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**Carbonaceous soil amendments to reduce plant uptake of Cd in
NZ's agricultural systems**

A Dissertation
submitted in partial fulfilment
of the requirements for the Degree of
Doctor of Philosophy

at
Lincoln University
by
Shamim Al Mamun

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2017

Note on the structure of the thesis

This thesis has been prepared as a series of manuscripts intended for publication in peer-reviewed international journals. At the time of submission, two of the papers have been published and third submitted for publication and further two awaiting approval from co-authors. As all of the papers in the thesis are multi-authored, I have written a short paragraph before each chapter explaining my contribution to the work.

Please note that as the chapters represent publications, there is necessarily some repetition in the introduction and methods sections in Chapters 3 – 7. The thesis contains an introduction and a background chapter (Chapters 1 and 2) that explain the problem at hand and the underlying general science respectively. The findings of the chapters as a whole are discussed in Chapter 7.

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Chapter 3

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Chapter 4

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Chapter 9

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Abstract of a Dissertation submitted in partial fulfilment of the
requirements for the Degree of Doctor of Philosophy.

Carbonaceous soil amendments to reduce plant uptake of Cd in NZ's agricultural systems

by

Shamim Al Mamun

Cadmium (Cd) is a non-essential trace element that accumulates in agricultural soils through the application of Cd-rich phosphate fertiliser and industrial activity. Plants can accumulate Cd to concentrations that sometimes exceed food safety standards presenting a human health risk. Cadmium is readily taken up by plants and can be transferred to grazing animals. In many agricultural systems, Cd concentrations in leafy vegetables and the offal products of grazing animals are at or above food safety standards. There is no practical means of removing Cd from contaminated agricultural soils. Various soil amendments have been used to reduce plant Cd-uptake, but these have mostly focused on heavily contaminated soils and mine tailings. This work aimed to determine whether low cost carbonaceous amendments could effectively reduce Cd uptake by crop plants in agricultural soils with moderate levels of Cd contamination.

We used two contrasting market garden soils (a silt loam and a brown granular allophanic soil) for these experiments, where Cd concentrations in selected vegetables were occasionally above food safety standards (0.1 mg/kg fresh weight). Batch sorption experiments were used to determine the ability of the soils and potential soil amendments to bind Cd from a solution of 0.05M Ca(NO₃)₂. The sorption experiments revealed that composts and lignite bound an order of magnitude more Cd than soils and other potential soil amendments. For all materials, sorption increased with increasing pH of the ambient solution up to a pH of 7.5.

Pot trials were used to determine the effect of various composts, lignite and lime on the uptake of Cd by spinach (*Spinacia oleracea* L.), lettuce (*Lactuca sativa* L.), onion (*Allium cepa* L.) and potato (*Solanum tuberosum* L.). All composts, added at a rate of 2.5% or 5% (w/w) reduced plant Cd uptake by up to 60%. The composts did not induce a deficiency in the uptake of plant nutrients, including essential trace elements such as zinc, and copper. Composts invariably increased plant biomass.

An incubation experiment, including treatments with increased temperature and nitrogen as well as regular disturbance, was used to determine the likely longevity of the Cd-immobilising

properties of the composts. After one year of incubation, there was no significant release of Cd from the compost-amended soils, despite a significant reduction in soil carbon. A pot trial using incubated soil also revealed that the beneficial effects of compost for reducing plant Cd uptake persisted for at least one year. The results indicated that mechanical disturbance of the soil may have resulted in the dissolution / suspension of iron moieties that subsequently occluded Cd on the surfaces of soil colloids.

Lignite generally reduced plant biomass and its effect on plant Cd-uptake was variable. In some cases, lignite caused a significant increase in plant Cd uptake. This was attributed to acidification, probably caused by oxidation of sulphide compounds in the lignite. Potentially, lignite-lime mixtures may be effective, however, the costs of lignite are significantly greater than composts. Using lime to increase the soil pH from 6.0 to 6.5 generally reduced the Cd concentration in soil solution and in vegetables. However, this effect was not consistent, with some treatments causing an increase in plant uptake. Moreover, liming significantly reduced the uptake of essential micronutrients, especially zinc, which offsets its usefulness as a tool to reduce Cd uptake.

I conclude that biological wastes, especially composts, are an underutilised resource that can not only reduce plant Cd-uptake but also improve plant production. Future research should include field trials to determine the performance of Cd in field conditions as well as agronomic practicalities.

Keywords: Biowastes, Lignite, Soil amendments, Heavy metals, Trace elements, Compost, Cadmium contamination, Phytoavailable Cd, Incubation, Potato, Organic amendment, Liming, White lupin, DGT, LA-ICP-MS and Nutrients.

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Chapter 1: General Introduction

1.1 Introduction

Cadmium (Cd) is a naturally occurring heavy metal that is not essential for life (Kabata-Pendias and Mukherjee, 2007). It causes various health related problems in humans and animals through accumulation in different organs. In the human body, Cd enters through ingestion and inhalation (Cadmium Working Group, 2011b; Merian, 1991). The acute effects of this metal can be seen in the respiratory and digestive tracts (Merian, 1991). Predominantly, Cd accumulates in the kidneys with a biological half-life of more than 10 years (Merian, 1991; World Health Organization, 2010). Respiratory tract yields 10% to 40% of the total inhaled Cd from particulate airborne Cd intake. For oral intake, the absorption of Cd ranges approximately from 0.3 to 3%. Higher absorption occurs at low calcium and protein uptake (Merian, 1991). Common toxicity symptoms occur after chronic exposure; and acute human toxicity is rare. Concentrations in the renal cortex increase over time, thus elderly people are more likely to suffer from toxicity. Renal cortex dysfunctions occur when Cd concentration is about 200 mg/kg. Other toxic effects of excess Cd on humans are hypertension, emphysema, carcinogenic changes (mainly of the kidney and prostate), skeletal deformation and low reproductive function (Kabata-Pendias and Mukherjee, 2007).

Humans are exposed to Cd mainly from two sources, inhalation from industrial activity (Kabata-Pendias and Mukherjee, 2007; Merian, 1991) and ingestion through consumption of foods grown in Cd elevated soils due to application of Cd contaminated phosphate fertilizers (Kabata-Pendias and Mukherjee, 2007; Taylor, 1997). In 1996, 300 tonnes of Cd was deposited in the soils of USA. The global use of Cd in industry has decreased since 1990 (Kabata-Pendias and Mukherjee, 2007).

Cadmium occurs naturally as a contaminant in all phosphate rocks, although the concentrations vary considerably, depending on the origin of the parent material. Rock phosphate originating from igneous rocks generally contains Cd concentrations of 0.7 - 30 mg/kg P (Oosterhuis et al., 2000), whereas rock phosphate refined from sedimentary rocks may contain Cd concentrations higher than 556 mg/kg P (Mar and Okazaki, 2012). Rock phosphate from sedimentary rock sources account for some 85-90% of world P production (Oosterhuis et al., 2000). Phosphate fertiliser use has resulted in an enrichment of Cd in agricultural soils worldwide (Hooda, 2010; Kabata-Pendias and Mukherjee, 2007). Historically, New Zealand and Australia manufactured superphosphate using phosphate rock from Nauru and Christmas Island, which contained relatively high Cd concentrations >600 mg Cd/kg P (Syers et al., 1986). Repeated application of this Cd-rich superphosphate fertilizers for most of the 20th century has resulted in significant increases in the Cd concentrations in New Zealand soils (Taylor, 1997).

The phytoaccumulation of Cd is primarily a concern for human health. Cadmium phytotoxicity is lower than for many other non-essential elements (Sanità di Toppi and Gabbrielli, 1999). Plants can readily take up Cd, leading to an accumulation in fodder and food products and subsequently in animals and humans through consumption (Cadmium Working Group, 2011b). Accumulation of Cd in soils has been reported worldwide (Hooda, 2010; Kabata-Pendias and Pendias, 2001; Kabata-Pendias and Mukherjee, 2007). Exceedance of the permissible limits of Cd in plants has been observed (Kim, 2008; McLaughlin et al., 1994b). Exceeding food standards of overseas partners might restrict export (Cadmium Working Group, 2011b) and a non-tariff trade barrier might be imposed by protectionist governments through the use of food safety standards (Roberts and Longhurst, 2002). Among the factors influencing the accumulation of Cd in plants, the elevated concentration of Cd in agricultural soils is one of the main reasons for increased concentration of Cd in plants

(Kabata-Pendias and Mukherjee, 2007). In NZ soils, enrichment of Cd is reported (Gray et al., 1999d; Kim, 2008; Roberts et al., 1994; Schipper et al., 2011; Taylor, 1997; Taylor et al., 2007). In some cases, soil Cd concentrations are more than 12 times higher in agricultural lands than in unfertilized soils with background concentrations of Cd. Phosphate fertilizer is considered the main culprit (Loganathan et al., 2003). Kabata-Pendias and Mukherjee (2007) reported that Cd enrichment in NZ soils is as high as 8.9 g/ha/yr whereas the average value for European Community countries is 2.5 g/ha/yr (Kabata-Pendias and Mukherjee, 2007). Thus, it is imperative to reduce the input of Cd in agricultural soils through contaminated fertilizer application although it is practically not viable to stop using the phosphate fertilizers, as this would drastically reduce agricultural production.

Researchers are investigating alternative ways of reducing the concentration of Cd in soils, and therefore decreasing the accumulation of Cd in plants, through different processes, including the application of less Cd-containing phosphate fertilizers, incineration of soils, adsorption and desorption processes, solubility, chemical treatment and bio extraction/phytoremediation (Kabata-Pendias and Mukherjee, 2007). Liming soil is one of the options that has been considered to reduce the transfer of Cd from soils to plants, although the effectivity depends mostly on soil pH and soil properties (Kabata-Pendias and Mukherjee, 2007). Organic matter and some soil amendments have a number of functional groups (Wild, 1993) and may reduce the movement of Cd in soil (Pusz, 2007). As well, some soil organic amendments contain significantly higher P and other plant nutrients, which might offset the need to use large amounts of phosphate fertilizers on agricultural land.

1.2 Objectives

This thesis aims to determine the potential of low-cost carbonaceous soil amendments to reduce Cd uptake by crop plants in agricultural soils with moderate levels of Cd contamination. The specific aims of this thesis were:

- 1) Compare the ability of potential soil amendments to remove Cd from soil solution.
- 2) Determine the efficacy of selected soil amendments to reduce Cd uptake by a range of vegetables and compare the growth and elemental uptake of compost-amended soils with limed soils.
- 3) Determine the persistence of a potential soil amendment and elucidate how such an amendment releases Cd as it decomposes.

Chapter 2 Literature Review

2.1 Cadmium

Cadmium (Cd) is a heavy metal, which has a density of 8.64 g/cm³ at 20°C, a melting point of 320°C, a boiling point of 767°C and is a silver-white, lustrous and ductile metal. The atomic number is 48 and atomic mass is 112.4 and there are eight naturally occurring isotopes (listed in order of abundance) ¹¹⁴Cd (29%), ¹¹²Cd (24%), ¹¹¹Cd (13%), ¹¹⁰Cd, ¹¹³Cd, ¹¹⁶Cd, ¹⁰⁶Cd and ¹⁰⁸Cd. Cadmium is the 67th most abundant element. Its oxidation state is 2⁺ in all compounds. It has a normal electrochemical potential of -0.40 relative to the hydrogen electrode and is slightly more noble than Zn. The size of the Cd ion (r = 103 pm) and Ca ion (r = 106 pm) is very close (Merian, 1991). Cadmium is known mostly for its toxicity to animals and humans (Merian, 1991; Sigel et al., 2013). In some places it occurs naturally at high concentrations (Jacob et al., 2013), however, most Cd contamination is anthropogenic. The magnitude and type of anthropogenic Cd sources vary between locations. A considerable amount of Cd contamination results from industrial activities. Nevertheless, in some agricultural countries, the application of Cd-rich phosphate fertilizers causes pervasive soil Cd contamination (Cadmium Working Group, 2011b). Sewage sludge or household leachate used for irrigation also increases the average Cd in soil (Gholami et al., 2011).

2.2 Cadmium and health

Cadmium enters the human body through food (plant or meat products) as an outcome of uptake of Cd by grass and crops from soil (Cadmium Working Group, 2011b). Adverse health effects of soil Cd have led to public concern over soil contamination (Dudka et al., 1996). Cadmium is non-essential for any regulatory function in humans and animals, although in some marine diatoms it is observed as a Zn-replacing element at the catalytic site of a

particular class of carbonic anhydrase (Sigel et al., 2013). Once absorbed, Cd is efficiently retained in the human body and accumulates throughout life (Bernard, 2008).

Many authors have reported that Cd is involved either directly or indirectly with many problems in human body. Cadmium accumulation in kidneys creates toxicity (Ferrari et al., 2013), especially through the proximal tubular cells, which is the main site of accumulation (Bernard, 2008). The half-life of Cd in kidneys is 10-30 years. Cadmium can cause bone damage (Merian, 1991) through decalcification. It also has the ability to damage bones indirectly as a result of renal dysfunction (Bernard, 2008; Järup and Åkesson, 2009). Cadmium exposure may increase important manifestations of cardiovascular disease (Peters et al., 2010; Sigel et al., 2013). Environmental exposure to Cd is associated with significantly increased stroke and heart failure prevalence. Cadmium might have a wide range of detrimental effects on human reproduction, through interference with DNA binding zinc (Zn), as has been observed in mammalian reproduction (Henson and Chedrese, 2004). Exposure to Cd is associated with altered gene expression in humans (Tvermoes et al., 2011). Prolonged exposure to low doses of Cd leads to high hepatic accumulation, which can then cause fibrosis (Baba et al., 2013). Cadmium affects the lungs and generates oxidative stress (Sigel et al., 2013). The toxicity of Cd accumulation in liver can be chronic (Cadmium Working Group, 2011b). Cadmium may be a human carcinogen as well (Ferrari et al., 2013; Jacob et al., 2013; Merian, 1991; Nawrot et al., 2008) and potentially transferred through trophic dietary bioaccumulation (Jacob et al., 2013). Heavy long-term Cd exposure might produce irreversible adverse health effects and in particular, cases of vitamin and protein deficiency (Merian, 1991).

2.3 Economic Significance

The economy of agriculture-based countries will be greatly affected due to the accumulation of Cd in soils and their subsequent transfer to plants, and ultimately to animals. Animals store Cd in their liver and kidneys and offal products may have elevated Cd concentrations. New Zealand already has an offal discard policy: kidneys from animals older than 30 months are not eligible for human consumption and must be discarded. It should be noted, considering the severity of Cd concentration, that the Cadmium Working Group (2008) commented that the discard of offal represents a significant loss of revenue for NZ (Cadmium Working Group, 2008). Agricultural, forestry and horticultural exports are generally 65% of New Zealand's total export (Cadmium Working Group, 2008). These products are intimately related with soil and its elemental composition. It is anticipated by the Cadmium Working Group (2008), that the elevated Cd concentration in soil is likely to affect the horticultural products and its export (Cadmium Working Group, 2008). New Zealand exports vegetables in the fresh, processed, and frozen form. New Zealand crops grown for export must meet domestic, as well as trading partners' food standards. Market access for exported products requires compliance with importing countries food standards, which include maximum limit or Maximum Residue Levels (MRLs). Food products exceeding the MRLs will be rejected, as they are considered unfit for consumption. The MRLs are usually tested at the ports of importing countries. In a report, the Cadmium Working Group (2008) expressed their anxiety about NZ products failing to pass the MRLs (Table 2.1) and subsequent loss to the NZ economy.

Table 2.1 MRL levels of various products in Australia and NZ and the EU (Cadmium Working Group, 2008)

Product	MRL for Cd (mg/kg)	
	Australia and NZ	EU
Liver of cattle, sheep and pigs	1.25	0.5
Kidneys of cattle, sheep and pigs	2.5	1.0*
Leafy vegetables	0.1	0.2

*The EU (European Union) includes poultry kidneys in its standard. MRL: Maximum Residue Level.

Recently, the increasing Cd concentrations in pasturelands have been flagged by the Cadmium Working Group (CWG) as an emerging environmental issue in NZ that could detrimentally affect NZ's export earnings and tarnish the image that NZ aims to portray in overseas markets (Cadmium Working Group, 2008).

2.4 Cadmium in phosphorus fertilizer

Phosphorus fertilizers add Cd to soils as Cd occurs naturally as an impurity in all phosphate rocks, although depending on the origin of the phosphate rocks, the Cd concentrations vary considerably. Sedimentary rocks contain high amounts of Cd. Conversely, igneous rocks contain low Cd (Table 2.2) as most of the Cd volatises at the temperatures at which these rocks are formed (Loganathan et al., 2003). In apatite, Cd substitutes calcium (Ca). The amount of Cd varies in rocks replacing Ca (Chien et al., 2011). Phosphate rocks with low Cd are difficult to find and the supply of these rocks is erratic. Igneous rock, or apatite, is found in the former Soviet Union, Finland, South Africa and South America and has low concentrations of Cd (often less than 2.29 mg Cd/kg P). Sedimentary rocks contain Cd in concentrations ranging from less than 46 to more than 458 mg Cd/kg P. These rocks account for some 85-90% of world's fertilizer production (Oosterhuis et al., 2000).

