminium humus complexes). Both the organic amendments (biosolid and lupin green manure) increased the amount of Fe in humus-complexes to a greater extent than the inorganic amendments (N and lime). The high percentage of Fe organically-bound in the overburden after the 24 week incubation period indicated that the overburden contained high amounts of Fe-humus complexes (Chapter 7 section 7.4.3). A combination of low overburden pH and high Fe-humus complexes implies that under these conditions Fe is highly soluble; this may speed up weathering processes and thus, element release. Lupin as a green manure will most likely contain organic acid and organic chelates; these will increase the incidence of Fe-humus complexes. In addition, the presence of Al-organic complexes will also contribute to increasing water retention capacity, variable charge, and lower values of soil bulk density in the overburden. During the weathering period, the lupin also increased the amount of ferrihydrite (Chapter 7 table 7.5). The high concentration of ferrihydrite indicates that the soils have a large surface area and reactive surface groups, and thus will be important for developing soil properties (Parfitt et al., 1988). Lupin as a green manure effectively enhanced the nutritional status and geochemistry properties of the overburden from OceanaGold Globe-Progress Mine. It created
conditions similar to a weakly developed soil; effectively the initial stages of pedogenesis from a mineral material.

Different plants have different responses to organic and inorganic amendments. Understanding the nutrient demand of different plant species and different growth mediums will lead to better management of site fertility for re-vegetation processes. For example, foliage with a high N content would lead to an increase in leaf litter turnover, an increase in N mineralization, and thus an increase in the N cycling rate (Ollinger et al., 2002).

Wineberry is a pioneer species for rehabilitation in the West Coast forest in the vicinity of Reefton. This native species, when grown in overburden had a greater internal N requirement than Red beech (which is a later successional species). Wineberry produced foliage with a high N content (Chapter 6 section 6.3.2). Both plant species required 200 kg N ha\(^{-1}\) for optimum shoot N. Application of high N (300 kg ha\(^{-1}\)) can cause the shoot N of Red beech and Wineberry to exceed the requirement for future revegetation during mine restoration (Chapter 4 section 4.4.2). However, Wineberry grown in overburden required less N (0 kg ha\(^{-1}\)) to produce optimal dry matter-yield, whilst Red beech required 200 kg N ha\(^{-1}\) for optimum yield. For the purposes of mine restoration revegetation, this indicated that Wineberry was able to grow in overburden which has no or very low N concentration in solution. However Wineberry still required more N for producing high shoot N. Supplying high N can be achieved through addition of N fertilizer, but only in the early stage of re-vegetation. For the next stage of re-vegetation, supplying N could be supplied from using lupin as a green manure - that would also effectively enhance weathering processes and the associated nutrient release from the overburden.

Both plant species had different sensitivities to heavy metal uptake (Chapter 4, section 4.4.2.9). During application of high N in the overburden, the shoot Mn of Red beech slightly reduced from 935.0 to 928.0 mg kg\(^{-1}\) (at toxic levels) (Figure 4.53b), while the shoot Mn of Wineberry increased from 173.0 to 980.0 mg kg\(^{-1}\) (from optimum to toxic levels) (Figure 4.54b). In addition, application of high N in the overburden slightly increased the concentration of shoot Al in Red beech from 70.3 to 71.0 mg kg\(^{-1}\) (Figure 4.45b), while the concentration of shoot Al in Wineberry increased from 32.0 to 151.0 mg kg\(^{-1}\) (Figure 4.46b). There was an indication that Wineberry was able to uptake heavy metal to a greater extent than Red beech. This might be a physiological characteristic that may contribute to removing heavy metals from contaminated materials in mining sites.
8.2 Recommendations for future research

- Biosolids effectively increased the nutritional status of the overburden. Further field trials are required to investigate the effect of biosolids on different overburden materials in different environments. Long-term trials to investigate the effect of biosolid application on heavy metal availability and bioavailability will provide information on the persistence of these in the environment. This information will contribute to determining realistic and sustainable strategies for managing overburden for restoration processes.

- Lupin green manure was an effective agent for releasing nutrients from the overburden and altering the geochemical properties of the overburden mineral, during the 24 week weathering incubation period. Future experiments are needed to identify the specific chemical properties of lupin (such as the production of organic acids and complexing agents) that affect the weathering processes. From this will follow further pot trials, incorporating the effect of longer-term weathering incubation, to determine the optimum application rate of lupin green manure and eventually. Field trials can then be located in a mine rehabilitation setting. As a result, a realistic protocol for managing overburden using this material for bio-restoration processes can be established.

- Sawdust was effective in reducing the EC level of growth medium substrates. Further experiments are required to investigate the chemical composition of the sawdust which affects the EC level. These results can be then included in further (incubation) pot trials, using different application rates of sawdust, and different weathering periods. This information will contribute to addressing the salinity issue in mine restoration.