Table 2.2 Cadmium concentration of main commercial phosphate rocks according to different sources
(Oosterhuis et al., 2000)

Origin	Cadmium content (mg/kg P ₂ O ₅)		
	Davister (1996)	Botschek and Van Balken (1999)	Demandt (1999)
<i>Igneous Rocks</i>			
Kola (Russia)	< 30	0.7	0.57
Pharlaborwa (South Africa)	< 30	0.23	0.87
<i>Sedimentary Rocks</i>			
Florida (USA)	53	45-75	55
Jordan	<69	28-64	41
Khouribga (Morocco)	105	39-144	126
Syria	119	30-105	50
Algeria	137	96-143	-
Egypt	169	-	-
Bu-Cra (Morocco)	229	231-263	222
Nahal Zin (Israel)	229	185-256	140
Youssofia (Morocco)	277	377	275
Gafsa (Tunisia)	314	215	396
Togo	371	376-410	337
North Carolina (USA)	380	286	275
Taiba (Senegal)	465	378-414	506
Nauru	556	-	-

Unprocessed rock phosphate is not suitable for direct application, since the phosphorus inside it is insoluble. Three kinds of acids are used to process the phosphate rock:

- * phosphoric acid, producing Triple Super Phosphate (TSP);
- * nitric acid, producing Ammonium Phosphate (NP), used in the manufacture of complex fertilisers; and
- * sulphuric acid, producing either Single Super Phosphate (SSP) or phosphoric acid, an intermediate product in the production of TSP, Mono- and Di-Ammonium Phosphate (MAP and DAP) and complex fertilisers. The process leads to gypsum (CaSO₄) as a by-product. The Cd in the phosphate rock is divided among the phosphoric acid and the gypsum (Oosterhuis et al., 2000).

The processes are important in determining the amount of Cd in P fertilizers. Among the processes, the use of phosphoric acid to produce phosphorus fertilizer keeps the least amount of Cd in P fertilizers compared to the other two processes. Many fertiliser industry representatives, however, argue that a large scale substitution (or blending low and high-Cd grades) to produce less Cd-containing P fertilizer would not be a feasible strategy, due to the limited production capacity and reserves of low-Cd phosphate rock (Oosterhuis et al., 2000). Only a limited amount of Cd is lost with the by-products during the production of P-fertilizers from P containing rocks. The Cd/P ratio remains the same in processed fertilisers which determines the degree of impurity and the risk of increasing Cd in agricultural lands (Nziguheba and Smolders, 2008).

2.5 Cadmium in NZ soil

Cadmium concentrations in NZ's soils are significantly higher than background concentrations and are continuing to increase (Gray et al., 1999d; Kim, 2008; Roberts et al., 1994; Schipper et al., 2011; Taylor, 1997; Taylor et al., 2007). Prior to agricultural use, the concentration of Cd in soils was low. Roberts et al. (1994) observed the total soil Cd concentration of about 0.20 mg/kg in the top soils (0-7.5 cm) of 86 non-agricultural sites in New Zealand. A similar result was found by Taylor et al. (2007), where 372 (unfertilized/background) top soils (mostly 10 cm) were sampled and the average concentration was 0.16 mg/kg soil. Taylor et al. (2007) collected data about Cd from 1794 soil samples from almost all types of land uses in NZ. Soils were analysed from cropping, pasture, horticulture and unfertilized soils amounting to 301, 825, 296 and 372, samples respectively (Table 2.3). The cropping, pasture and horticulture soils had Cd concentrations of 1.5 times, more than 2.5 times and more than three times, respectively than the unfertilized soils. The average Cd concentration of land used for agricultural purposes demonstrates the increase of Cd in all types of agricultural land use in NZ. The highest average Cd

concentration was observed in horticulture soils. The depth of soil was also considered, as ploughing and plant root depth varies for different types of cropping and fertilizer mixing.

Table 2.3 Cd concentration in NZ soils by land use (Taylor et al., 2007)

Land use	Number of samples	Average sampling depth (cm)	Average Cd (mg/kg)	Range (mg/kg)
Cropping	301	14.3, mostly 0 - 15	0.24	0.00 - 0.99
Pasture	825	9.39, mostly 0 - 7.5, 0 - 10 or 10 - 5	0.43	0.00 - 2.52
Horticulture	296	13.1, mostly 0 - 10	0.50	0.00 - 2.00
Background ("unfertilised")	372	10.0, mostly 0 - 10	0.16	0.00 - 0.77
All land use	1794		0.35	0.00 - 2.52

Zanders (1998) showed that the Cd concentration in agricultural soils decreases with depth in 17 soil types on NZ farms, which implies that the parent rock's contribution to Cd deposition in the top soils is low. The status of Cd in some specific region's soils of NZ is severe. Based on sampling, it is estimated that 17% (approximately 1775 hectares) of Waikato's horticultural soils and 11% (approximately 15700 hectares) of Waikato's pastoral soils already exceed 1 mg Cd/kg soil (Kim, 2008).

There is a positive correlation between the fertilizer and tillage history and the amount of Cd present in agricultural land in NZ (Cadmium Working Group, 2011a) that are comparable to concentrations reported in other industrialised countries (Hooda, 2010; Traina, 1999). According to Loganathan et al. (2003) the major anthropogenic sources of Cd in NZ are P fertilisers, biosolids (sewage sludge) and industrial waste application. In NZ, P fertiliser is the most relevant anthropogenic source of Cd in cultivated soils, while atmospheric deposition and biosolids application are only important in some localised areas (Loganathan et al., 2003). The Cadmium Working Group (2011a) also reported that every year a large amount of P

fertilizer is added to the agricultural land in NZ, which contributes to the enrichment of Cd. In soils with intensive agricultural practices are usually observed to have high concentrations of Cd. These lands usually receive P fertilizers of different amounts. Taylor et al. (2007) blamed the Cd-rich superphosphate in the build-up of Cd in NZ soils and increasingly, soil Cd concentrations around the country are exceeding the self-imposed limit of 1 mg/kg (Taylor et al., 2007).

Oceanic sedimentary and guano-based rocks from the Christmas Islands and Nauru Island were the main source of P rock in NZ up to the early 1990's, and these are considered high-Cd rocks on the international scale (Gray et al., 1999d; Loganathan et al., 2003). Initially, the Cd concentration in P-rock used in NZ was around 340 mg/kg P (Cadmium Working Group, 2011a).

Before 1995, it was revealed that the Nauru P rocks are one of the highest sources of Cd in the world (Table 2.4). From 1995, the concentration of Cd in P Fertilizer was voluntarily reduced to 180 mg/kg P which is below the upper limit of 280 mg/kg P set in 1997 (Cadmium Working Group, 2011a). The source of low Cd phosphate rocks has some strategic problems. North Carolina Rocks are only exported to NZ in their value-added form (fertilizer) (Cadmium Working Group, 2011a), resulting in higher costs. A similar problem applies to Chinese rock phosphates, which is further complicated by export taxes and logistical difficulties (Cadmium Working Group, 2008). The current main low-Cd source from Morocco is mined in the Western Sahara, which is subject to a United Nations mediated process and this may affect the long-term supply (Cadmium Working Group, 2008).

Table 2.4 Estimated rock blends for manufactured superphosphate 1952-2005 in NZ (Cadmium Working Group, 2008)

Year	Phosphate rock source/blend	Cadmium (mg Cd/kg P)
1952-1968	Dominantly Pacific Island rocks	200-490
1968-1975	Mostly Nauru/ some Christmas Island	200-450
1975-1983	50:50 Nauru/Christmas Island	200-500*
1983-1996	Nauru/Christmas Island/North Carolina	200-450
1996-2005	China/Morocco/Togo	10-340

*Original reference contained a typographical error “200-50”

At the current Cd loading rate it is projected that the average Cd concentration in all horticultural potato growing soils (Waikato is the NZ’s second largest potato growing region) and pastoral soils of Waikato region will exceed the 1 mg Cd/kg soil in 13 years and under 40 years, respectively (Kim, 2008). In NZ agricultural soils the Cd concentration has increased to a concentration which is alarming for future agricultural practices of NZ and the Cd concentration is still much higher in P fertilizers used in NZ than the limit values in P fertilizers of EU member states (Table 2.4 and Table 2.5) (Oosterhuis et al., 2000). NZ-grown export products containing high Cd concentrations, may negatively affect exports in the future, as the “100% pure” image and current good quality of export produce, is slowly eroded.

Table 2.5 Limit values for Cd in fertilizers and soils in EU Member States. Adapted from (Oosterhuis et al., 2000)

Country	Max. concentration of Cd in fertilizer (mg/kg P)	Max. amount of Cd input to agricultural soils (g/ha/year)	Max. concentration of Cd in agricultural soils (mg/kg dry soils; guidance level)
Austria	172 (since 1994)	10	1.0
Belgium/Lux.	206	150	1.0-3.0
Denmark	108 (since 1995)	-	0.5
Finland	49	3	0.5
Germany	92-206	16.7	1.0
Netherlands	40	-	0.5-1.0
Portugal	92-160	-	-
Sweden	98	1.75	-
UK	-	0.15	3.0

There is no commercially viable process for the removal of Cd from phosphate rock (Cadmium Working Group, 2011a). As the low Cd-containing P rocks are depleted at an ever-faster rate, farmers will be forced to apply poor-quality high-Cd phosphate rocks. The estimation of the time for low Cd-containing P rock to be depleted, ranges from 30 to 300 years (Cordell and White, 2011) indicating the potential use of higher Cd containing P rocks in fertilizers in future.

It is important to maintain the application of P rock fertilizers to NZ soils as NZ has few sources of recyclable organic P, and these are in the form of manure from sewage or housed animal production (Hedley et al., 2010). It is estimated that less than 5% of the national maintenance P application can come from poultry and pig manure and raw sewage sludge (Hedley et al., 2010). Therefore, the demand for P in agricultural use will mainly be fulfilled by mineral P fertiliser. In NZ, single superphosphate is the dominant P fertilizer, followed by diammonium phosphate (25%) and other P fertilisers (10%), mainly reactive phosphate rock (Hedley et al., 2010).

Due to the preference for higher quality phosphorus fertilizers, it is expected that in respect to P percentage and Cd concentration, the quality of P fertilizers will decrease eventually (Cordell and White, 2011) leading to more Cd input with increased application of P fertilizers in future in NZ soils. New Zealand's dependency on phosphate fertilizers is unlikely to decrease significantly in the coming years, there are no low-cost means of removing Cd from P fertilizers, and Cd concentrations in New Zealand's soils will continue to increase. So, it can be assumed that to maintain the P status of its agricultural lands, New Zealand will face big challenges if it wants to avoid fertiliser -derived contamination in agricultural lands. As Cd is increasing in NZ soils, so more studies related to Cd should be undertaken to ensure safe food products (Römken et al., 2009).

2.6 Solubility of Cd in soils

The term soluble can be defined as dissolved in a media (Priester et al., 2009; Viipsi et al., 2010), eg. water. Thus, soluble Cd is the fraction of the total Cd in soil, which is present in soil solution (Robinson et al., 2009). An important distinction in the heavy metals distribution in soils is whether the heavy metals are inert, able to interact with plants referred as phytoavailable, or whether able to interact with any biological organism, including humans that is referred as bioavailable. These terms phytoavailable and bioavailable are used to indicate a heavy metal's physicochemical potential but not its biological action. For example, phytoavailable heavy metals may be toxic to plants, or can be accumulated in the plant's shoots, but they are not necessarily so. The Toxicity and accumulation of heavy metals are dependent upon plant species (Robinson et al., 2009).

Cadmium in soil is partitioned between soluble and insoluble forms. Phytoavailable Cd is only a fraction of the total Cd concentration in soil solution that is accessible to plants. There are many factors that influence the availability of Cd to plants (Kabata-Pendias, 2004). The uptake of Cd by plants is dependent on both the total amount of Cd in soil and factors that

affect the phytoavailability of Cd in soil. Thus, the concentration of Cd in dilute salt extractants or soil solution may be a better predictor of the accumulation of Cd in plants, besides the total Cd concentration in soil (Smolders, 2001).

Although some complexes in soil solution are known to contribute to the overall transfer of Cd from soil to plants, the free Cd ion is the most phytoavailable and therefore a prime factor in the accumulation of Cd by plants (Hooda, 2010; Silveira et al., 2003). Many authors reported the influence of Cl^- in soil and soil solution on the transfer of Cd from soil to plants. They observed the increase of Cd uptake with increasing Cl^- in soil or soil solution (Ghallab and Usman, 2007; Smolders and McLaughlin, 1996; Weggler-Beaton et al., 2000). A similar result was also observed with the increasing amount of SO_4^{2-} in soil solution, which might be due to the phytoavailability of Cd-sulphate complexes (Berkelaar and Hale, 2003; Lopez-Chuken and Young, 2010; McLaughlin et al., 1998).

Cadmium extraction in soils using diluted NH_4OAc , $\text{Ca}(\text{NO}_3)_2$ (Black et al., 2012; Gray et al., 1999b) and CaCl_2 (Andrews et al., 1996; Gray et al., 1999b) was conducted in studies and reported that, the concentration of Cd in plants is highly correlated with the extractable Cd. Clays, oxides and soil organic matter influences the mobility of elements through formation of complex bonds (Wild, 1993).

2.6.1 Effect of pH

Soil pH affects the transfer of Cd from soil to plants. Most studies show that a high pH usually increases the binding of Cd with materials in soil, leading to less available Cd in soil and less accumulation by plants (Loganathan et al., 2003; McLaughlin et al., 1996) although in some studies the opposite scenario was also observed by McLaughlin et al. (1996). McLaughlin et al. (1996) and Smolders (2001) found a high accumulation of Cd in plants at higher pH values although there was less Cd available in soil solution for plant uptake (Smolders, 2001). At low pH the low uptake may be due to the competition of Cd^{2+} with proton (H^+) (McLaughlin

et al., 1996) and at high pH Zn deficiency in plants (Smolders, 2001) may enhance the uptake of Cd.

2.6.2 Organic matter

The addition of organic matter to soil can modify the phytoavailability of heavy metals (Chami et al., 2013). Tachibana et al. (2013) observed that the use of organic matter significantly decreases the peroxidative stress and Cd uptake in barley.

According to Brady and Weil (2013), organic compounds vary greatly in their rate of decomposition and they decompose in the following order; (listed fastest to slowest) sugar, starches, simple proteins; crude protein; hemicelluloses; cellulose; fats, waxes, etc.; lignin and the end product of these are humus. The surface area of humus colloids per unit mass is high, generally exceeding that of silicate clays. The colloidal surfaces of humus are negatively charged, the sources of the charge being hydroxyl (-OH), carboxylic (-COOH), or phenolic groups. The extent of the negative charge is pH dependent (high at high pH values). At high pH values the CEC of humus on a mass basis (150-300 Cmol_c/kg), far exceeds that of most silicate clays. Humus has a favourable effect on aggregate formation and stability. The carboxylic and phenolic groups of humus, when dissociate, form pH dependent negative charges. At pH 7, in well-drained soils, the value of the charge is about 3 moles of charge per kg of humus, which is mainly from dissociation of carboxylic acid (Wild, 1993). Chelates involve a direct bond between metal and ligand in more than one place. Adsorption due to CEC is electrostatic attraction between a hydrated ion and the negative surface charge of a colloid. Humic substances have a high amount of carboxylic and phenolic OH groups, which in dissociation form negative charges and increase CEC of soil (Brady and Weil, 2013).

The physical and chemical properties of soils are improved by organic matter. Humic acid, fulvic acid, humin, polysaccharides, polyuronides etc. have many functions in soil, leading to better soil physical and chemical conditions for all organisms present in soil (Brady and Weil,

2013). The humic and fulvic acid fractions are prominent in cation adsorption or immobilization by high molecular weight organic substances such as lignin or complexation by initially soluble organic substances that form insoluble salts (Brady and Weil, 2013). The mobility and form of metal contaminants in soil are influenced by the physical and chemical properties of the soil (Brady and Weil, 2013). Adsorption greatly influences the mobility of metals in soil and controls the behaviour and phytoavailability of metals in soils (Brady and Weil, 2013). Organic matter is highly capable of binding cations through the formation of coordinate complexes or ion exchange between soil solution and solid phase (Senesi, 1992).

2.6.3 Clay fraction

The clay fraction usually has a high CEC compared to sand and silt. Thus, clay particles play a vital role in fixing elements in soil. Not all clay particles sorb Cd in the same way as their CEC (Table 2.6) and surface area vary. Allophanic clay has a low ability to adsorb Cd^{2+} (Shahriari et al., 2010), whereas vermiculite and montmorillonite might be more effective. The fractionation of 12 NZ topsoils using the sequential fractionation procedure were conducted and reported that 13% Cd was associated with amorphous oxides and for crystalline oxides it was 12% (Gray et al., 2000) indicating the capability of clay to adsorb Cd.

Table 2.6 Typical CEC values of soil colloids (McLaren and Cameron, 1996)

Colloid	CEC (Cmol _c /kg)
Humus	100-300+ ¹
Illite (hydrous mica)	10-40
Vermiculites	100-200
Smectites	60-150
Pedogenic chlorite	10-30
Kaolinite, halloysite	2-15
Allophane, imogolite	30-150
Fe and Al hydrous oxides	<1 ¹
Kaolinite	3-15
Halloysite 2H ₂ O	5-10
Halloysite 4H ₂ O	40-50
Montmorillonite-group	70-100

¹ Varies greatly with pH

Controversy exists about the way to affect movement of Cd through various particles in soil. The mechanism by which CEC affects, specific adsorption, solubility, occlusion and/or anything else, is not yet clearly established.

2.6.4 Competing Ions

Other cations present in soil solution play an important role determining the availability of Cd in soil solution. It is observed that Cd competes with other cations for the binding sites in temperate soils (Christensen and Haung, 1999b). As Cd is not expected to form inner sphere complexes with soil components, so competition is expected to occur at ion exchange sites (Scheffer et al., 2010; Silveira et al., 2003).

The Ca content in soil is sometimes considered an important parameter influencing the availability of Cd for plants, as Ca may compete for exchangeable sites in soil depending on the selectivity of other ions towards different exchangeable positions in soil (Merian, 1991).

The elements Mg, K and Na compete less than Ca for Cd-binding sites because of their different sizes and/or charges (Christensen and Haung, 1999b). Trace metals are also known to compete with Cd for adsorption sites. The sorption coefficient K_d for specific adsorption

on pedogenic oxides increases in the order $Cd < Ni < Co < Zn < Cu < Pb \ll Hg$ (Scheffer et al., 2010).

Zinc is considered the most important competing trace element, as Cd is chemically similar to Zn, and Zn is normally present in higher concentrations (Christensen and Haung, 1999b). It is observed that with the increase of Zn concentration (application) in solution, the concentration of Cd also increases in the solution which indicates that the same sorption sites are available for Cd and Zn (Christensen, 1987). Other researchers also mentioned the competition of Cd with other trace elements in soil, such as Pb (Serrano et al., 2005), Ni (Liao and Selim, 2009) and Cu (Vergara and Schalscha, 1992).

Increased Cl^- has been reported to be associated with Cd^{2+} in soil thus increasing $CdCl^+$ species activity in soil and therefore increased Cd concentration in Wheat (*Triticum aestivum* cv. Halberd) and Swiss chard (*Beta vulgaris* cv. Foodhook Giant) (Ghallab and Usman, 2007; Smolders and McLaughlin, 1996; Weggler-Beaton et al., 2000). The $CdCl^+$ in soil is reported to be available both in acidic and alkaline solution (Sposito and Page, 1984).

2.7 Cadmium uptake by plants

Plants have no metabolic requirement for Cd although it is relatively available to plants. Its concentration in food and feed plants is of great concern and its content in food plants varies between 2-400 $\mu g/kg$ (Kabata-Pendias and Mukherjee, 2007; Kim, 2008) (Table 2.7).

Table 2.7 Cadmium in food plants (Kabata-Pendias and Mukherjee, 2007)

Plant	Range (µg/kg)
Cereal, grains	5.6-32
Wheat, grains	20-70
Barley, grains	13-22
Legumes	1-30
Broccoli	10
Cabbage	5-10
Lettuce	29-400
Carrot	30-240
Onion	80
Potato	16-300
Tomato	30
Spinach	43-150

Both soil and air may supply Cd to plants. In areas with low direct atmospheric deposition of Cd, i.e. <2 g/ha/y, the aerial contribution to plant Cd is low (Smolders, 2001). The Cd in plants of NZ can be mostly attributed to uptake from soil, as atmospheric deposition in NZ is much lower than 2 g/ha/y (Gray et al., 2003). The level of Cd found in plants grown and animals grazed was related to the Cd concentration in the soil (Gray et al., 2003).

Many researchers have observed the transfer of Cd from soil to plants (Berkelaar and Hale, 2003; Lopez-Chuken and Young, 2010; McLaughlin et al., 1998; Meharg et al., 2013). Increasing Cd concentration in soil increases Cd accumulation in crops (Meharg et al., 2013; Nan et al., 2002). High Cd concentrations were found in potato tubers (Dudka et al., 1996). Wang (2012) reported that in a farmland of Tianjin, more than 60% of the vegetable samples had Cd concentrations above the standard level (0.05 mg/kg f.w.). It is forecast that increased soil Cd levels will cause increased levels of Cd uptake in specific agricultural products without intervention and in excess of food standards (Cadmium Working Group, 2008). Kim (2008) reported the exceedance of Cd concentration in 1.5% of the potato samples collected

from the Waikato. Per capita intake of a particular food is also important in considering the effect of transfer of Cd from soil to plants (Meharg et al., 2013) and from plants to humans through crop products and animal products (as animals consume plants).

2.8 Plant variety

The uptake of Cd is dependent not only on soil factors but also on plant species. Many researchers have observed the differential uptake of Cd by different plant varieties and species (Loganathan et al., 2003; Welch and Norvell, 1999). In a pot trial of vegetable crops, it was found that lettuce and carrot accumulated more Cd than the common pasture species perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) where 10 New Zealand soils were used (Gray et al., 1999b). High Cd concentrations were found in potato tubers (Dudka et al., 1996).

Roberts et al. (1994) found in a comprehensive survey (including 312 pastoral and 86 non-agricultural sites), similar Cd concentrations in grass and legumes, but significantly higher concentrations in weeds. The mean plant concentrations on the pastoral soils were 0.10, 0.06 and 0.28 mg/kg d.w. for the grass, legume and weed species respectively (Roberts et al., 1994). Selective breeding of low-Cd varieties is widely discussed as a means to cope with increasing pasture Cd concentrations (Grant et al., 1999a; Redjala et al., 2009). In a study with 11 different perennial ryegrass varieties grown on a contaminated soil showed that Cd accumulation varied among the varieties and this might be important in managing Cd in agricultural lands (Gray and McLaren, 2005). High concentrations of Cd were observed in rice grains deemed unsafe by international and national regulators (Meharg et al., 2013). As it has been observed that different species uptake Cd in different amounts, the development of genetically modified varieties that uptake Cd in smaller amounts, could decrease the threat of Cd in agricultural systems.

2.9 Cadmium mitigation strategies in agricultural systems

2.9.1 Eliminate or reduce the use of P fertilizer

The P is a macro essential element for plants. There is no substitute for P for plant growth. The elimination or reduction of P fertilizer use in the agricultural lands of NZ is not possible as an organic source of P is not abundant in NZ. Moreover, the plant's requirement for P is higher and a significant amount of P is immobilized and fixed in soil. So, the elimination or reduction of Cd input to NZ soils is not actually practical, as the organic P source in NZ soils is low and estimated at less than 5% of the national maintenance from different manures (Hedley et al., 2010). Globally there is an increasing awareness about the diminishment of phosphate rock resources (Beardsley, 2011; Cordell and White, 2011; Neset and Cordell, 2012). In addition, it is expensive to remove Cd from superphosphate rocks. The estimation of the time for P rock to be depleted ranges from 30 to 300 years (Cordell and White, 2011) indicating that increasingly high Cd-contaminated P fertilizers will need to be used, as the lower Cd-containing materials are depleted.

2.9.2 Tiered fertilizer management strategy

A tiered fertilizer management system (a system that links soil Cd levels to overall Cd management action) might be used to lessen the effect of continued application of Cd-rich phosphate fertilizers that is increasing the Cd concentration in agricultural lands. According to this system, soils with <0.6 mg/kg Cd have no restriction placed on the application of P fertilizers. Soils with concentrations between >0.6 and <1.0 mg/kg Cd are permitted restricted use of P to ensure that the soil does not exceed 1.8 mg/kg Cd after 100 years. More intensive monitoring and modelling is required for soils with Cd concentrations >1.4 and <1.8 mg/kg. No further Cd accumulation is permitted in soils with Cd concentrations >1.8 mg/kg (Rys, 2011).

2.9.3 Phytoextraction

Phytoextraction has been reported as an economically and ecologically sound alternative for the remediation of metal-contaminated soils. Willow (*Salix alba* L.) is a metal phytoextractor, which combines a gradual contaminant removal with production of biomass. It was observed that changing the bacterial community in the plants' rhizosphere, developed the resistance of the plants against metal contamination, and doubled those plants metal accumulation (Weyens et al., 2013).

Soil remediation through phytoextraction requires the concentrations of the contaminating TEs (Trace Elements) be reduced to levels that complies with environmental regulations (Robinson et al., 2009). Hyperaccumulator plants can be used to uptake trace elements from soil. Hyperaccumulator plants can accumulate a particular trace element 10-1000 times higher than a normal plant from contaminated lands (Brooks et al., 1977). In this process, the hyperaccumulator plant, which is usually selective for a particular element, is grown in the same land repeatedly. Table 2.8 shows Cd accumulation in some cropping plants when grown in Cd contaminated soils. It is to be ensured that the concentration of the trace element is significantly higher in the plant than the input of the element in agricultural land (Robinson et al., 2009).

Table 2.8 Crops accumulating Cd from contaminated soils (Kabata-Pendias and Mukherjee, 2007)

Plant	Harvest yield (t/ha)	Cd in plants (mg/kg)
Yellowtuft (<i>Alyssum murale</i>)	0.8	34
Alpine penny-cress (<i>Thaspi caerulescens</i>)	16	12
Tobacco (<i>Nicotiana tabacum</i>)	9	10
Corn (<i>Zea mays</i>)	10	8
Mustard (<i>Brassica juncea</i>)	21	3
Osier Willow (<i>Salix viminalis</i>)	10	22

McGrath et al. (1993) and Baker et al. (1994) found that phytoextraction of Zn was possible with *Thlaspi caerulescens* (J. & C. Presl.), which acted as a hyperaccumulator plant. The plant is then burnt or fermented or used in gasification to reduce its volume (Robinson et al., 2009). Specialized incineration facilities may be required to prevent TE-loss in the smoke (Keller et al., 2005). Margni et al. (1997) reported that most existing waste incinerators can safely process metal-enriched biomass. The residual material could be reprocessed to recover the trace element (Robinson et al., 2009).

Some plants can transform soil contaminants into volatile compounds that scatter in the atmosphere is referred as phytovolatilization. Plant-microbial systems have been discovered that volatilise Hg, As and Se (Brooks, 1998). Phytoextraction through volatilisation does not need regular harvesting. The plant can be left onsite until the soil's TE concentrations comply with environmental regulations. For essential TEs such as Se, phytovolatilization can offer the possibility of redistributing Se from areas where Se toxicity exists to downwind areas where there is Se deficiency (Zayed et al., 2000). There are mainly two drawbacks of

phytovolatilization, the limited number of plant-microbial systems that volatilise a limited number of TEs and there is no control on the destination of the volatilised elements (Robinson et al., 2009).

However, the phytoextraction to remove metals, including Cd is discredited as it takes extremely long time to clean a contaminated land (Robinson et al., 2015). The problem with phytoextraction is that even to clean a moderately contaminated soil takes decades (Robinson et al., 2009). Moreover, there is a noticeable absence of successful phytoextraction field trials or commercial operations. One of the few examples of the successful field application of phytoextraction is the selenium volatilisation using genetically engineered *Brassica juncea* (L.) (Bañuelos et al., 2005).

2.9.4 Soil washing, thermal desorption and soil removal

Soil washing is one of the ways to remove Cd from contaminated soils (Abumaizar and Smith, 1999) and is effective in treating heavy metals in the soil matrix (Virukyte et al., 2002). Thermal desorption treats halogenated and non-halogenated volatiles and semi-volatiles, as well as fuel hydrocarbons and pesticides. Thermal desorption method was ineffective in removing heavy metals from contaminated soils (Virukyte et al., 2002). The removal of top soil is also not a good solution as it leaves the land infertile. In spite of the good performance of some of these methods in some specific arenas, it is probably not a good choice for agricultural land in NZ where the Cd level is not very high compared to the lands those are contaminated from industrial activities in other countries.

2.9.5 Selection of plants with lower uptakes

Selecting plants with lower uptake of Cd might be a good solution for lands to be used for agricultural purposes where the concentration of Cd is low. In this case, it is also important to choose a particular plant variety and it may be that some demanding vegetables cannot be

grown. Another option may be to grow crops that we do not consume (eg. Flower plants). However, it is not possible for everyone to grow flower plants commercially and it might not be economical, as well as decreasing the number of different varieties grown in agricultural land.

2.9.6 In situ fixation of cadmium

Different soil conditioners might be applied to agricultural land to remove the threat of Cd accumulation in plants through making the Cd less mobile. The following materials may be tried in this regard.

2.9.6.1 Liming agents

Liming may be a good way to make Cd less available in soils through increasing the pH of soil. Many studies have shown that when the pH is increased the availability of Cd to plants is decreased (Kim et al., 2016; Maier et al., 2002), which may be due to the fact that lime decreases the exchangeable Cd and increases the Fe and Mn oxide bound Cd that is less available to plants (Chen et al., 2016). Some experiments show that increased Ca from lime competes with Cd for exchangeable sites and again increases the solubility of Cd leading to increased plant uptake (Bolan et al., 2003a; Christensen and Haug, 1999b). The competition of Cd and Ca take place in the ion exchange sites as Cd is not expected to form inner sphere complexes with soil components (Scheffer et al., 2010; Silveira et al., 2003). In addition, liming can reduce the fertility of soil by rendering all cations less available, especially Zn (Andersson and Siman, 1991; Merian, 1991), and is only suitable within a limited pH range. Liming may have a role in the NZ environment where fertility is limited by a low pH, because it may increase fertility and reduce Cd uptake.

2.9.6.2 Organic matter

Organic matter has different functional groups and has sites producing different negative charges during decomposition and may immobilize Cd in soil making it less available for plants (Pusz, 2007). Organic matter that can be used for this purpose are:

2.9.6.2.1 Compost

Organic material that is collected from by-products or waste, and decomposed for the purpose of recycling, is usually known as compost. Both trace metal loading and organic matter in the soil are increased by the application of municipal solid waste compost. Composts have been tested to be used in agricultural lands for a long time for its beneficial properties ranging from supplying nutrient elements, enhancing carbon sequestration and nutrient cycling and reducing disposal costs of solid wastes (Ding et al., 2017; Gabhane et al., 2012; Paulin, 2014). Previously, composts were discredited in the use of fixing heavy metal pollution in agricultural lands due to its high heavy metal content eg. Cd, Cr, Zn and Hg. Due to the improvement of the sorting of raw materials, municipal composts contain less heavy metals and pathogens compared to composts prepared without sorting (Cook and Beyea, 1998; Ding et al., 2017; Farrell and Jones, 2009).

There is much research into reducing the toxic effect of Cd on plants by using composts. Compost together with lime significantly reduced the accumulation of Cd, compared to the lime only treatment in a high Cd contaminated soil (55 mg Cd/kg soil) (Kim et al., 2016). In a pot experiment with flooded soil, no foliar symptoms of Cd toxicity were observed even at Cd concentrations of 100 mg/kg. Rice grain and straw yields decreased when Cd was applied above 10 mg/kg, irrespective of compost, lime or P application (Sarkunan et al., 1991). When compost was applied to decrease the Cd concentration in soil, it was observed that compost incorporation at rates up to 30% decreased lettuce Cd concentration but higher rates had a less marked effect (Costa et al., 1994). In general, the roots had a higher content than the shoots. Cadmium rates had no effect on yield, both fresh weight and dry weight (Costa et al., 1994).

In soils with little organic matter, compost addition will significantly increase the amount of highly reactive organic complexing agents for trace metals in the soil (Kaschl et al., 2002a) and may decrease the phytoavailability of Cd.

Van et al. (2007) found that compost amended with different inorganic amendments (clinoptilolite or bentonite) had a limited effect on reducing the transfer of Cd from soil to ryegrass (*Lolium perenne* L.). In another study, compost enriched with inorganic amendments which had been evaluated in laboratory-based experiments for its effectiveness to immobilise heavy metals in contaminated soils where naturally occurring zeolite-clinoptilolite and synthetic iron oxide (Fe_2O_3) were used, found them effective for reducing Cd uptake in ryegrass (Gadepalle et al., 2009). It was concluded that zeolite and/or iron oxide enriched compost can be used effectively for immobilising Cu and Cd in contaminated soils (Gadepalle et al., 2009).

Scientists observed that peroxidative stress of barley exposed to Cd was reduced in the presence of water-extractable organic matter from compost-like materials in a hydroponic culture and it was also observed that compost significantly reduced Cd uptake (Tachibana et al., 2013). In another study, it was found that the use of two composts derived from green waste and sewage sludge amended with minerals (clinoptilolite or bentonite) to convert a contaminated site to green space, successfully decreased leaching of Cd. They found compost effective in binding Cd but bentonite had a limited effect (Van et al., 2007). The fungus, XJ-1, isolated from chicken manure compost was observed as an efficient biosorbent for Cd (Xu et al., 2012). Different plants have a different response to compost application, especially rice and vegetables, implying that the growth condition is also important to the good result from compost (Juang et al., 2012). Tomato was the highest Cd accumulator (Hosobuchi et al., 2011). The addition of compost on transfer of Cd from soil to plants did not affect the growth of tomato (*Solanum lycopersicum* L.), cabbage (*Brassica oleracea* L.), and daikon (Japanese

radish; *Raphanus sativus* L.) in soils treated with fertilizer or compost (Hosobuchi et al., 2011). Cabbage took up the least amount of Cd (Hosobuchi et al., 2011).