- The nature of the overburden was critical to the success of the pot trials. It is important for further pot trials to be conducted using a variety of overburden materials and both organic and inorganic amendments. For example, a quartz sandstone overburden will respond differently to organic amendments, having fewer nutrients to release from the primary minerals during weathering.
References


Appendix A – Application rates calculation of amendments

(Chapter 4)

Pot size: 2.5 L (diameter = 17 cm; high = 15.5 cm)

Pot area = \( \pi r^2 = 3.14 \times (0.17 \text{ m}^2/2) = 0.0227 \text{ m}^2 \)

- **Biosolid**
  - Source: fresh biosolid from Bromley-Christchurch
  - Application rate: 20 ton ha\(^{-1}\)
    - Dosage per pot: \( (0.0227 \text{ m}^2/10'000 \text{ m}^2) \times 20'000 \text{ kg} \)
      = 0.0454 kg pot\(^{-1}\)
      = 45.4 g pot\(^{-1}\)
  - Application rate: 40 ton ha\(^{-1}\)
    - Dosage per pot: \( (0.0227 \text{ m}^2/10'000 \text{ m}^2) \times 40'000 \text{ kg} \)
      = 0.0908 kg pot\(^{-1}\)
      = 90.8 g pot\(^{-1}\)

- **Sawdust**
  - Source: commercial retail outlet from Parkhouse-Christchurch
  - Application rate: 50 ton ha\(^{-1}\)
    - Dosage per pot: \( (0.0227 \text{ m}^2/10'000 \text{ m}^2) \times 50'000 \text{ kg} \)
      = 0.1135 kg pot\(^{-1}\)
      = 113.5 g pot\(^{-1}\)
  - Application rate: 100 ton ha\(^{-1}\)
    - Dosage per pot: \( (0.0227 \text{ m}^2/10'000 \text{ m}^2) \times 100'000 \text{ kg} \)
      = 0.227 kg pot\(^{-1}\)
      = 227 g pot\(^{-1}\)

- **N fertilizer**
  - Source: Ammonium Nitrate (NH\(_4\)NO\(_3\))
  - Application rate: 150 kg N ha\(^{-1}\)
    - Dosage per pot: \( (0.0227 \text{ m}^2/10'000 \text{ m}^2) \times 150 \text{ kg N} \)
      = 0.00034 kg N pot\(^{-1}\)
      = 0.34 g N pot\(^{-1}\)
    - Moles = Mass / Molar Mass
      = 0.34 / 14.01 = 0.0243 moles N
    - 1 mole of NH\(_4\)NO\(_3\) produces 2 moles of N
    - Moles of NH\(_4\)NO\(_3\) = 1/2 moles of N
    - Moles NH\(_4\)NO\(_3\) = 1/2 \times 0.0243 = 0.0122 mol
    - MM of NH\(_4\)NO\(_3\) = 80.082
    - Mass = 0.0122 \times 80.082 = 0.977
    - Mass of NH\(_4\)NO\(_3\) = 1 g pot\(^{-1}\)
  - Application rate: 300 kg N ha\(^{-1}\)
    - Dosage per pot: \( (0.0227 \text{ m}^2/10'000 \text{ m}^2) \times 300 \text{ kg N} \)
      = 0.000681 kg N pot\(^{-1}\)
      = 0.681 g N pot\(^{-1}\)
Moles = Mass / Molar Mass
= 0.681 / 14.01 = 0.0486 moles N
1 mole of NH₄NO₃ produces 2 moles of N
Moles of NH₄NO₃ = 1/2 moles of N
Moles NH₄NO₃ = 1/2 x 0.0486 = 0.0243 mol
MM of NH₄NO₃ = 80.082
Mass = 0.0243 x 80.082 = 1.945
Mass of NH₄NO₃ = 2 g pot⁻¹

- Lupin as a green manure
  Source: Fresh *Lupinus angustifolius* (blue lupin)
  Dosage per pot: 20 g pot⁻¹ (equivalent to 8.81 kg ha⁻¹)

(0.0227 m²/10 000 m²) x 20 g = 8810 g pot⁻¹ = 8.81 kg ha⁻¹
Appendix B – Application rates calculation of amendments  
(Chapter 5)

Pot size : 2.5 L (diameter = 17 cm; high = 15.5 cm)
Pot area = \( \pi r^2 = 3.14 \times (0.17 \text{ m}^2/2) = 0.0227 \text{ m}^2 \)

- N fertilizer
  Source : Ammonium Nitrate (NH\(_4\)NO\(_3\))
  Application rate : 150 kg N ha\(^{-1}\)
  Dosage per pot : \((0.0227 \text{ m}^2/10 000 \text{ m}^2) \times 150 \text{ kg N} = 0.00034 \text{ kg N pot}^{-1} = 0.34 \text{ g N pot}^{-1} \)