In China, it was observed that the application of heavy metal-contaminated compost resulted in toxicity to soil microbes (Chen et al., 2010a). A greenhouse study with alfalfa and corn, where soil was treated with 25 t/ha sewage sludge, compost and/or cow manure including three rates of Cd, concluded that Cd phytoavailability depends on the Cd source, loading rate and plant species (Sharifi et al., 2010). Cattle compost is better than swine or poultry compost as it has a high affinity for Cd and lower P content than others (Sato et al., 2010). The maximum Cd concentration in compost was proposed 0.8 mg Cd/kg (Saha et al., 2010). Poultry manure compost was effective in reducing Cd phytoavailability and increasing pH and it was more pronounced in higher Cd-contaminated soils (Chen et al., 2010b).

Compost components, i.e. macro- and micronutrients, organic matter, humic substances, hormone-like substances, biotic agents, emission of carbon dioxide and nitric oxide and many others, effectively contributed to the physiological metabolism to counteract oxidative stress induced by Cd²⁺ contaminated soil (Tartoura and Youssef, 2010). The effect of temperature on metal availability from compost was studied and found that it depends on metal type, compost formulation and waste type (Adekunle, 2009).

Composted pig manure supplied more Cd to rice and the response was different in two soils (Li et al., 2009). The direct, and subsequent influence of added organic materials on changes to Cd and Cu phytoavailability in soil and their accumulation in aboveground oat (*Avena sativa* L.) biomass was studied in a three-year experiment (Gondek, 2008). After application of poultry manure the concentration of available Cd increased in soil which is likely to be due to Cd containing poultry manure (Gondek, 2008; Hanc et al., 2008). After the addition of compost and Cd to soil, 80% of added Cd was converted to carbonate Cd and organically bound Cd immediately. Calcareous nature of soils plays a key role in Cd retention because a

major portion of the soluble Cd entered the carbonate fraction immediately after addition to soils (Rajaie et al., 2006). In a greenhouse experiment cherry-red radish (*Raphanus sativus* L.) was grown in two soils amended with different levels of Cd with chicken manure and pig manure compost, compared with those of Cd applied in metal salt. The Cd source, loading rate, soil pH and plant tissue were important factors in evaluation of plant uptake of Cd (Li et al., 2006).

The order of metals reacting with humic substances was found as $Pb > Cu > Cd > Zn$ (Chien et al., 2006), which is in agreement with the sequence reported by judging the thermodynamic stability constants (Chien et al., 2006). To immobilize Cd in soil, NovoGro (NG), chicken manure compost and *Bacillus subtilis*, as well as their mixtures, were used as soil amendments. Results showed that the amendments increased the residual fraction of Cd in the soils, but decreased Cd plant uptake (Wang et al., 2012). In sugar beet (*Beta vulgaris* L.) plants, Cd accumulation was higher in leaves than in roots and its content was dependent on compost rate, organ of plant and locality (Gaj and Gorski, 2005). Ammonium nitrogen content was observed to have a negative impact on Cd accumulation in plant leaves. Moreover, the total Cd content in leaves was determined by the Cd content in roots (Gaj and Gorski, 2005).

Soil amended with municipal solid waste compost had a higher concentration of Cd in the organic fraction (Zinati et al., 2004) and this organic fraction was not available for plants to accumulate. The agricultural practice of amending soils with composted MSW adds significant amounts of organic matter and trace metals, including Cd. The highest complexing capacities for Cd were found for the most humified ligands (Kaschl et al., 2002b). Compost manure was found to both increase and decrease the accumulation of Cd, indicating accumulation differences with different aquatic organisms (Ghosal and Kaviraj, 2002). All doses of compost manure significantly reduced the bioaccumulation of Cd in plankton, but

maximum reduction was found under cumulative treatment at a low dose of the manure, and application of compost manure markedly increased the growth of fish and primary productivity of water (Kaviraj and Ghosal, 1998).

Pot experiments evaluating the yield, P and Cd contents of rice (*Oryza sativa* L.) grown as a second crop on an Ultisol repeatedly fertilized with three Indian rock phosphates with and without addition of vegetable compost, indicated that Mussoorie rock phosphate was significantly superior to other two rock phosphates in enhancing the dry matter yields of rice. Vegetable compost addition significantly enhanced the yields and P concentration of rice plant tissue (Ramachandran et al., 1998). The Cd content of rice grain was more than that of rice shoots (Ramachandran et al., 1998). In general, incorporation of vegetable compost effectively reduced the Cd content of both shoots and grains of rice (Ramachandran et al., 1998). Compost manure contains humic acid, which can chelate metals in water and reduce toxicity and bioavailability.

The addition of compost manure significantly reduced the concentration of dissolved Cd in water and whole-body Cd in fish and plankton (Kaviraj et al., 1998). Fish growth - length, weight, and yield - was reduced by Cd exposure (Kaviraj et al., 1998). Addition of compost manure reduced the ill effects on fish growth produced by Cd (Kaviraj et al., 1998). Even when soil was amended with MSW, containing Cd, Cu, Pb, Ni, and Zn, higher amounts of Cd was not found in tomato and squash (OzoresHampton et al., 1997). Urban waste increased foliar contents of Cd but root contents did not reach maximum tolerance limits as specified by Brazilian legislation (Costa et al., 1997).

2.9.6.2.2 Biosolids

Biosolids can be defined as sewage sludges that have undergone a series of treatments to maintain with the prevailing local and international regulations to permit its land application (Lu et al., 2012). In NZ, sewage treatment generates annually between 700'000 and 1'000'000

tonnes of biosolids (Ministry for the Environment, 2002) and typically contains between 1 and 4 mg Cd/kg d.w. (Wang et al., 2008). In NZ, biosolids are used as amendments on production forest and agricultural lands to improve the fertility of soils (Gibbs, 2003). According to NZ guidelines, soil that contains Cd less than 1 mg/kg may have biosolids applied (Gibbs, 2003).

Cadmium uptake by crops from biosolids amended soil is a major route of Cd exposure in food chain (Logan and Chaney, 1983). Plant Cd uptake varies with the type of plant (Chaney et al., 1987), trace element, cumulative application rate of biosolids (Chang et al., 1987), biosolids chemistry (Sommers et al., 1987), and soil chemistry (Corey et al., 1987).

Studies reported that biosolids contain Cd more than 1 mg/kg (Azizi et al., 2013; Logan et al., 1997b). Logan et al. (1997) observed that biosolids contained 45-48 mg/kg Cd and mentioned that the concentration was higher than the 39 mg/kg concentration established for EQ sludges under the US EPA 503 rule (US EPA, 1993) and the mean for US sludges of 7 mg/kg (US EPA, 1990).

When applied to soil, biosolids increase the amount of Cd in soils and subsequent transfer to plants (Ramachandran and D'Souza, 1999). A six-year experiment with high amount of separately collected biosolids showed an increase in total Cd in soil as well as a decrease in the soil microbial community (Moreno et al., 1999). In another study, the impact on heavy metal accumulation and lability due to repeated application of biosolids was evaluated using composite soils (at 0-15 and 15-30 cm depths) from 0, 2, 5, and 25-year biosolids applied to Genesee silt loam soils. Biosolids application significantly influenced heavy metal concentration in soil. Among the heavy metals, the concentration of total and residual Cd was the highest (3 and 2.8 times respectively) (Islam et al., 2013). In a field experiment the effect of application rates of biosolids and mineral N and P fertilizers on As, Ba, Cd, Cr, Cu, Ni, Pb, Se, and Zn concentration in soil, cane plant (*Saccharum officinarum*), and first ratoon

(residual effect) in a Typic Hapludult soil was studied. It was observed that biosolids application increased As, Cd, Cu, Ni, Pb, and Zn concentrations in soil and biosolids increased the Cd uptake in sugarcane (Nogueira et al., 2013). A greenhouse pot experiment with various amounts of added biosolids: 20 ton/ha, 50 ton/ha and 100 ton/ha established that increasing the biosolids application rate significantly increased the total amounts of Cd in all the soils (Tsadilas and Shaheen, 2013). Greenhouse pot culture experiments evaluated that the uptake of Cd by two successive maize (*Zea mays*) varieties was increased when biosolids were applied, and reduced plant shoot growth. It was further suggested that care has to be taken while amending soils (acidic soils in particular) with biosolids and biosolids containing a high amount of Cd should be refused (Ramachandran and D'Souza, 1999).

In some experiments, biosolids did not increase the Cd availability in the soil (Sato et al., 2010; Vaca-Paulin et al., 2006; Xu et al., 2012). Moreover, in some studies biosolids were effective in reducing the accumulation of Cd from soil to plants (Sato et al., 2010; Xu et al., 2012). The results of a study indicated that composted biosolids can reduce Cd uptake by plants from contaminated soil and may bring about an increase in plant growth (Shuman et al., 2002). It is also observed that the intensive fertilization with biosolids compost did not influence the Cd contents in the harvest products, however, the fertilization with superphosphate led to significantly higher Cd concentrations in potato (*Solanum tuberosum*) tubers (Bartl et al., 1999). The capacity of biosolids compost to decrease the toxicity of trace elements in soils depends on the different plant variety. Besides, the combination of calcareous soil pH and higher organic matter, Fe, and P levels of biosolids-compost amended plots improved the overall success of vegetation (Li et al., 2000). The reaction of composts produced from biosolids gradually increased during their 9-month fermentation and Cd content was not increased more than the permissible range (Krzywy et al., 1999). It was observed that biosolids can change the form of Cd in soil, while increasing total Cd

concentration in soil. Biosolids decrease the toxicity of Cd through complexation and makes Cd less available to plants (Bolan et al., 2003b). Logan et al. (1997a) measured the uptake of selected trace elements (Cd, Cu, Ni, Pb, and Zn) in a field experiment by six vegetable crops namely cabbage (*Brassica oleracea*), carrot (*Daucus carota*), dry bean (*Phaseolus vulgaris*), lettuce (*Lactuca sativa*), potato (*Solanum tuberosum*), and tomato (*Solanum lycopersicum*), from a single 500 t/ha application rate of an advanced alkaline stabilized biosolids product. The biosolids were applied in 1992 and crops were grown for 3 years, 1993, 1994 and 1995. Differences among the metals for uptake by the different crops were in the order: Zn > Cu > Ni > Cd > Pb. Cadmium uptake declined from 1993 to 1995. Low plant Cd uptake response slopes were observed compared with literature values and often negative. Logan et al. (1997a) also suggested that large applications of the biosolids may cause no threat to the food chain from Cd uptake by crops. Biosolids were more effective at immobilizing Cd, due to the greater humification of its organic matter and higher content of Fe (Tapia et al., 2010). Due to the increased cost of fertilizers and disposal of biosolids, the importance of biosolids as a soil amendment may be favourable (Food and Agriculture Organisation of the United Nations, 2008) after proper treatment and Cd concentration consideration.

2.9.6.2.3 Biochar

Charcoal/biochar is an emerging material that is being trialled on contaminated land. Charcoal is organic matter. In an experiment, charcoals were prepared from the stalk of the giant reed (*Arundo donax* L.) at various temperatures (400-700°C) under nitrogen stream. In the experiment, it was observed that mesopores within the range of 20 to 100 Å were abundant in charcoals prepared under 400°C and 500°C. At low Cd concentrations, charcoal was highly effective in removing Cd from aqueous solution (Sagehashi et al., 2010). It was observed that about 70-75% Cd from an aqueous solution could be removed by activated charcoal in a single step (Qadeer and Khalid, 2005).

Wood charcoal was used to remove Cd from acidic wastewater (Nath et al., 1997). The adsorption of Cd depends on various adsorption parameters such as pH, temperature, metal ion concentration and amount of adsorbent. Adsorption kinetics are fast initially, followed by slower kinetics, and a stationary phase attained within one hour (Nath et al., 1997). The capability of biochar to immobilise and retain As, Cd and Zn from a multi-element contaminated sediment-derived soil was explored by a column leaching experiment and scanning electron microanalysis. Sorption of Cd and Zn to biochar's surfaces assisted a 300-fold and a 45-fold reduction in the leachate concentration, respectively. It was concluded that biochar can rapidly reduce the mobility of contaminants in polluted soil system (Beesley and Marmiroli, 2011).

2.9.6.2.4 Lignite

Lignite (brown coal) is a source of soil organic matter that is used in degraded soils to improve soil fertility where the organic matter content is low (Kwiatkowska et al., 2008) and also a fixing additive of metal-contaminated soils to fix metals (Ciecko et al., 2001; Pusz, 2007; Skłodowski et al., 2006).

Ion exchange and specific adsorption are the two prevalent mechanisms of lignite that play an important role sorbing metals in soil (Pentari et al., 2009b). Lignite samples have a CEC of 40 to 400 Cmolc/kg (Jochova et al., 2004; Karczewska et al., 1996; Lao et al., 2005; Pentari et al., 2009b) whereas the CEC of soil organic matter ranges from 100 to 300 Cmolc/kg (Hooda, 2010). Large amounts of humic and fulvic acids are present in lignite (Pehlivan and Arslan, 2007) that is the same with other equivalents in soil (Kwiatkowska et al., 2008). There are many carbonyl (C=O), carboxyl (COOH) and hydroxyl (OH) groups in lignite (Pehlivan and Arslan, 2007). In ion exchange, carboxyl and hydroxyl groups are the main functional groups that participate. Between pH 2.5 and 7, carboxyl groups in humic acids increasingly dissociate and between pH 8 and 13.5, phenolic groups dissociate. The pH value of the

surrounding solution determines the number and type of negatively charged functional groups (COO^- and O^-) available for ion exchange (Pehlivan and Arslan, 2006). The surface area of hydrated coal is $1000 \text{ m}^2/\text{g}$ (Burns et al., 2004). Dry coal particles have a surface area of $5 \text{ m}^2/\text{g}$ and $170 \text{ m}^2/\text{g}$ obtained with $\text{N}_2(\text{g})$ -BET and $\text{CO}_2(\text{g})$ respectively. High concentration of carboxylic and phenolic groups ($5 - 7 \text{ mmol/g}$) and the large specific surface area might increase the capacity of lignite to sorb metals (Burns et al., 2004). Lignite is relatively resistant to decomposition (Pusz, 2007).

2.9.6.2.5 Sawdust

Sawdust is a waste product of the wood industry, where during the sizing and cleaning of trees a significant amount of sawdust is produced. If sawdust is not managed properly and simply used as land fill, it can contaminate surface and ground water. During decomposition, it produces several organic acids that leach into the soil. Environmental benefits of sawdust have been observed (Roy and Dutta, 2013) and through proper use sawdust can be a resource.

2.9.6.3 Inorganic amendments

Utilization of minerals, such as zeolites (zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents), as substrates for horticultural crop production has been receiving attention (Mohammad et al., 2004). In some studies zeolite was used in soil to improve the soil's nutrient status by decreasing nutrient leaching (Wang et al., 2005) and producing good crops. Broschart (2011) showed that where Downy jasmine (*Jasminum multiflorum* (Burm. f.) Andr.) and areca Palms (*Dyopsis lutescens* (H. Wendl., Beentje & Dransf.)) were grown in containers filled with a fine sandy soil or with a pine bark-based potting substrate, zeolite can stop the leaching loss of some cations (ammonium (NH_4)-N and potassium) (Broschat, 2001). A growth chamber experiment determined the response of croton (*Codiaeum variegatum* L.) grown in a substrate composed of a mixture of zeolitic tuff. It concluded that the use of zeolite tuff as a growth medium for croton can provide the plant

with adequate amounts of N, P, and K for the growth period investigated. Zeolite addition also lowered the cost of production of container-grown plants in the greenhouse and nursery industries (Mohammad et al., 2004). Bentonite $[(Al_{1.56}Fe_{0.03}Mg_{0.19})(Si_{3.85}Al_{0.15})O_{10}(OH)_2]$ (Theng, 2012) is an Al phyllosilicate, essentially impure clay consisting mostly of montmorillonite (Theng, 2012). The CEC of bentonite is higher than many minerals in soil (Carroll, 1959) that might be capable of reducing the mobility of Cd in soil.

Most scientific studies with heavy metals were done with highly contaminated soils such as mine spoil, where it was important to decrease leaching of Cd, reduce metal phytoavailability to humans and ecological receptors, and re-establish vegetation (Martin and Ruby, 2004). Cadmium concentration was lower in agricultural soils than in mine spoil. Technologies used to clean agricultural land are very expensive. So, a method that will stabilize soils at their present position should be developed that will incur less cost. To reduce the availability of heavy metals for plant roots, sorption, ion exchange, and precipitation are principle mechanisms to convert soluble and pre-existing potentially soluble solid phase forms of heavy metals to more geochemically stable solid phases (Cheng and Hseu, 2002).