  Moles = Mass / Molar Mass
  \[ = 0.34 / 14.01 = 0.0243 \text{ moles N} \]
  1 mole of NH\(_4\)NO\(_3\) produces 2 moles of N
  Moles of NH\(_4\)NO\(_3\) = 1/2 moles of N
  Moles NH\(_4\)NO\(_3\) = 1/2 x 0.0243 = 0.0122 mol
  MM of NH\(_4\)NO\(_3\) = 80.082
  Mass = 0.0122 x 80.082 = 0.977
  Mass of NH\(_4\)NO\(_3\) = 1 g pot\(^{-1}\)

  Application rate : 300 kg N ha\(^{-1}\)
  Dosage per pot : \((0.0227 \text{ m}^2/10 000 \text{ m}^2) \times 300 \text{ kg N} = 0.000681 \text{ kg N pot}^{-1} = 0.681 \text{ g N pot}^{-1} \)

  Moles = Mass / Molar Mass
  \[ = 0.681 / 14.01 = 0.0486 \text{ moles N} \]
  1 mole of NH\(_4\)NO\(_3\) produces 2 moles of N
  Moles of NH\(_4\)NO\(_3\) = 1/2 moles of N
  Moles NH\(_4\)NO\(_3\) = 1/2 x 0.0486 = 0.0243 mol
  MM of NH\(_4\)NO\(_3\) = 80.082
  Mass = 0.0243 x 80.082 = 1.945
  Mass of NH\(_4\)NO\(_3\) = 2 g pot\(^{-1}\)

- P fertilizer
  Source : Potassium dihydrogen orthophosphate (KH\(_2\)PO\(_4\))
  Application rate : 50 kg P ha\(^{-1}\)
  Dosage per pot : \((0.0227/10 000) \times 50 \text{ kg P ha}^{-1} = 0.0001135 \text{ kg P pot}^{-1} = 0.11 \text{ g P pot}^{-1} \)

  Moles = Mass / Molar Mass
  \[ = 0.11 / 30.97 = 0.00355 \text{ moles P} \]
  1 mole of KH\(_2\)PO\(_4\) produces 1 mole of P
  MM of KH\(_2\)PO\(_4\) = 136.09 g/mol
  Mass of KH\(_2\)PO\(_4\) = 0.00355 x 136.09 = 0.5 g pot\(^{-1}\)
Application rate : 100 kg P ha$^{-1}$

Dosage per pot : \((0.0227 \text{ m}^2 / 10000 \text{ m}^2) \times 100 \text{ kg P} \)
\[= 0.0000227 \text{ kg P pot}^{-1} \]
\[= 0.227 \text{ g P pot}^{-1} \]

Moles = \frac{\text{Mass}}{\text{Molar Mass}}
\[= \frac{0.0227}{30.97} = 0.000733 \text{ moles P} \]

1 mole of KH$_2$PO$_4$ produces 1 moles of P

MM of KH$_2$PO$_4$ = 136.09

Mass of KH$_2$PO$_4$ = 0.00733 \times 136.09
\[= 1.0 \text{ g pot}^{-1} \]

- **Lime**
  
  Source: Calcium carbonate (CaCO$_3$)

Application rate : 37.5 ton CaCO$_3$ ha$^{-1}$

Note:
- 15 ton lime increase 1 unit pH
- Topsoil pH was 3.5
- pH 3.5 to 6 = 2.5 unit pH
- 15 ton x 2.5 = 37.5 ton

Dosage per pot : \((0.0227 \text{ m}^2 / 10000 \text{ m}^2) \times 37500 \text{ kg lime} \)
\[= 0.085 \text{ kg lime pot}^{-1} \]
\[= 85 \text{ g lime pot}^{-1} \]

Moles = \frac{\text{Mass}}{\text{Molar Mass}}
\[= \frac{85}{40.078} = 2.12 \text{ moles Ca} \]

1 mole of CaCO$_3$ produces 1 mole of Ca

Moles CaCO$_3$ = 1 \times 2.12 = 2.12 \text{ mol}

MM of CaCO$_3$ = 100.09 g mol$^{-1}$

Mass = \(2.12 \times 100.09 = 212.19 \text{ g CaCO}_3 \text{ pot}^{-1} \)
Appendix C - Application rates calculation of amendments

(Chapter 6)

**Pot size**
- 1.5 L (diameter = 13.2 cm; high = 14 cm)
  
  Pot area = $\pi r^2 = 3.14 \times (0.132 m^2/2)^2 = 0.0137 m^2$

**Source**
- Ammonium Nitrate ($\text{NH}_4\text{NO}_3$)

- **Application rate 1**
  - 50 kg N ha$^{-1}$
  - **Dosage per pot**
    
    $\frac{(0.0137/10\ 000) \times 50\ \text{kg N ha}^{-1}}{10\ 000} = 0.000685\ \text{kg N pot}^{-1}$
    
    $= 0.0685\ \text{g N pot}^{-1}$

    Moles = Mass / Molar Mass
    
    $= \frac{0.0685}{14.01} = 0.04889$ moles N

    1 mole of $\text{NH}_4\text{NO}_3$ produces 2 moles of N

    Moles of $\text{NH}_4\text{NO}_3 = 1/2$ moles of N

    Moles $\text{NH}_4\text{NO}_3 = 1/2 \times 0.04889 = 0.0244$ mol

    MM of $\text{NH}_4\text{NO}_3 = 80.082$

    Mass = 0.0244 x 80.082 = 0.196

    Mass of $\text{NH}_4\text{NO}_3 = 0.2\ \text{g pot}^{-1}$

- **Application rate 2**
  - 100 kg N ha$^{-1}$
  - **Dosage per pot**
    
    $\frac{(0.0137/10\ 000) \times 100\ \text{kg N ha}^{-1}}{10\ 000} = 0.000137\ \text{kg N pot}^{-1}$
    
    $= 0.137\ \text{g N pot}^{-1}$

    Moles = Mass / Molar Mass
    
    $= \frac{0.137}{14.01} = 0.00978$ moles N

    1 mole of $\text{NH}_4\text{NO}_3$ produces 2 moles of N

    Moles of $\text{NH}_4\text{NO}_3 = 1/2$ moles of N

    Moles $\text{NH}_4\text{NO}_3 = 1/2 \times 0.00978 = 0.00489$ mol

    MM of $\text{NH}_4\text{NO}_3 = 80.082$

    Mass = 0.00489 x 80.082 = 0.392

    Mass of $\text{NH}_4\text{NO}_3 = 0.4\ \text{g pot}^{-1}$

- **Application rate 3**
  - 200 kg N ha$^{-1}$
  - **Dosage per pot**
    
    $\frac{(0.0137/10\ 000) \times 200\ \text{kg N ha}^{-1}}{10\ 000} = 0.000274\ \text{kg N pot}^{-1}$
    
    $= 0.274\ \text{g N pot}^{-1}$

    Moles = Mass / Molar Mass
    
    $= \frac{0.274}{14.01} = 0.0196$ moles N

    1 mole of $\text{NH}_4\text{NO}_3$ produces 2 moles of N

    Moles of $\text{NH}_4\text{NO}_3 = 1/2$ moles of N

    Moles $\text{NH}_4\text{NO}_3 = 1/2 \times 0.0196 = 0.00978$ mol

    MM of $\text{NH}_4\text{NO}_3 = 80.082$

    Mass = 0.00978 x 80.082 = 0.783

    Mass of $\text{NH}_4\text{NO}_3 = 0.8\ \text{g pot}^{-1}$

- **Application rate 4**
  - 400 kg N ha$^{-1}$
  - **Dosage per pot**
    
    $\frac{(0.0137/10\ 000) \times 400\ \text{kg N ha}^{-1}}{10\ 000} = 0.000548\ \text{kg N pot}^{-1}$
    
    $= 0.548\ \text{g N pot}^{-1}$

    Moles = Mass / Molar Mass
    
    $= \frac{0.548}{14.01} = 0.039$ moles N

    1 mole of $\text{NH}_4\text{NO}_3$ produces 2 moles of N

    Moles of $\text{NH}_4\text{NO}_3 = 1/2$ moles of N

    Moles $\text{NH}_4\text{NO}_3 = 1/2 \times 0.039 = 0.0195$ mol

    MM of $\text{NH}_4\text{NO}_3 = 80.082$

    Mass = 0.0195 x 80.082 = 1.56

    Mass of $\text{NH}_4\text{NO}_3 = 1.6\ \text{g pot}^{-1}$
Appendix D - Application rates calculation of amendments

(Chapter 7)

Pot size : 1.5 L (diameter = 15 cm; high = 11.5 cm)
Pot area = \( \pi r^2 = 3.14 \times (0.15 \text{ m}^2/2) = 0.0177 \text{ m}^2 \)

- **N fertilizer**
  
  Source : Ammonium Nitrate (NH\(_4\)NO\(_3\))
  Application rate : 200 kg N ha\(^{-1}\)
  
  Dosage per pot : \((0.0177/10 000) \times 200 \text{ kg N ha}^{-1} = 0.000354 \text{ kg N pot}^{-1}\)
  
  \[
  \text{Moles} = \frac{\text{Mass}}{\text{Molar Mass}}
  \]
  \[
  = \frac{0.354}{14.01} = 0.0253 \text{ moles N}
  \]
  
  1 mole of NH\(_4\)NO\(_3\) produces 2 moles of N
  
  Moles of NH\(_4\)NO\(_3\) = 1/2 moles of N
  
  Moles NH\(_4\)NO\(_3\) = 1/2 x 0.0253 = 0.0126mol
  
  MM of NH\(_4\)NO\(_3\) = 80.082
  
  Mass = 0.0126 x 80.082 = 1.011
  
  Mass of NH\(_4\)NO\(_3\) = 1 g pot\(^{-1}\)