Cadmium is increasing in soils, so more studies related to Cd should be done in order to produce safe foods (Römkens et al., 2009). It is important to develop some techniques that will improve the fertility and physical condition of soil, will be friendly for different macro and microorganisms in soil, can be used for agricultural as well as contaminated sites, will not increase the cost of production and finally will be environmentally sustainable. Keeping all these views in mind an experiment was designed to see the ability of different carbonaceous soil amendments with different inorganic soil amendments to decrease the solubility, as well as phytoavailability, of Cd.

Chapter 3 **Municipal composts reduce the transfer of Cd from soil to vegetables**

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My contribution to the article: I designed and setup the experiments with the help of my co-authors, particularly Guilhem Chanson. I collated and interpreted the data and wrote the article in collaboration with my co-authors.

3.1 Abstract

Cadmium (Cd) is a non-essential trace element that accumulates in agricultural soils through the application of Cd-rich phosphate fertiliser. Vegetables can accumulate Cd to concentrations that sometimes exceed food safety standards. We investigated the potential of low-cost soil amendments to reduce Cd uptake by spinach (*Spinacia oleracea* L.), lettuce (*Lactuca sativa* L.) and onion (*Allium cepa* L.). Batch sorption experiments revealed the relative sorption of Cd by biosolids, charcoal, lignite, sawdust, two types of compost, bentonite and zeolite. Lignite and composts had the greatest ability to sorb Cd and were subsequently selected for pot trials, which elucidated their effect on Cd uptake by onions, spinach and lettuce in two market garden soils with native Cd concentrations of 1.45 mg/kg and 0.47 mg/kg. The addition of 2.5% (dry w/w) municipal compost reduced the Cd concentration in onions, spinach and lettuce by up to 60% in both soils. The addition of lignite gave variable results, which depended on the soil type and rate of addition. This Cd

immobilisation was offset by soil acidification caused by the lignite. The results indicate that municipal compost is a low-cost soil conditioner that is effective in reducing plant Cd uptake.

3.2 Introduction

Cadmium (Cd) is a non-essential element that can cause many negative health effects at high concentrations (Kabata-Pendias and Mukherjee, 2007). It occurs naturally as a contaminant in all phosphate rocks, although the concentrations vary considerably, depending on the origin of the parent material. Rock phosphate originating from igneous rock generally has Cd concentrations of 0.7 - 30 mg/kg P (Oosterhuis et al., 2000), whereas rock phosphate refined from sedimentary rocks may contain Cd concentrations higher than 556 mg/kg P (Mar and Okazaki, 2012). Rock phosphate from sedimentary rock sources account for some 85-90% of world P production (Oosterhuis et al., 2000). Phosphate fertiliser use has resulted an enrichment of Cd in agricultural soils worldwide (Hooda, 2010; Kabata-Pendias and Mukherjee, 2007). Historically, New Zealand and Australia manufactured superphosphate using phosphate rock from Nauru and Christmas Island, which contained relatively high Cd concentrations >600 mg Cd/kg P (Syers et al., 1986). Repeated application of this Cd –rich superphosphate for most of the 20th century has resulted the significant increases in the Cd concentrations in NZ soils (Taylor, 1997).

The transfer of Cd from soil to plants and thence into food products is well documented (Alloway et al., 1990; Arcella et al., 2012; Berkelaar and Hale, 2003; Lopez-Chuken and Young, 2010; McLaughlin et al., 1998). Enriched soil Cd concentrations cause increased Cd accumulation in crops (Kabata-Pendias and Mukherjee, 2007; Nan et al., 2002). Cadmium accumulation varies between plant species, varieties and cultivars (Crews and Davies, 1985; Gartler et al., 2013; Grant et al., 2008; Kabata-Pendias and Mukherjee, 2007; McLaughlin et al., 1994a). Different parts of the plant have distinct Cd concentrations. For example, vegetable species such as spinach (*Spinacia oleracea* L.) and lettuce (*Lactuca sativa* L.), accumulate higher concentrations of Cd in the edible portions than perennial ryegrass (*Lolium perenne* L.) (Gartler et al., 2013). An increase in soil pH decreases plant Cd-uptake (Kabata-

Pendias and Mukherjee, 2007). Although Zn can have both synergistic and antagonistic effects on plant Cd-uptake (Grant et al., 1999b), Cd is often a food-chain toxicity risk in Zn deficient agricultural systems (Hooda, 2010). Soil Cl^- increases the mobility of Cd in soil resulting elevated Cd concentrations in plants (McLaughlin et al., 1994b).

In New Zealand (NZ), these concerns led to the formation of the Cadmium Working Group (CWG)-established by the NZ government in 2006. The CWG identified vegetable production as being the industry most at risk from superphosphate-derived Cd (Cadmium Working Group, 2008). The fertilizer industry, in collaboration with regulators has developed a Tiered Fertilizer Management System (TFMS) (Rys, 2011). Here, soils with <0.6 mg/kg Cd have no restriction placed on the application of P fertilizers. Soils with concentrations >0.6 and <1.0 mg/kg are permitted restricted use of P fertilizers to ensure that the soil does not exceed 1.8 mg/kg Cd after 100 years. Intensive monitoring and modelling is required for soils with Cd concentrations >1.4 and <1.8 mg/kg. No further Cd accumulation is permitted in soils with Cd concentrations >1.8 mg/kg (Rys, 2011).

Plants in soil take up Cd from the soil pore water. While most of the Cd in soils is usually associated with soil colloids ($>98\%$), with only a small fraction of the total is available for plant uptake in soil solution (Christensen and Haug, 1999a). By manipulating the amounts of available cation binding sites in soils, the amount of dissolved Cd can be reduced, resulting in a subsequent reduction in uptake by plants (Kabata-Pendias and Mukherjee, 2007). This can be achieved by a number of different methods, such as changing the soil pH (*e.g.* by liming) or by introducing additional binding sites. For example, Fe and Mn oxides sorb Cd (Backes et al., 1995; Zasoski and Burau, 1988) and can be used to reduce the movement of Cd in soil solution. Humic substances, produced during the decomposition process of organic materials, include a large group of amorphous, colloidal organic polymers (McLaren and Cameron, 1996). These molecules carry a predominantly negative charge arising from

ionizable carboxyl and phenolic hydroxyl functional groups, which enable humic substances to act as a cation exchanger in soil and thus remove metal cations from solution (McLaren and Cameron, 1996). Specific sorption also plays an important role (Pentari et al., 2009a). As Cd is a chalcophilic trace element, it is expected to bind relatively strongly to organic sulphur groups (Kabata-Pendias and Mukherjee, 2007), R-SH, R-S-R, R-SS-R and heterocyclic S, which might be present in organic matter (*e.g.* lignite) (Calkins, 1994).

Various organic and inorganic amendments are used in agricultural lands for improving the physical and chemical conditions of soil (Sarwar et al., 2008). Moreover, both organic (*e.g.* sawdust, peat, compost, etc.) and inorganic (*e.g.* lime) soil amendments can effectively reduce Cd solubility and plant uptake in highly contaminated soils (Bolan et al., 2003b; Guo et al., 2006). Lignite (added at a rate of 1%) reduced the solubility of Cd and decreased the transfer of Cd from soil to *Lolium perenne* (L.) by 30%, while not detrimentally affecting soil fertility (Simmler et al., 2013).

To date, most studies investigating the use of lignite or compost to reduce the plant uptake of Cd have considered highly contaminated soils (Ciecko et al., 2001; Pusz, 2007; Skłodowski et al., 2006; Tapia et al., 2010) that are not representative of most agricultural soils where Cd concentrations typically reach a few mg/kg at most (Alloway and Steinnes, 1999). Other studies that investigated the fate of Cd in compost-amended land focused on the endogenous Cd in the compost itself (Chang et al., 1997; Hanc et al., 2009; Rutzke et al., 1993), which may be contaminated through industrial emissions into wastewater treatment plants.

We aimed to investigate potential soil amendments that could reduce the transfer of Cd from soils to plants in two different NZ market garden soils with elevated Cd concentrations. To achieve these aims, we used batch sorption experiments to identify promising amendments and then used selected amendments in targeted pot trials to assess the efficacy of these amendments to reduce Cd uptake by vegetables.

3.3 Materials and Methods

3.3.1 Soil sample collection

Soils were collected from two commercial vegetable growing areas in Pukekohe (37°13'18.92"S 174°52'5.94"E) and Levin (40°38'17.49"S 175°14'23.61"E) in the North Island of NZ. Soil from the top 0.25 m were collected and large stones and roots removed manually. The soils were dried, ground, passed through a 7 mm sieve, and homogenised. Three 500 g sub samples of each soil were collected which were then ground and sieved through a 2 mm Nylon mesh. Table 3.1 and Table 3.2 show the chemical and physical properties of the soils. Both soils had elevated total Cd concentrations (1.45 mg/kg and 0.47 mg/kg respectively).

3.3.2 Soil amendment collection

Eight materials were considered as potential soil amendments for reducing the phytoavailability of Cd in soils. These were: commercially available bentonite, which is an aluminium phyllosilicate, essentially impure clay consisting mostly montmorillonite (Theng, 2012), zeolite powder which is a microporous aluminosilicate mineral commonly used as commercial adsorbent; charcoal; lignite; sawdust; biosolids and two types of compost. Zeolite powder and bentonite were provided by Commodities NZ Ltd., Wellington. Charcoal was produced by Solid Energy New Zealand Ltd. Biosolids were collected from Kaikora sewage waste treatment plant, NZ. Solid Energy New Zealand Ltd. provided the lignite in powdered form; it originated from the New Vale open cast mine in Southland, NZ. Living Earth compost (municipal compost) was collected from Living Earth Ltd. (Christchurch branch, NZ) and Parkhouse compost was collected from Parkhouse Garden Supplies (Christchurch, New Zealand) outlets. Living Earth compost is produced from municipal green waste including lawn clippings, tree prunnings, and food waste, while Parkhouse compost is made from sawdust composted and animal residues (manure and carcasses). The sawdust was collected

from a local sawmill (Shands Road Saw mill Ltd., Rolleston, Christchurch, NZ) produced from *Pinus radiata*. After collection, samples were dried, ground and passed through a 2 mm Nylon sieve. Table 3.1 and Table 3.2 show the chemical and physical properties of the materials.

Table 3.1 Properties and macronutrient concentrations (total) of the materials used in the experiments

Properties	Lignite	Living Earth Compost	Parkhouse compost	Sawdust	Charcoal	Biosolids	Zeolite Powder	Bentonite	Pukekohu soil	Levin soil
pH	4.6	7.4	7.0	4.8	6.7	3.6	5.9	8.8	6.0	6.5
CEC (Cmolc/kg)	45	45 (0)	47 (0)	9.3 (0)	3.3 (0)	11 (1)	21 (0)	44 (0)	22*(Hesse, 1971)	15* (Hesse, 1971)
C (%)	59 (1)	21	21	48	40	26 (0)	<0.02	0.7	2.1* (Keeney and Nelson, 1982)	1.2* (Keeney and Nelson, 1982)
N (%)	0.83 (0.00)	2.3	1.6	0.1	0.13	2.6 (0.03)	0.03	<0.02	0.23* (Keeney and Nelson, 1982)	0.13* (Keeney and Nelson, 1982)
P	201 (1.7)	4178 (37)	5159 (227)	23 (1)	118 (10)	3805 (66)	<1	124 (9)	3414 (26)	2247 (20)
S	4942 (94)	2644 (27)	3610 (70)	49 (10)	58 (2)	6395 (201)	<1	768 (16)	491 (6)	296 (1)
Ca	14216 (314)	24903 (588)	37416 (1456)	556 (16)	1505 (39)	4967 (66)	12084 (89)	17131 (306)	4147 (117)	7008 (99)
Mg	2496 (40)	4177 (16)	2186 (34)	158 (5)	458 (21)	2305(3) (1)	3663 (29)	6838 (189)	2400 (95)	2873 (43)
K	200 (6)	14938 (33)	5412 (67)	425 (1)	975 (25)	1564 (16)	10506 (46)	1621 (265)	1951 (59)	2242 (54)

Values are in mg/kg unless otherwise indicated. Standard errors are given in brackets (n=3). * Data from Hill Laboratories, NZ.

Table 3.2 Total trace element concentrations (mg/kg) of the materials used in the experiments

Properties	Lignite	Living Earth Compost	Parkhouse compost	Sawdust	Charcoal	Biosolids	Zeolite Powder	Bentonite	Pukekohe soil	Levin soil
B	36 (0)	20* (Wolf, 1971)	<1	5.9 (0.1)	<1	14 (0)	<1	17 (1)	33 (0)	9 (0)
Cd	0.31 (0.15)	0.70 (0.10)	0.45 (0.10)	0.03 (0.01)	0.05 (0.03)	1.6 (0.05)	<0.01	0.93 (0.29)	1.5 (0.03)	0.47 (0.01)
Cu	2.8 (0.2)	59 (1)	25 (1)	37 (3)	2.4 (0.2)	555 (15)	1.9 (0.0)	25 (1)	65 (1)	20 (0.2)
Zn	4.3 (0.5)	310 (11)	34 (2)	5.3 (0.3)	16 (2)	912 (16)	34 (2)	72 (2)	173 (1)	67 (1)
Cr	2.1 (0.1)	28 (1)	37 (1)	63 (5)	0.74 (0.04)	33 (1)	0.71 (0.1)	4.2 (0.1)	40 (2)	15 (0.3)
Ni	3.7 (0.3)	9.3 (1)	5.2 (0.1)	<1	0.42 (0.1)	18 (0.5)	<1	1.9 (0.1)	25 (1)	7.4 (0.5)
Pb	3.5 (1)	123 (3)	4.5 (1)	<1	<1	101 (1)	4.5 (1)	5.9 (0.3)	55 (0.5)	7.4 (0.1)

Standard errors are given in brackets (n=3). * data from Hill Laboratories, NZ

3.3.3 Sample analysis

The pH values of the sieved samples were determined using a (Mettler Toledo pH meter in high purity water (18.2 MΩ resistivity; Heal Force® SMART Series, SPW Ultra-pure Water system, Model-PWUV) at a solid/water ratio of 1:2.5 (1:10 for composts, charcoals and lignite). The mixtures were left to equilibrate for 24 hr before measurement (Blakemore, 1987).

The Cation Exchange Capacity (CEC) of the materials was measured using the 0.01 M Silver Thiourea (AgTU) method (Blakemore, 1987). Briefly, 35 mL of 0.01 M AgTU was added to 0.70 g of dry sample in a 50 mL centrifuge tube and then agitated in an end-over-end shaker for 16 hours. Samples were centrifuged at 2000 rpm for 10 minutes. The supernatant was filtered through a Whatman no. 40 filter and analysed using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Varian 720 ES - USA). The total carbon and nitrogen were analysed in soil and compost samples using an Elementar Vario-Max CN Elementar analyser (Elementar ®, Germany).

For both plants and soils, pseudo-total elemental analyses were carried out using microwave digestion in 8 mL of Aristar™ nitric acid ($\pm 69\%$), diluted with milliQ water to a volume of 25 mL and filtered using Whatman no. 52 filter paper (pore size 7 μm). The concentrations of Cd together with other elements (Ca, Mg, K, P, S, B, Cu, Zn, Cr, Ni and Pb) were determined using inductively coupled plasma optical emission spectrometry (ICP-OES Varian 720 ES – USA) in soils (Kovács et al., 2000) and in plants (Gray et al., 1999a). Reference soil and plant material (International Soil analytical Exchange – ISE 921 and International Plant analytical Exchange IPE 100) from Wageningen University, the Netherlands, were analysed for quality assurance. Recoverable concentrations were 91% - 108% of the certified values.

An estimation of the phytoavailable fraction of Cd in the soils and soil amendments was determined using 0.05 M $\text{Ca}(\text{NO}_3)_2$ extraction (Black et al., 2012; Gray et al., 1999b). Significant correlations between concentrations of Cd in extractions that simulate soil solutions and plant (*cereals, pasture and several vegetable species*) Cd have been reported (Black et al., 2012; Gray et al., 1999b), in both spiked and unspiked soils. Briefly, 5 g of soil was mixed with 30 mL of

extractant in a centrifuge tube and a suspension was formed using a vortex mixer. The centrifuge tube was then agitated on an end-over-end shaker for 2 hours after which it was centrifuged at 3000 rpm for 15 minutes. After filtering (Whatman no. 52 filter paper), the samples were analysed to determine the concentration of Cd and other elements using inductively coupled plasma optical emission spectrometry (ICP-OES Varian 720 ES – USA) in soils. Five blank samples were also run along with samples during the analysis following all steps.