- **Biosolid**
  
  Application rate : 200 kg N ha\(^{-1}\)
  Source : Fresh biosolid from Bromley-Christchurch
  
  Dosage per pot : \((0.0177/10 000) \times 200 \text{ kg N ha}^{-1} = 0.000354 \text{ kg N pot}^{-1}\)
  
  \[
  \text{Biosolid content} \ 5.62 \% \ \text{of N}
  \]
  
  \[
  5.62/100 \times X = 0.354 \text{ gram}
  \]
  
  \[
  X = (0.354/5.62) \times 100
  \]
  
  \[
  X = 6.30 \text{ g N in dry biosolid}
  \]
  
  Biosolid water content = 80.325 %
  
  \[
  \text{WC} = \frac{\text{Wet} - \text{Dry}}{\text{W}} \times 100
  \]
  
  \[
  80.325/100 = \frac{\text{Wet} - 6.30}{\text{W}} \times 100
  \]
  
  \[
  0.80 = (\text{Wet/Wet}) - (6.30/\text{Wet})
  \]
  
  \[
  0.80 = 1 - (6.30/\text{Wet})
  \]
  
  \[
  0.80 - 1 = - 6.30/\text{Wet}
  \]
  
  \[
  \text{Wet} = - 6.30 / (0.80-1)
  \]
  
  \[
  \text{Wet} = - 6.30 / 0.20
  \]
  
  \[
  = 31.5 \text{ g fresh biosolid pot}^{-1}
  \]

- **Green manure**
  
  Application rate : 200 kg N ha\(^{-1}\)
  Source : Blue Lupin
  
  Dosage per pot : \((0.0177/10 000) \times 200 \text{ kg N ha}^{-1} = 0.000354 \text{ kg N pot}^{-1}\)
  
  \[
  = 0.354 \text{ g N pot}^{-1}
  \]
Lupin contain 3.39 % of N
\[
3.39 / 100 \times X = 0.354 \text{ gram}
\]
\[
X = (0.354/5.54) \times 100
\]
\[
X = 10.44 \text{ gram N in dry lupin}
\]
Lupin water content = 81.5 %
\[
WC = (\text{Wet} - \text{Dry}) / \text{W} \times 100
\]
\[
81.5 / 100 = (\text{Wet} - 10.44) / \text{W} \times 100
\]
\[
0.815 = (\text{Wet/Net}) - (10.44/\text{Wet})
\]
\[
0.815 = 1 - (10.44/\text{Wet})
\]
\[
0.815 - 1 = -10.44/\text{Wet}
\]
\[
\text{Wet} = -10.44 / (0.815-1)
\]
\[
\text{Wet} = -10.44 / -0.185
\]
\[
= 56.43 \text{ g fresh lupin pot}^{-1}
\]

- Lime
  Application rate : 19.5 tonnes ha\(^{-1}\)
  Note: - 15 tonnes lime increase 1 unit pH
    - Fresh overburden pH 5.2
    - pH 5.2 to 6.5 = 1.3
    - 15 tonnes x 1.3 = 19.5 tonnes
  Source : Calcium Carbonate (CaCO\(^3\))
  Dosage per pot :
\[
(0.0177/10 000) \times 19 500 \text{ kg lime ha}^{-1} = 0.0345 \text{ kg lime pot}^{-1}
\]
\[
= 34.5 \text{ g lime pot}^{-1}
\]
  Moles = Mass / Molar Mass
\[
= 34.5 / 40.078 = 0.86 \text{ moles Ca}
\]
  1 mole of CaCO\(^3\) produces 1 mole of Ca
  Moles CaCO\(^3\) = 1 x 0.86 = 0.86 mol
  MM of CaCO\(^3\) = 100.09 g/mol
  Mass = 0.86 x 100.09 = 86.07
  Mass of CaCO\(^3\) = 86 g pot\(^{-1}\)
Appendix E – The chemical and physical characteristics of the substrate and plant used

Table E1. The chemical properties of topsoil, overburden, and mullock substrates planted with the Red beech (Chapter 4)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>EC (µs cm⁻¹)</th>
<th>NH4-N</th>
<th>NO3-N Extractable (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Topsoil</td>
<td>Overburden</td>
<td>Mullock</td>
<td>Topsoil</td>
</tr>
<tr>
<td>Control</td>
<td>4.75</td>
<td>4.13</td>
<td>7.56</td>
<td>27.09</td>
</tr>
<tr>
<td>Biosolid-1</td>
<td>4.30</td>
<td>4.23</td>
<td>7.11</td>
<td>236.43</td>
</tr>
<tr>
<td>Biosolid-2</td>
<td>4.17</td>
<td>4.35</td>
<td>7.03</td>
<td>202.80</td>
</tr>
<tr>
<td>Lupin</td>
<td>4.86</td>
<td>4.25</td>
<td>7.60</td>
<td>33.68</td>
</tr>
<tr>
<td>Sawdust-1</td>
<td>4.68</td>
<td>4.41</td>
<td>7.69</td>
<td>48.93</td>
</tr>
<tr>
<td>Sawdust-2</td>
<td>4.47</td>
<td>4.37</td>
<td>7.61</td>
<td>37.60</td>
</tr>
<tr>
<td>Nitrogen-1</td>
<td>4.24</td>
<td>4.18</td>
<td>7.24</td>
<td>81.50</td>
</tr>
<tr>
<td>Nitrogen-2</td>
<td>4.03</td>
<td>4.15</td>
<td>6.78</td>
<td>174.40</td>
</tr>
</tbody>
</table>

Table E2. The chemical properties of topsoil, overburden, and mullock substrates planted with the Wineberry (Chapter 4)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>EC (µs cm⁻¹)</th>
<th>NH4</th>
<th>NO3 Extractable (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Topsoil</td>
<td>Overburden</td>
<td>Mullock</td>
<td>Topsoil</td>
</tr>
<tr>
<td>Control</td>
<td>4.85</td>
<td>3.99</td>
<td>7.65</td>
<td>93.73</td>
</tr>
<tr>
<td>Biosolid-1</td>
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<td>4.37</td>
<td>7.09</td>
<td>329.00</td>
</tr>
<tr>
<td>Biosolid-2</td>
<td>4.38</td>
<td>4.30</td>
<td>6.86</td>
<td>522.25</td>
</tr>
<tr>
<td>Lupin</td>
<td>4.85</td>
<td>4.32</td>
<td>7.56</td>
<td>123.80</td>
</tr>
<tr>
<td>Sawdust-1</td>
<td>4.81</td>
<td>4.33</td>
<td>7.65</td>
<td>129.35</td>
</tr>
<tr>
<td>Sawdust-2</td>
<td>4.69</td>
<td>4.39</td>
<td>7.63</td>
<td>150.65</td>
</tr>
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<td>Nitrogen-1</td>
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<td>4.06</td>
<td>7.33</td>
<td>359.25</td>
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<tr>
<td>Nitrogen-2</td>
<td>3.82</td>
<td>4.08</td>
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Table E1...continued

<table>
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<tr>
<th></th>
<th>Ca</th>
<th>Mg</th>
<th>Exchangeable (cmolc kg⁻¹)</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Topsoil</td>
<td>Overburden</td>
<td>Mullock</td>
<td>Topsoil</td>
<td>Overburden</td>
</tr>
<tr>
<td>0.98</td>
<td>0.67</td>
<td>2.28</td>
<td>0.29</td>
<td>0.25</td>
<td>1.55</td>
</tr>
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<td>2.97</td>
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<td>2.88</td>
<td>0.57</td>
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<td>1.55</td>
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<td>3.15</td>
<td>3.76</td>
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<td>1.51</td>
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<td>1.44</td>
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<td>2.43</td>
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<td>0.31</td>
<td>0.26</td>
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<tr>
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<td>0.83</td>
<td>2.28</td>
<td>0.25</td>
<td>0.26</td>
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</tr>
<tr>
<td>1.23</td>
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<td>2.26</td>
<td>0.26</td>
<td>0.27</td>
<td>1.20</td>
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<td>0.23</td>
<td>0.23</td>
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<td>2.63</td>
<td>0.30</td>
<td>0.23</td>
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Table E2...continued

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<th>Mg</th>
<th>Exchangeable (cmolc kg⁻¹)</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Topsoil</td>
<td>Overburden</td>
<td>Mullock</td>
<td>Topsoil</td>
<td>Overburden</td>
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<td>0.67</td>
<td>2.28</td>
<td>0.20</td>
<td>0.29</td>
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<td>2.88</td>
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<td>1.58</td>
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<td>3.15</td>
<td>3.76</td>
<td>2.75</td>
<td>0.32</td>
<td>0.41</td>
<td>1.54</td>
</tr>
<tr>
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<td>0.40</td>
<td>2.43</td>
<td>0.22</td>
<td>0.35</td>
<td>1.57</td>
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<tr>
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<td>0.83</td>
<td>2.28</td>
<td>0.22</td>
<td>0.41</td>
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Table E3. The chemical concentration of shoot Red beech planted in the topsoil, overburden, and mullock substrates (Chapter 4)

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<th>Ca (mg kg⁻¹)</th>
<th>Mg (mg kg⁻¹)</th>
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<td>Mullock</td>
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<td>1.00</td>
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Table E4. The heavy metal concentration of shoot Red beech planted in the topsoil, overburden, and mullock substrates (Chapter 4)

<table>
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<th>Treatment</th>
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<th>Cd (mg kg⁻¹)</th>
<th>As (mg kg⁻¹)</th>
<th>Al (mg kg⁻¹)</th>
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Table E5. The chemical concentration of shoot Wineberry planted in the topsoil, overburden, and mullock substrates (Chapter 4)