3.3.4 Batch Sorption Experiment

The batch sorption experiment was conducted with eight soil amendments and two soils, at four different pHs (six for lignite) ranging from 3.4 to 7.5 and six Cd concentrations. Each treatment was replicated three times. Following the method of Simmler et al. (2013), we prepared spiked solutions in 0.05 M $\text{Ca}(\text{NO}_3)_2$ solution using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (BDH AnalaR). We added $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (BDH AnalaR) in 0.05 M $\text{Ca}(\text{NO}_3)_2$ solution to achieve Cd concentrations of 0, 1.4, 6.8, 13.2, 18.9 and 24.5 mg/L in 0.05 M $\text{Ca}(\text{NO}_3)_2$ solution. Five grams of soil or amendment was mixed with 30 ml of each of the spike and control (0 mg Cd/L) solutions. The pH was adjusted close to the target pH using HNO_3 (made from BDH ARISTAR nitric acid 70%) or 2M KOH (BDH AnalaR KOH) to decrease or increase pH, respectively. Pilot studies were carried out with each material following the batch sorption experiment steps and by adding different amounts of HNO_3 or KOH solution to determine how much of HNO_3 or KOH solution would be needed to get a desired pH.

The mixture was agitated using a vortex mixer for 3 minutes, shaken on an end-over-end shaker for two hours, and centrifuged at 10,000 rpm for 10 minutes. The supernatant was filtered through a Whatman no. 52 filter paper in to 30 mL vials and was analysed using Flame Emission Atomic Absorption Spectrophotometer (AAS). A parallel ICP-OES analysis was carried out on randomly

selected samples from the bulk samples to confirm the results of the AAS. The monitoring validated the Flame Emission Atomic Absorption Spectrophotometer's performance in detecting low concentrations of Cd after Cd sorption by different soil amendments.

The Cd adsorption coefficient (K_d) for the different soil amendments were determined according to the following equation (Simmler et al., 2013),

$$K_d = \frac{\text{Cd sorbed by the soil or soil amendments (mg/kg)}}{\text{Cd in solution } (\frac{\text{mg}}{\text{L}})}$$

$$= \frac{(C1 - (C2 - C3)) * \frac{0.03}{0.005}}{(C2 - C3)}$$

where, K_d is the solid-solution distribution co-efficient. In the equation, C1 is the initial Cd concentration in solution (for our batch experiment they were 1.4, 6.8, 13.2, 18.9 and 24.5 mg/L), C2 is the Cd concentration in solution (mg/L) after equilibrium in a given batch (either with soil or soil amendments) with Cd spiking and C3 is the Cd solution concentration (mg/L) in the corresponding batch without Cd spiking (only with 0.05 M $\text{Ca}(\text{NO}_3)_2$ solution).

3.3.5 Pot trial

A pot experiment was conducted with lignite and one compost. The coarsely-sieved soils were mixed with the amendments using a concrete mixer to give the following treatments (d.w.): control, 1.05% (w/w) lignite (henceforth “1% lignite”), 2.63% (w/w) lignite (henceforth “2.5% lignite”, henceforth “lignite”), and 2.7% (w/w) compost (henceforth “2.5% compost”, henceforth “compost”). The soil amendments were added on a dry weight basis. Subsamples of each soil treatment were transferred into 2.5 L pots (approx. 3 kg dry weight) into which onion (*Allium cepa* L. var Pukekohe long keeper), spinach (*Spinacia oleracea* L.) and lettuce (*Lactuca sativa* L. var. Buttercrunch) were planted with five replicates for each treatment-vegetable combination. The

pots were placed in a randomised block design in the Plant Growth Unit (greenhouse) at Lincoln University, where they were watered daily to field capacity. Before sowing, the soils, mixed with different soil amendments, were kept for two weeks in the green house and watered daily to equilibrate. The nutrient status of the pots was maintained by periodic applications of Ruakura solution (Smith et al., 1983). A total of 0.25 g N/pot, 0.04 g P/pot and 0.23 g K/pot was applied together with other micro nutrients, those are present in Ruakura solution in each pot throughout the growing period in to two split applications, one at first week and other at the 4th week.

The plants were grown for 6-10 weeks before harvest (February-April). Temperatures ranged between 9°C and 20°C during the nighttime (10 pm until 6 am) and between 14°C and 28°C during the daytime. At harvest, the edible portions of the plants were excised and the fresh weight determined. Both the edible portions and the residual material was washed thoroughly with deionised water and placed in a drying cabinet at 70°C until a constant weight was obtained. Samples were then ground and stored in airtight containers until chemical analyses. After harvest, soil was sampled from each of the spinach treatments, ground, and sieved to < 2 mm through a Nylon mesh. Soil pH and total and $\text{Ca}(\text{NO}_3)_2$ -extractable Cd concentrations were determined as described above.

The data was analysed using ANOVA with Fisher's Least-Significant-Difference post-hoc test to compare means using Minitab® 17 (Minitab Inc, State College, Pennsylvania, USA). The level of significance was 0.05.

3.4 Results and discussion

3.4.1 Batch sorption experiment

The Figure 3.1 shows the Cd sorption, expressed as $\log(K_d)$ (sorbed / solution concentration coefficient), by the potential soil amendments in a solution of 1.4 mg/L Cd. K_d values for the 6.8, 13.2, 18.9 and 24.5 mg/L Cd solutions were significantly lower (data not shown), indicating saturation of the binding sites on the materials tested. While a soil solution concentration of 1.4 mg/L Cd is well above concentrations found in most agricultural soils, our results indicate that the K_d values obtained were still within the linear range for the materials tested and thus can be considered analogous to lower Cd concentrations.

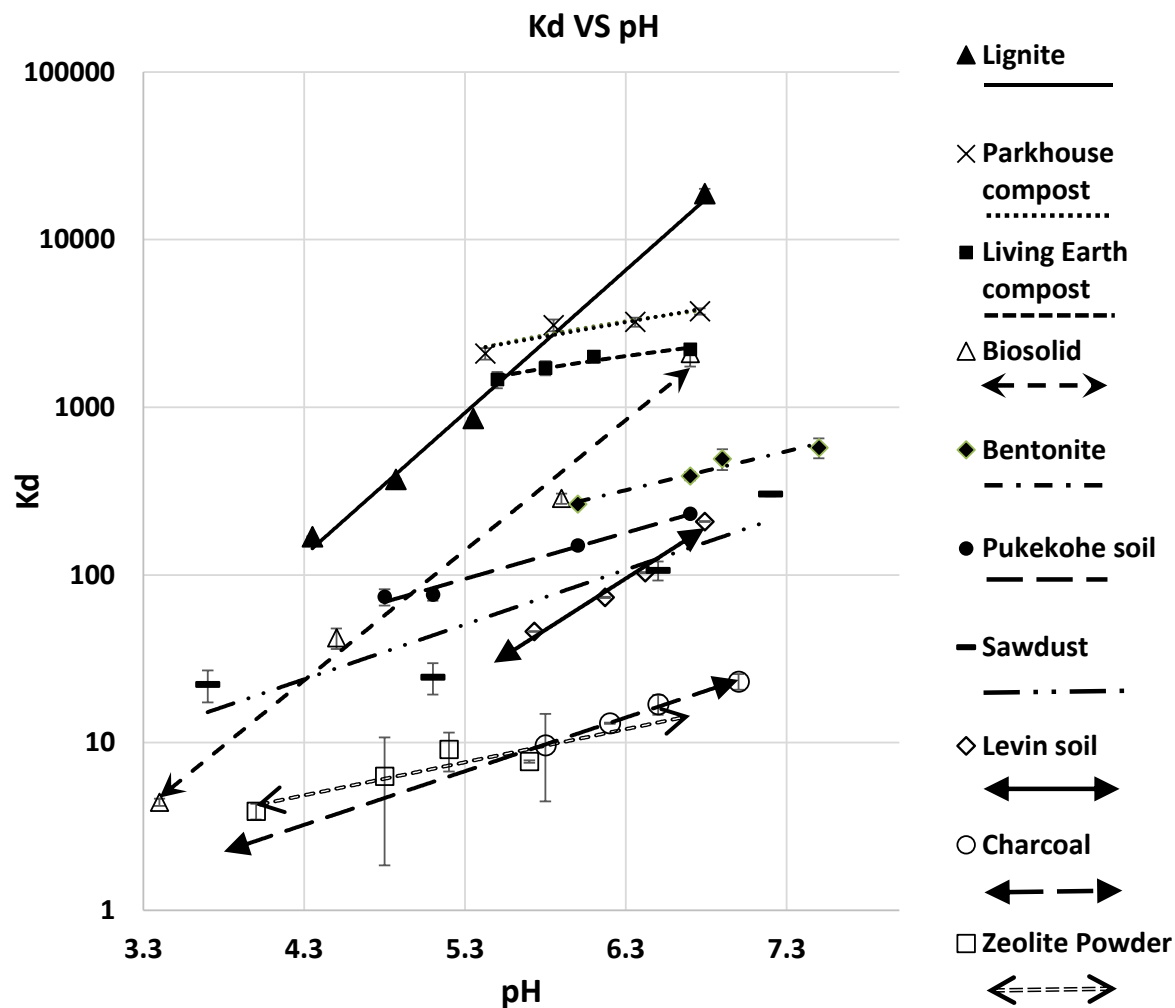


Figure 3.1 The K_d values of Pukekohe and Levin soil and different soil amendments through a range of pH values. Error bars represent the standard error of the mean ($n=3$).

At controlled pH values, the two composts and lignite had the greatest capacity to bind Cd across a range of pHs (Figure 3.1), which is consistent with the findings of similar batch sorption experiments (Simmler et al., 2013; Ulmanu et al., 2003). Charcoal and zeolite had low K_d values, which is consistent with the findings of Hanauer et al. (2012). Kelly et al. (2014) suggested that this may be because the charcoal sorbs more Cd in soil than in the batch experiments due to the longer contact time with the Cd in soil solution. The effectiveness of charcoal in sorbing Cd may

have been better if it were more weathered (Cui et al., 2014). Fard et al. (2011) reported that biosolids were an effective sorbent for Cd and that the K_d value for biosolids increased substantially with increasing pH. While biosolids may be an effective sorbent for highly contaminated soils, Simmler et al. (2013) reported that in agricultural soil, biosolids increased extractable Cd and increased plant Cd uptake. Our K_d values for bentonite were similar to those reported by Ulmanu et al. (2003). Sawdust, zeolite powder and charcoal had similar or only slightly higher K_d values than the Pukekohe and Levin soils. This indicates that these amendments are unlikely to provide a significant increase in Cd sorption in these soils.

The Cd K_d values of all materials increased with increasing pH (Figure 3.1), consistent with other work carried out using lignite and soil (Simmler et al., 2013). The sensitivity of K_d to pH differed between materials. The binding of Cd by lignite was more sensitive to pH than the composts, with the composts sorbing more Cd at lower pH values.

We chose the Living Earth compost and lignite for the pot trial because the batch experiment revealed that they had high K_d values over a range of solution pHs. Living Earth compost was selected over Parkhouse compost because of its lower cost (NZ\$12 / tonne c.f. NZ\$100 / tonne).

3.4.2 Plant uptake of cadmium

On a fresh weight basis, spinach grown in the Levin soil accumulated the highest shoot Cd concentration (0.10 mg/kg f.w., Figure 3.2), similar to the World Health Organisation's and Food Standards of Australia and New Zealand's limit for Cd in vegetables of 0.1 mg/kg (Bigdeli and Seilsepour, 2008a; FSANZ, 2015) and lower than the CODEX limit of 0.5 mg/kg f.w. (Chaney et al., 2009). This soil contained just 0.49 mg/kg Cd (Table 3.2), less than the lowest tier on the TFMS (Rys, 2011). The Cd concentrations in the shoots of lettuce grown on the same soil were significantly lower, as were the Cd concentrations in spinach and lettuce grown on the Pukekohe

soil. The Cd concentrations in the onions growing in both soils were significantly lower than the Cd concentrations found in spinach or lettuce. This is consistent with other findings (Gartler et al., 2013) that also showed high Cd uptake by shoot material of a variety of commercially grown vegetables, including lettuce and spinach. Moreover, genetic variations between cultivars can result in significant differences in Cd uptake (Crews and Davies, 1985; Grant et al., 2008; Kabata-Pendias and Mukherjee, 2007; McLaughlin et al., 1994a).

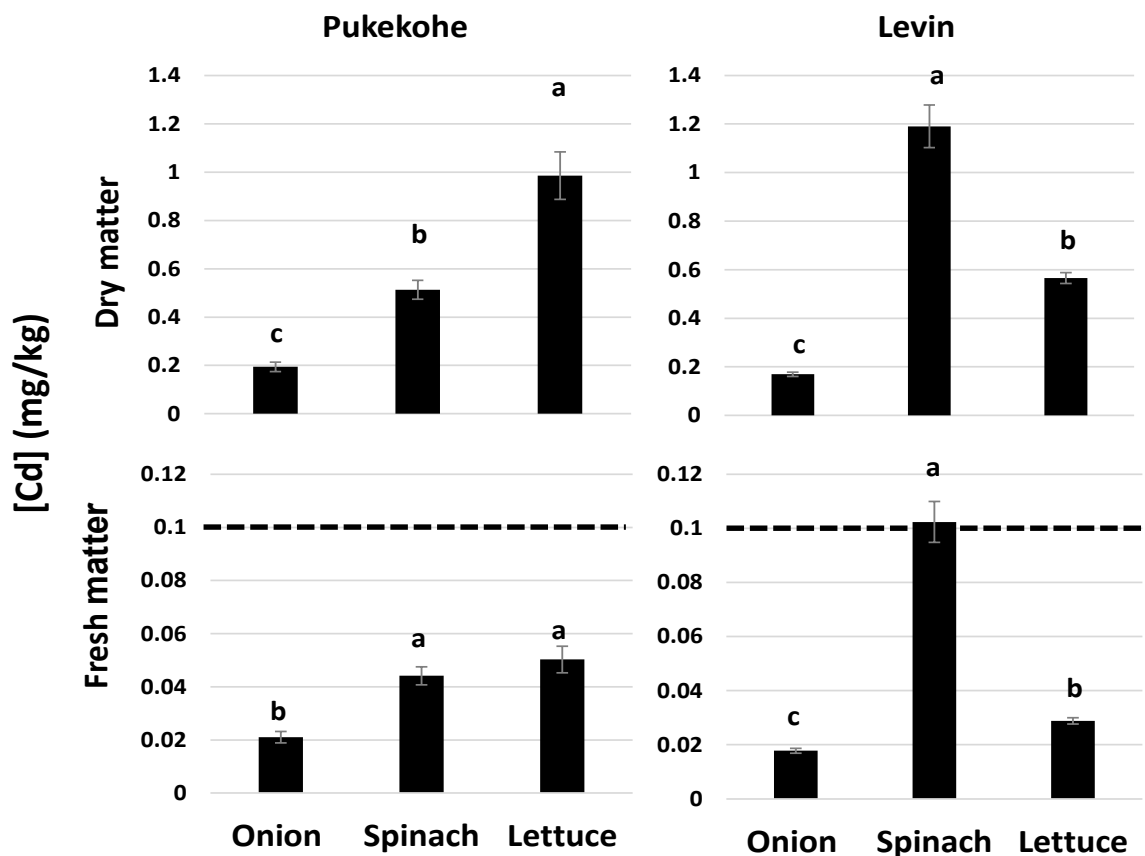


Figure 3.2 Average dry matter and fresh matter Cd concentrations in the edible portions of selected vegetables grown in control soil. The dotted line illustrates the World Health Organisation's and Food Standards of Australia and New Zealand's limit for Cd in vegetables (Bigdeli and Seilsepour, 2008a; FSANZ, 2015). Error bars represent the standard error of the mean (n=5). Values with the same letter are not significantly different.

The 0.05 M $\text{Ca}(\text{NO}_3)_2$ -extractable Cd concentrations in the two soils reflected the concentrations of Cd in the shoots of the lettuces grown in those soils. However, the concentrations of Cd in the shoots of spinach grown on the two soils do not reflect either the total or the extractable Cd concentrations in those soils (Table 3.1 and Table 3.2). The higher Cd accumulation by vegetables grown in Levin soils compared to Pukekohe soils may be partially due to the lower Zn

concentrations in the Levin Soils. Many authors reported that increased soil Zn concentrations could reduce Cd accumulation by plants (Chaney et al., 2009; Grant et al., 1999b; Kabata-Pendias and Mukherjee, 2007; McKenna et al., 1992). Zinc also affects the transfer of Cd from plants to animals or humans. McKenna et al. (1992) reported that Cd in spinach was less bioavailable to quail than Cd in lettuce. They also report that increased Zn concentrations in lettuce and spinach Zn reduced the retention of Cd in kidney and liver.

The compost treatment decreased Cd uptake by more than 20% in onions, spinach and lettuce in both the Pukekohe and Levin soils (Figure 3.3). This finding is consistent with reports of Cd decreases using other composts in highly contaminated soils (Tapia et al., 2010). This decrease is consistent with the addition of function groups that may bind Cd through cation exchange or specific adsorption (Simmler et al., 2013). The composts contained significant Zn concentrations (Table 3.2), which may have further reduced plant uptake as described above. In the Pukekohe soil, compost addition increased the pH from 6.0 to 6.2, which would likely reduce plant Cd uptake (Kabata-Pendias and Mukherjee, 2007). The compost had no significant effect on the pH of the Levin soil.