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Table E6. The heavy metal concentration of shoot Wineberry planted in the topsoil, overburden, and mullock substrates (Chapter 4)

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<th>As (mg kg⁻¹)</th>
<th>Al (mg kg⁻¹)</th>
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<td>Mullock</td>
<td>Topsoil</td>
</tr>
<tr>
<td>Control</td>
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<td>2.11</td>
<td>0.21</td>
</tr>
<tr>
<td>Lupin</td>
<td>4.69</td>
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<td>2.27</td>
<td>0.13</td>
</tr>
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Table E7. The chemical properties of topsoil from different inorganic amendments (Chapter 5)

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<th>NO₃</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>CEC</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Cd</th>
<th>Pb</th>
<th>As</th>
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Table E8. The chemical properties of shoot Red beech from different inorganic amendments (Chapter 5)

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<th>S</th>
<th>Ca</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>Al</th>
<th>Total shoot concentration (mg kg⁻¹)</th>
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Table E9. The chemical properties of Red beech and Wineberry grown in the topsoil and overburden from different N rates (Chapter 6)

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<th>Overburden DM (g plant⁻¹)</th>
<th>Total N (%)</th>
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Table E10. The chemical and physical properties of overburden, before (To) and after (Ti) the short-term weathering period from 4 different water regime status (Chapter 7)

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<th>Clay (%)</th>
<th>Silt (%)</th>
<th>Sand (%)</th>
<th>Ca Exchangeable (cmolc kg⁻¹)</th>
<th>Na</th>
<th>Mg</th>
<th>K Exchangeable (cmolc kg⁻¹)</th>
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<td>To</td>
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Table E11. The chemical and physical properties of overburden, before (To) and after (Ti) the short-term weathering period from 4 different soil amendments (Chapter 7)

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<th>Clay (%)</th>
<th>Silt (%)</th>
<th>Sand (%)</th>
<th>Ca Exchangeable (cmolc kg⁻¹)</th>
<th>Na</th>
<th>Mg</th>
<th>K Exchangeable (cmolc kg⁻¹)</th>
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</thead>
<tbody>
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<td>To</td>
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<td>To</td>
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<td>4.78</td>
<td>332.1</td>
<td>265.8</td>
<td>1.93</td>
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<td>61.7</td>
<td>66.1</td>
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<td>Lupin</td>
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<td>5.37</td>
<td>133.7</td>
<td>239.1</td>
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<td>2.11</td>
<td>60.6</td>
<td>57.8</td>
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<td>Lime</td>
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<td>9.61</td>
<td>62.7</td>
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</table>
### Appendix F – Determination of field capacity

Determination of field capacity

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Rep</th>
<th>AD soil (g)</th>
<th>Tin (g)</th>
<th>FC soil+ tin (g)</th>
<th>OD soil + Tin (g)</th>
<th>FC soil (g)</th>
<th>OD soil (g)</th>
<th>Water at FC (g)</th>
<th>FC moisture (%)</th>
<th>AD moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topsoil</td>
<td>1</td>
<td>480</td>
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<td>620.80</td>
<td>490.84</td>
<td>545.55</td>
<td>415.59</td>
<td>129.96</td>
<td>31.3</td>
<td>15.5</td>
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<td>2</td>
<td>480</td>
<td>77.27</td>
<td>621.54</td>
<td>494.44</td>
<td>544.27</td>
<td>417.17</td>
<td>127.10</td>
<td>30.5</td>
<td>15.1</td>
</tr>
<tr>
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<td>480</td>
<td>75.36</td>
<td>625.92</td>
<td>494.12</td>
<td>550.56</td>
<td>418.76</td>
<td>131.80</td>
<td>31.5</td>
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<tr>
<td>Overburden</td>
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<td>595</td>
<td>73.37</td>
<td>710.14</td>
<td>636.79</td>
<td>636.77</td>
<td>563.42</td>
<td>73.35</td>
<td>13.0</td>
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<td>595</td>
<td>74.61</td>
<td>708.47</td>
<td>639.85</td>
<td>633.86</td>
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<td>68.62</td>
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<td>562.91</td>
<td>70.82</td>
<td>12.6</td>
<td>5.7</td>
</tr>
</tbody>
</table>

**Determination of the substrate and water added per pot**

NB: Removed 200 g to leave space for plant on substrate surface

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Weight (2.5 L pot) (kg)</th>
<th>Add to pot (kg)</th>
<th>AD soil (kg)</th>
<th>AD moisture (%)</th>
<th>OD soil (kg)</th>
<th>FC moisture (%)</th>
<th>90% FC moisture (%)</th>
<th>Weight of 90% FC soil in pot (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topsoil</td>
<td>2.485</td>
<td>2.300</td>
<td>2.300</td>
<td>15.06</td>
<td>2.00</td>
<td>31.07</td>
<td>27.96</td>
<td>2.558</td>
</tr>
<tr>
<td>Overburden</td>
<td>3.022</td>
<td>2.800</td>
<td>2.800</td>
<td>5.52</td>
<td>2.65</td>
<td>12.58</td>
<td>11.32</td>
<td>2.954</td>
</tr>
</tbody>
</table>

AD = air dry
FC = field capacity
OD = oven dry
**Formulation to determine the overburden field capacity**

FC soil = (FC substrate+ tin) - tin
OD soil = (OD soil - tin) - tin
Water at FC = (FC soil - OD soil)
FC moisture = Water at FC / OD soil x 100
AD moisture = (AD soil - OD soil) / OD soil x 100

**Formulation to determine the substrate and water added per pot**

OD soil = (AD soil / ((AD moisture/100) + 1))
90% FC moisture = 0.9 x FC moisture
Weight of 90% FC soil in pot = (90% FC moisture / 100 x OD soil) + OD soil

Note: the weight of 90% FC soil in the pot would change after adding by the soil amendments. For example: the weight of 90% FC soil in pot was 2.954 kg, the biosolid weight added to the overburden was around 100 g, then the weigh of 90% FC soil in pot become 3.054 kg.
Appendix G – Determination and calculation of topsoil buffer capacity (Chapter 5)

Experimental Procedure:

1. Measure out 20 g samples of soil into a set of ten 120 ml plastic beakers.
2. Add the following volumes of water and 0.2 M NaOH or 0.2 M HCl (Table 1).
3. Stir the soil and leave it incubated for 25 minutes.
4. Add 42 ml water to each beaker (1:2.5 soil : solution ratio).
5. Stir the soil suspension, leave for 5 minutes and record the soil pH. Record your results in Table 1.
6. Calculate the amounts of H\(^+\) or OH\(^-\) added (mmol/kg soil) and enter the values in Table 1.
7. Plot pH (X axis) against the amounts of H\(^+\) or OH\(^-\) added (split Y axis, amounts of H\(^+\) descending, amounts of OH\(^-\) ascending). Join the points with a curve of best fit.

Table 1. pH buffer curve

<table>
<thead>
<tr>
<th>Beaker No.</th>
<th>Volume added (ml/beaker)</th>
<th>Amounts of H(^+) or OH(^-) added (mmol/kg soil)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H(_2)O</td>
<td>0.2M NaOH</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>3</td>
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<td>5</td>
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<td>8</td>
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<tr>
<td>9</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

*Amount of OH\(^-\) or H\(^+\) added (mmol/kg) = Volume of NaOH or HCl added x 10 = [Volume x 0.2 x (1000/20)]

8. Calculate the pH buffering capacity of the soil, by drawing a tangent to the curve of best fit you have drawn (pH buffer capacity is defined as the amounts of H\(^+\) or OH\(^-\) ions require to alter the soil pH by one pH unit – mmol H\(^+\) or OH\(^-\) ions/kg soil/pH).

From this experiment, the topsoil buffer capacity was 4 mmol kg\(^{-1}\) soil pH\(^{-1}\)
Example calculation:

pH buffering capacity is defined as the amount of H⁺ or OH⁻ ions required to alter pH by 1 unit. From the following data calculate the amount of liming material required per hectare to a depth of 5 cm to alter the pH by 1 unit. The lime (CaCO₃) content of the liming material is 80%.

- pH buffering capacity = 4 mmol H⁺ or OH⁻/kg soil/pH
- Molecular weight of CaCO₃ = 100
- 1 mole of CaCO₃ = 2 moles of OH⁻
- Bulk density of soil = 0.8 tonne/m³
- 1 ha = 10,000 m²

Answer:

pH buffering capacity = 4 mmoles of H⁺ or OH⁻/kg soil (8 moles/ton)

Weight of soil/ha = volume x bulk density
= (Area x depth) x bulk density
= 10,000 x 0.05 x 0.8 = 400 tonnes soil/ha

Amount of H⁺ or OH⁻ required per ha to alter the pH by 1 unit

= pH buffering capacity x wt. of soil
= 4 x 400 moles/ha
= 1600 moles OH⁻ or H⁺/ha

1 mole of CaCO₃ = 2 moles of OH⁻

Therefore number of moles of CaCO₃ required per hectare:

= 1600/2 = 800 moles CaCO₃

Therefore weight of CaCO₃ required per hectare:

1 mole of CaCO₃ = 100 g
CaCO₃ required per hectare = 800 x 100 g = 80 kg CaCO₃

But the liming material contains only 80% CaCO₃, therefore (100/80) x 80 kg liming material is required.

Amount of liming material required per ha (5cm depth) to alter the pH by one unit = 100 kg/ha

(Amount of CaCO₃ required per kg soil to alter the pH by one unit = 400mg CaCO₃/kg soil = 500mg liming material/kg soil)