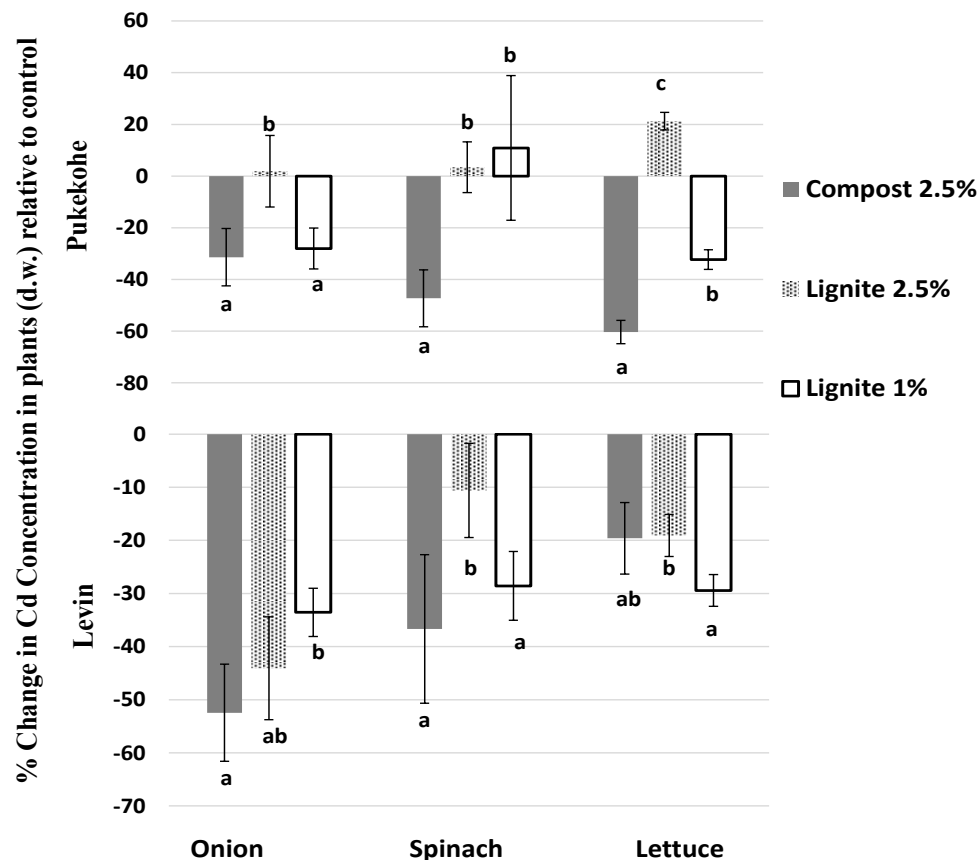


Figure 3.3 Changes in Cd concentrations (dry matter) in the edible portions of selected vegetables relative to the control. Error bars represent the standard error of the mean (n=5). Values for the same plant with the same letter are not significantly different.

The 2.5% lignite treatment in the Levin soil significantly reduced the Cd concentrations in the plant shoots by at least 10%. However, there were no significant differences between the Cd concentrations in onion and spinach grown in treated and control Pukekohe soils. Moreover, the 2.5% lignite treatment significantly increased the Cd concentration in the lettuce grown in the Pukekohe soil. The 1% lignite treatment of the Levin soil reduced the transfer of Cd from soil to the shoots of the vegetables by 28-34% when compared to the untreated soil (Figure 3.3). A similar

result was observed in the 1% lignite treated Pukekohe soil, with the exception of spinach, where no significant decrease was observed. Overall, the lower rate of lignite treatment appears to have been more effective in reducing Cd uptake by vegetables grown on these soils. In contrast, the higher rate may increase Cd uptake by lettuce. The difference between the two treatments may be due to the change in pH: the 2.5% lignite treatment decreased the pH significantly from 6.5 to 6.2 in the Levin soil and 6.0 to 5.7 in Pukekohe soil, while the pH change caused by the 1% treatment was less (0.1 pH unit decrease in both soils). As shown in the batch sorption experiment, a pH decrease may result in less Cd being bound by the lignite and the soil particles (Figure 3.1).

Overall, the compost treatment was the most effective and consistent in reducing the transfer of Cd from soil to vegetables in both the soils. This may be partly due to the high CEC of the compost, which enables Cd immobilisation through non-specific or specific adsorption retention of the Cd onto soil colloids (Kabata-Pendias and Mukherjee, 2007). However, as shown in the batch sorption experiment, the nature of the binding sites (*c.f.* inorganic: zeolite powder, bentonite; and organic: compost, biosolids) may also be important, especially under variable pH conditions.

3.4.3 Practical implications of lignite or compost addition

With the exception of lettuce growing in the Pukekohe soil and spinach growing in the Levin soil, the compost treatment did not significantly change the biomass of the vegetables grown in the pot trial, despite the additional nutrients provided by the compost. This is unsurprising given the high nutrient status of the soils prior to treatment (Table 3.1 and Table 3.2) and addition of nutrient solution in all pots. Importantly, none of the treatments caused a significant reduction in the biomass production of the plants in either soil (Table SI 3.1). No chlorosis or malformation of the plants was observed, which indicates that the use of these amendments are unlikely to cause fertility problems in the short-term.

Translating the rates of 1% and 2.5% into tonnes per hectare gives 33 and 81 t/ha respectively, assuming a ploughing depth of 0.25 m and a soil density of 1.3 g/cm³. The cost of adding 1% lignite @ NZ\$350 per tonne is therefore \$11,550 per hectare, which is prohibitively expensive. Compost on the other hand is more effective and the addition of 2.5% @ NZ\$12 per tonne would cost just \$975 per hectare. Moreover, the high N and P concentrations in the compost (Table 3.1) could reduce fertiliser costs and also reduce further Cd increase in the soils which could be expected with injudicious applications of fertiliser derived from phosphate rock.

Living Earth compost (municipal compost) achieved significant and consistent reductions in plant shoot Cd concentrations in the three vegetables grown in the two soils without causing any reduction in plant growth or the uptake of other essential nutrients. In nutrient poor soils, compost could provide an additional source of important plant macronutrients, such as N, P and K while improving the structural properties and water retention characteristics of the soil. Reusing municipal compost reduces the expense of disposing this material into landfills. Monitoring is required to ensure that further contaminants are not added with the composts. Composts may be a low-cost means of extending the useful life of the soil before Cd concentrations proscribe food production. Composts are heterogeneous mixtures of highly variable composition. The composition of municipal compost varies seasonally and by location, and the performance of various composts in reducing plant uptake of Cd over the long-term is a fertile area for future research. Determination of the mechanisms by which composts immobilise Cd in the soil-plant system could elucidate how other composts might perform and how variability in the compost parent material might affect its ability to bind Cd.

3.4.4 Acknowledgements

The senior author would like to thank NZAID for a doctoral scholarship. This research was supported by the Centre for Integrated Biowaste Research (CIBR). We gratefully acknowledge the constructive and detailed comments provided by the reviewers of this manuscript.

Supplementary Information

Table SI 3.1 Average edible biomass of the vegetables (g dry weight)

Treatment	Onion	Lettuce	Spinach
Pukekohe soil			
Control	0.97(0.43) ^a	0.53(0.06) ^b	0.25(0.06) ^a
Compost	1.22(0.62) ^a	1.02(0.23) ^a	0.35(0.14) ^a
Lignite 1%	1.31(0.49) ^a	0.88(0.12) ^{ab}	0.35(0.14) ^a
Lignite 2.5 %	1.54(0.58) ^a	0.59(0.06) ^b	0.26(0.08) ^a
Levin soil			
Control	1.19(0.33) ^a	1.33(0.34) ^a	2.32(0.40) ^{ab}
Compost	1.71(0.92) ^a	1.29(0.15) ^a	2.77(0.62) ^a
Lignite 1%	0.54(0.18) ^a	1.52(0.46) ^a	1.83(0.24) ^{ab}
Lignite 2.5%	2.01(1.64) ^a	1.19(0.19) ^a	1.50(0.31) ^b

Values in brackets represent the standard error of the mean (n=5). Values in the same column for a soil with the same letter are not significantly different.

Table SI 3.2 pH and elemental concentrations in Ca(NO₃)₂ extracts of soil and soil amendments (mg/kg)

Elements	Lignite	Living Earth Compost	Parkhouse compost	Sawdust	Charcoal (solid energy)	Biosolids	Zeolite Powder	Bentonite	Pukekohe soil	Levin soil
pH	3.4	6.7	6.4	3.7	6.5	3.4	4	7.5	5.1	6.2
P	0.05 (0.005)	31 (0.68)	18 (0.26)	2.5 (0.18)	5.6 (2.6)	48 (1.22)	0.03 (0.02)	0.13 (0.01)	3.7 (0.15)	5.5 (0.16)
S	ND	280 (31)	515 (3.2)	0.19 (0.13)	145 (14)	832 (24)	2.15 (0.49)	319 (84)	43 (13)	11 (0.58)
Mg	251 (3.6)	1262 (116)	655 (29)	38 (2.0)	64 (25)	354 (4.7)	113 (10)	38 (8.7)	115 (5.7)	93 (3.6)
K	6.1 (0.19)	4677 (325)	1517 (64)	834 (2.0)	204 (2.7)	174 (7.0)	292 (24)	60 (15)	183 (13)	71 (18)
Cd	0.0002 (0.00008)	0.004 (0.0001)	0.005 (0.001)	0.03 (0.01)	0.15 (0.15)	1.56 (0.06)	0.0007 (0.0007)	0.0009 (0.0005)	0.015 (0.002)	0.008 (0.002)
Cu	0.018 (0.002)	0.06 (0.004)	0.033 (0.01)	3.0 (0.16)	1.7 (1.6)	10 (0.23)	0.02 (0.003)	0.0089 (0.003)	0.13 (0.015)	0.12 (0.006)
Zn	0.36 (0.04)	0.044 (0.01)	0.09 (0.02)	0.80 (0.02)	6.04 (2.87)	57 (9.5)	0.28 (0.03)	0.019 (0.002)	0.37 (0.06)	0.18 (0.017)
Cr	0.003 (0.003)	0.003 (0.0001)	0.005 (0.001)	0.88 (0.02)	0.005 (0.002)	0.09 (0.02)	0.001 (0.0002)	0.0014 (0.0014)	<0.0008	<0.0008
Ni	0.003 (0.003)	0.037 (0.036)	0.064 (0.004)	0.006 (0.004)	0.026 (0.006)	5.2 (0.14)	0.003 (0.00003)	0.003 (0.002)	0.09 (0.01)	0.01 (0.001)
Pb	<0.007	0.038 (0.03)	0.07 (0.04)	0.009 (0.0002)	0.11 (0.06)	0.21 (0.01)	0.033 (0.009)	0.01 (0.002)	<0.007	<0.007

ND= Not Detected. Values in brackets represent the standard error of the mean (n=3)

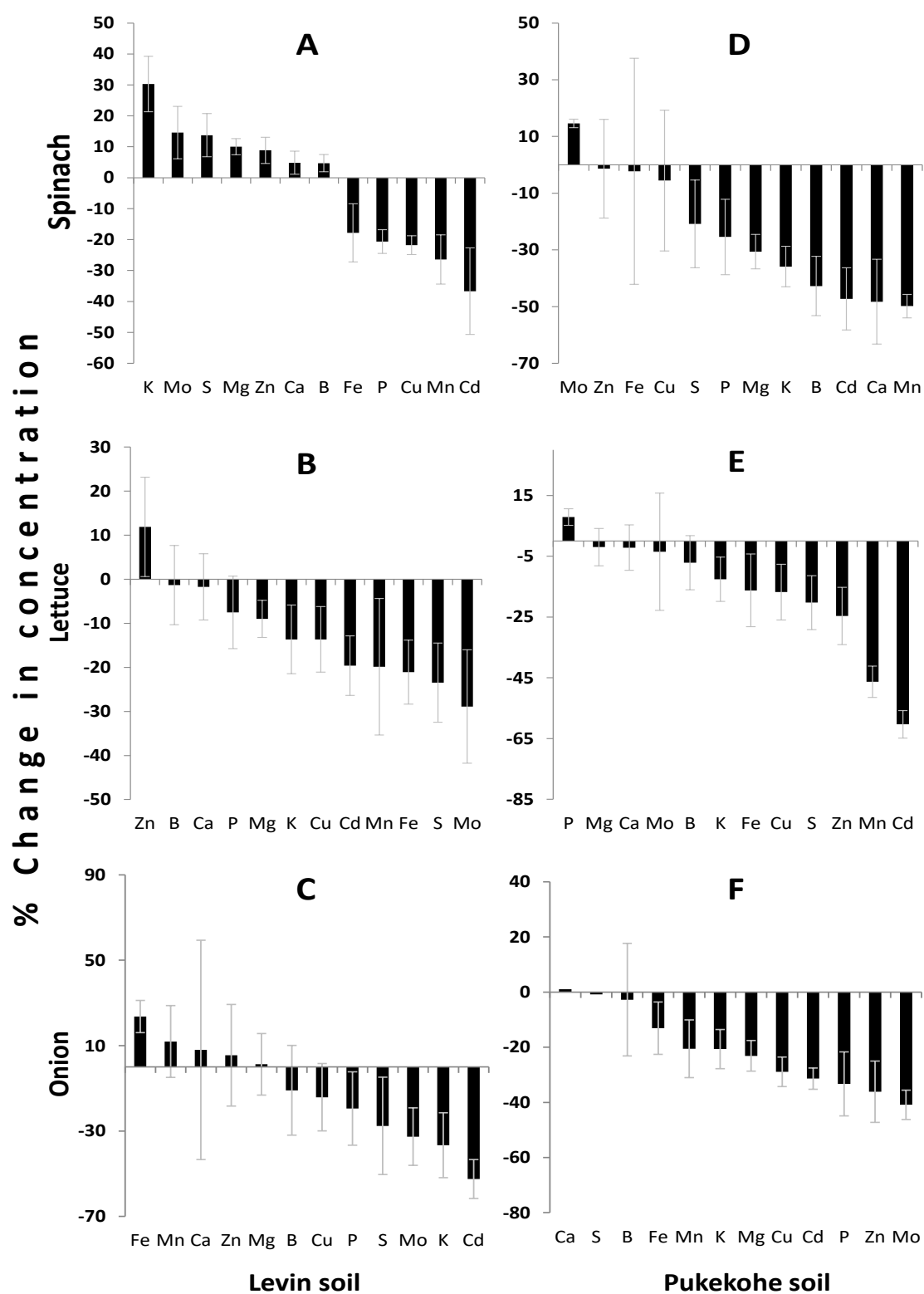


Figure S1 3.1 (A-F) Elemental change in spinach, lettuce and onion grown in Levin and Pukekohe soils treated by 2.5% compost compared to control soils. Error bars represent the standard error of the mean. (n=5).

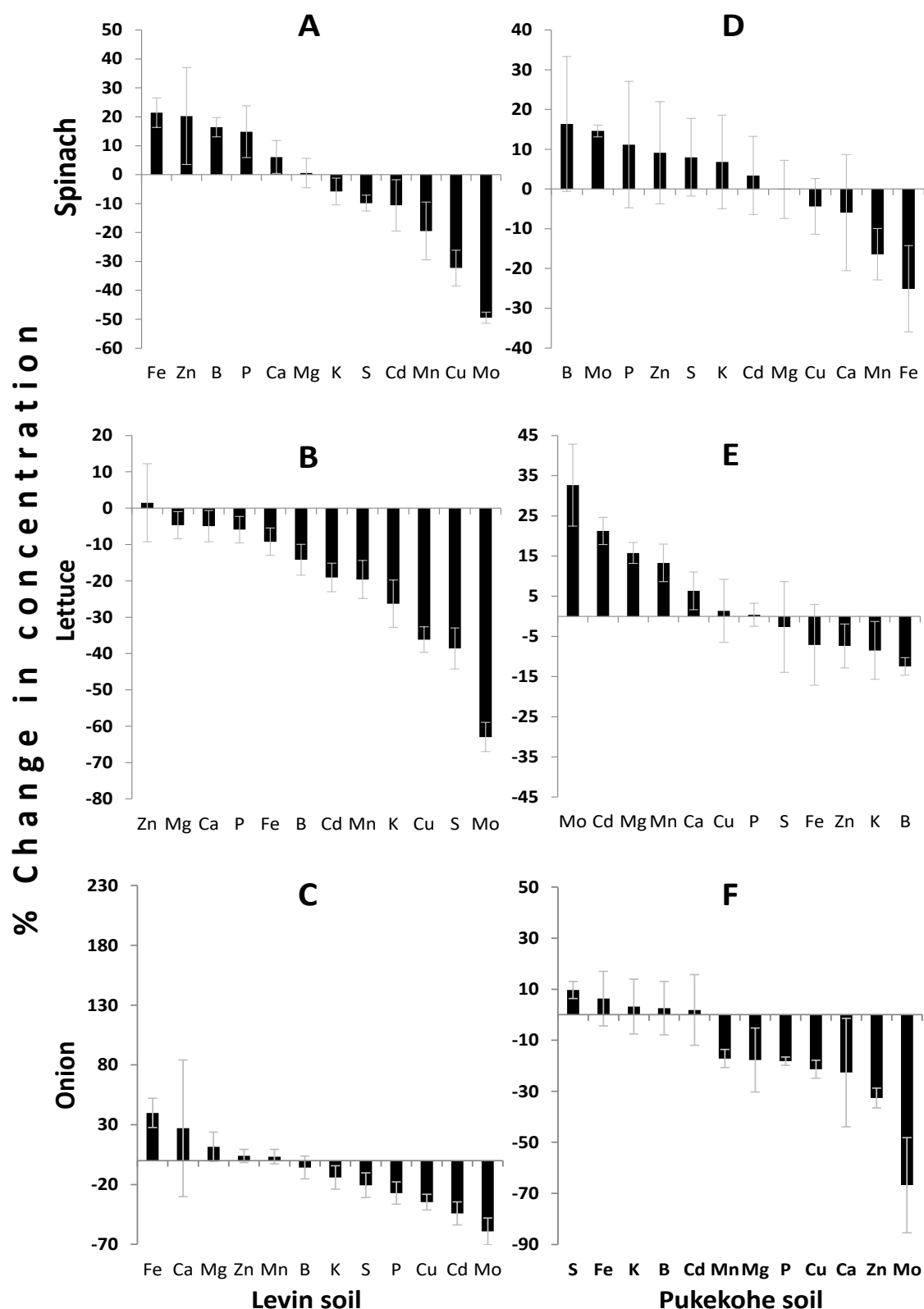


Figure SI 3.2 (A-F) Elemental change in spinach, lettuce and onion grown in Levin and Pukekohe soils treated by 2.5% lignite compared to control soils. Error bars represent the standard error of the mean. (n=5).

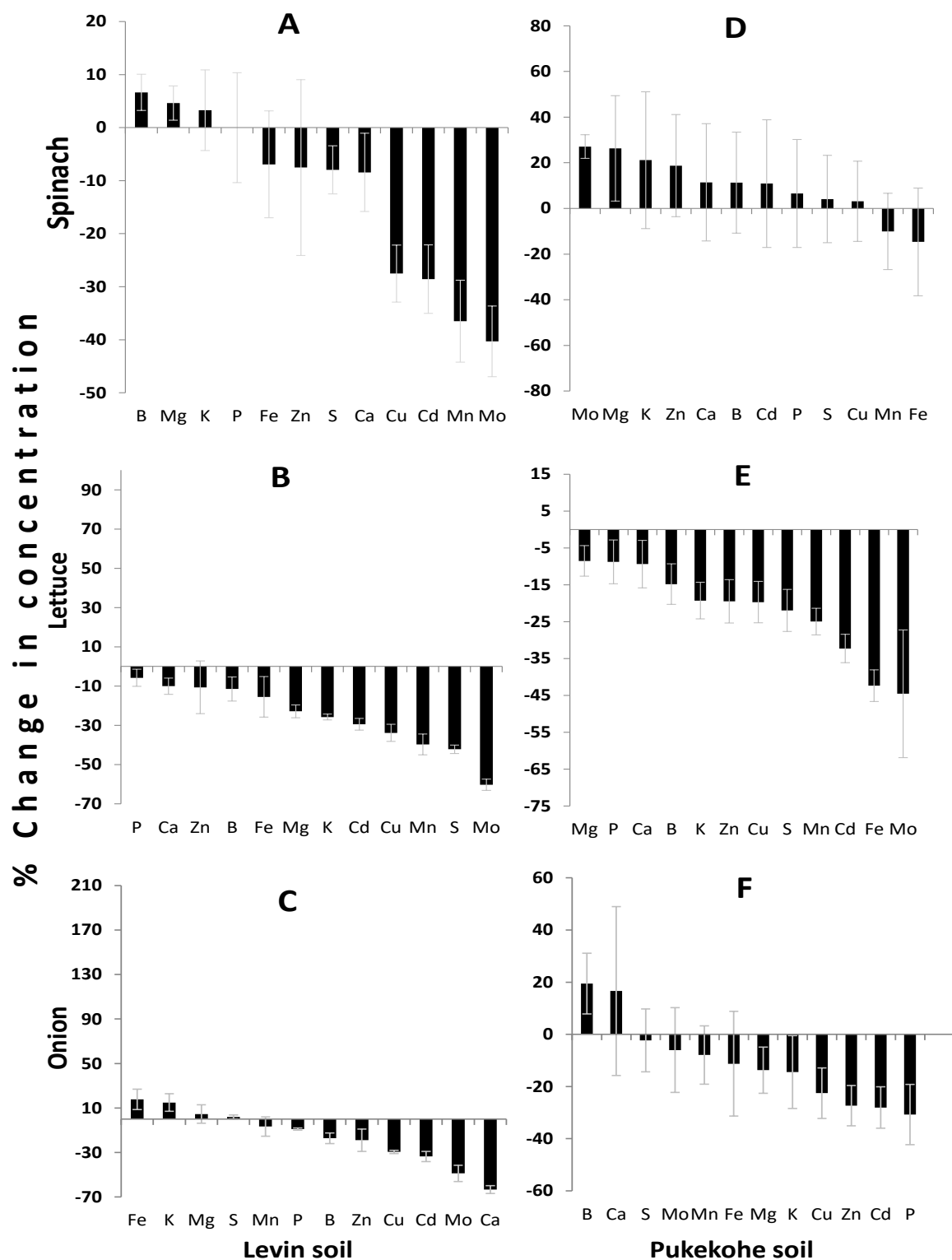


Figure SI 3.3 (A-F) Elemental change in spinach, lettuce and onion grown in Levin and Pukekohe soils treated by 1% lignite compared to control soils. Error bars represent the standard error of the mean (n=5).

Chapter 4 Effects of Lime and Organic amendments derived from varied source materials on Cd uptake by potato

Publication arising from Chapter: Al Mamun S., Lehto N, Cavanagh J, McDowell R, Aktar M, Benyas E, Robinson BH (2017). Organic amendments derived from varied source materials reduce Cd uptake by potatoes. Published in the *Journal of Environmental Quality*, 46, 836-844.

My contribution to the article: I designed and setup the experiments with the help of my co-authors. I collated and interpreted the data and wrote the article in collaboration with my co-authors.

4.1 Abstract

Repeated applications of Cd-rich phosphate fertilisers have resulted in elevated concentrations of this toxic element in some New Zealand soils. Exceedance of the food safety standard for Cd (0.1 mg/kg f.w.) has been reported for potato (*Solanum tuberosum* L.). Composts may efficiently sorb Cd in soil and therefore reduce its phytoavailability leading to reduced uptake by plants. We aimed to determine potential of various composts, shredded corn stover, and lime at two different rates, to reduce the transfer of Cd from a soil (containing 1.45 mg/kg Cd) to potato (var. 'Nadine'). In the control, the peeled tubers, skins, leaves, and stems had Cd concentrations of 0.04, 0.09, 0.26, and 0.53 mg/kg dry weight, respectively. There was a 71% reduction in tuber Cd concentrations in potatoes grown in soil amended with 5% (w/w) shredded corn stover. Potatoes grown in soil amended with pig manure compost, mushroom compost, sawdust-animal waste compost, and municipal compost at rates of either 2.5% or 5% (w/w) reduced tuber Cd concentrations by 58-66%, 46-63%, 52-53% and 29-49%, respectively. Lime (1.3%) application in soil reduced tuber Cd concentrations by 50%. Composts significantly increased tuber biomass. Composts manufactured from contrasting source

materials, all reduce Cd uptake by potatoes, however, this does not imply that all composts will do so. Further work is warranted to identify the key components of composts that result in reduced Cd uptake by plants.

Keywords: compost; lime; cadmium contamination; Nadine;

4.2 Introduction

Cadmium (Cd), a non-essential trace element (Kabata-Pendias and Mukherjee, 2007), has accumulated in many soils worldwide (Hooda, 2010; Kabata-Pendias and Pendias, 2001; Kabata-Pendias and Mukherjee, 2007). Humans are exposed to Cd through contaminated food products, which may in turn result in adverse health effects (Bernard, 2008; Dziubanek et al., 2015; Fekete et al., 2001; Järup and Åkesson, 2009; Peters et al., 2010; Sigel et al., 2013). The concentration of Cd in the renal cortex of the kidneys increases with time (Kabata-Pendias and Mukherjee, 2007).

Cadmium accumulates in agricultural soils from the repeated application of P fertilizers (Gray et al., 1999d; Loganathan et al., 2003; Pérez and Anderson, 2009; Roberts et al., 1994; Schipper et al., 2011; Taylor, 1997; Taylor et al., 2007) as well as industrial activities and the land application of biosolids (Kabata-Pendias and Mukherjee, 2007). Kim (2008) reported that Cd may be accumulating in NZ soils, with market garden soils accumulating more than other agricultural practices because of higher fertiliser inputs (Cadmium Working Group, 2011b). Cadmium in agricultural land is of concern in New Zealand and Australia as both countries historically manufactured superphosphate using phosphate rock from Nauru and Christmas Island containing relatively high Cd concentrations (>600 mg Cd/kg P) (Syers et al., 1986).

Increased Cd in soil has been linked to increased uptake by plants (Dziubanek et al., 2015; Fekete et al., 2001; Krauss and Diez, 1997; Maclean, 1976; McLaughlin et al., 1997; Pérez and Anderson, 2009; Rai et al., 2015; Weggler-Beaton et al., 2000) and accumulation in the food chain (EFSA, 2012; Kim, 2008).

Potatoes (*Solanum tuberosum* L.) are a staple food in many countries and can accumulate Cd at a concentrations (f.w.) of 0.002-0.3 mg/kg (Kabata-Pendias and Mukherjee, 2007; Kim, 2008; McLaughlin et al., 1994a; McLaughlin et al., 1994b), which is equivalent to 0.01 to 1.5 mg/kg dry weight (considering the moisture percentage is around 80%). A survey of potatoes

grown in the Waikato Region of NZ was conducted by Kim (2008), who reported that 1.5% of the potatoes exceeded the WHO and Australia and New Zealand Food Standard of 0.1 mg/kg fresh weight (f.w.) basis (Bigdeli and Seilsepour, 2008b; FSANZ, 2015). In Australia, McLaughlin et al. (1997) reported Cd concentrations more than double the guideline value (0.232 mg/kg f.w.) in potatoes in some samples. Per capita potato consumption rate in the USA, UK, USSR, Poland, Germany and New Zealand are 55, 105, 110, 149, 146 kg/year (Lisinska and Leszczynski, 1989) and 66 kg/year (Russell et al., 1999), respectively. In high potato consuming countries, even potato Cd concentrations below the permissible limits may also pose risk to human health (EFSA, 2012). Therefore, there is an imperative to reduce the transfer of Cd from soil to potato tubers.

Soil properties significantly affect the uptake of Cd by plants (Kabata-Pendias and Mukherjee, 2007; McLaughlin et al., 1994b; Merian, 1991). Soil properties can be modified by the use of soil amendments that have high numbers of functional groups that can reduce the phytoavailability of Cd (Pusz, 2007). Simmler et al. (2013) showed that certain organic amendments sorb significant amounts of Cd. In particular, composts have more than fourfold higher Cd sorption capacity than soils (Al Mamun et al., 2016). Increasing metal sorption in soil through the use of pH manipulation or introducing sorbing agents decreased the uptake of Cd by plants (Simmler et al., 2013; Valentinuzzi et al., 2015). Municipal composts reduced Cd uptake in spinach, lettuce and onion by up to 60% (Al Mamun et al., 2016). Only one type of compost (municipal compost, made from lawn clippings, tree pruning and food debris) was tested in the study. Other types of composts may be more or less effective in reducing Cd uptake.

The use of composts may improve soil fertility and reduce the need for mineral fertilizers and associated Cd inputs. Composts improve the physical properties of soils by increasing total pore space, aggregate stability, nutrient and water holding capacity, erosion resistance,

temperature insulation and decreasing apparent soil density and also chemical properties of soils by modifying the soil pH (Sarwar et al., 2008; Shiralipour et al., 1992), cation exchange capacity, and soil nutrient content (Shiralipour et al., 1992). Composts can significantly increase the growth of plants (Barkoczi et al., 2008; Khan et al., 2007; Muhammad et al., 2007).

Liming can either decrease or increase the transfer of Cd from soil to plants in field conditions (Chaney et al., 2009; Hong et al., 2007; Maier et al., 1997; Tillar et al., 1997). Maier et al. (2002) observed that liming effectively reduced the accumulation of Cd in potato tubers in three soils where the initial pH of the soils ranged between 4.1-4.7. Maier et al. (1997) reported that when calcite lime was applied at a rate of 20 t/ha in field conditions and potato was grown, liming of the soil did not reduce the concentration of Cd in potato tuber. In some cases liming increased plant Cd-uptake even though soil pH increased by 2 units. Shaheen and Rinklebe (2015) observed that liming the soil decreased the phytoavailable and exchangeable Cd in soil but increased concentration of Cd in rapeseed in the field trial. The increase in Cd uptake may be due to an induced Zn deficiency at high soil pH, which persuades the plant to produce more root Zn transport proteins to obtain adequate soil Zn to check the Zn deficiency stress (Chaney et al., 2009). As the Zn transport proteins also accumulate Cd, so increased Zn transporting protein production by plants may cause even higher Cd accumulation during Zn deficiency stress in plants (Hart et al., 2002). Moreover, liming can create an imbalance among the nutrient elements in soil specifically through significantly decreasing the concentration of essential nutrient elements K, Mn, B and S (Maier et al., 2002).

We aimed to determine the potential of various composts, and shredded corn stover at 2.5% and 5% (w/w), to reduce the transfer of Cd from a soil (containing 1.5 mg/kg Cd) to potato (var. 'Nadine'). We sought to compare the effect of compost with lime added at 0.6% and 1.3%

(w/w). Furthermore, we aimed to elucidate the effect of these soil amendments on the growth and nutrient uptake of potato.

4.3 Materials and Methods

4.3.1 Soils

We collected soil from a market garden in Pukekohe (37°13'18.92"S 174°52'5.94"E) in the North Island of NZ. Samples were collected evenly across an area of 30 m² within the plough depth (0-0.25 m), and large stones and roots were removed manually. Soils were homogenised using a spade. A sub-sample was dried in an oven at 70°C for one week, ground, and passed through a 2 mm plastic sieve before analysis. The Table 4.1 shows the soil properties.

Table 4.1 Physico-chemical Properties of soil and soil amendments (includes total elements digested by conc. HNO₃). Standard errors are given in brackets (n=3)

Properties	SC	MC	MS	SD	PG	Pukekohe soil
Source	A local farm at Leeston, Christchurch, New Zealand	Living Earth Ltd, Christchurch, New Zealand	Parkhouse Garden Supplies Ltd, Christchurch, New Zealand			From a commercial vegetable garden at Pukekohe, Auckland, New Zealand 37°13'18.92"S 174°52'5.94"E
Raw ingredients	Corn stover	Municipal compost originated from municipal green waste including lawn mowing and tree pruning	Residual compost waste generated by the mushroom production industry	Animal residues and sawdust	pig manure added with sawdust	soil
pH (H ₂ O)	5.5 (0.2)	7.3 (0.06)	6.8 (0.01)	7.1 (0.2)	7.0 (0.01)	5.9 (0.02)
CEC (Cmolc/kg)	11 (1)	46 (2)	42 (3)	46 (2)	44 (1)	21 (2)
Moisture (%)	30 (2)	24 (3)	73 (4)	42 (3)	42 (2)	25 (2)
C (%)	47 (2)	19 (2)	34 (3)	20 (2)	41 (3)	2.7 (0.3)
N (%)	0.09 (0.02)	2.0 (0.3)	2.0	1.4 (0.2)	1.2	0.24 (0.01)
P (mg/kg)	341 (16)	4120 (40)	4860 (116)	4879 (198)	6559 (357)	3424 (31)
S (mg/kg)	642 (13)	2547 (110)	16352 (74)	3725 (140)	2618 (61)	498 (15)
Ca (mg/kg)	1907 (48)	25132 (434)	67427 (1131)	37159(981)	10372 (298)	4170 (149)
Mg (mg/kg)	503 (6.4)	4217 (150)	2957 (100)	2431 (122)	2790 (52)	2464 (91)
K (mg/kg)	19666 (13)	14351 (149)	7306 (91)	5119 (172)	5882 (106)	1995 (53)
B (mg/kg)	<0.0003	18 (2)	13 (0.07)	<0.0003	20 (0.3)	28 (4)
Cd (mg/kg)	<0.00026	0.68 (0.1)	0.24 (0.07)	0.47 (0.1)	0.16 (0.027)	1.45 (0.03)
Cu (mg/kg)	2.3 (0.35)	57 (1)	68 (2.6)	27 (1)	296 (0.43)	64 (1)
Zn (mg/kg)	18 (1.9)	319 (20)	230 (2.5)	35 (2)	304 (13)	174 (4)
Cr (mg/kg)	1.02 (0.60)	28 (1)	18 (0.10)	39 (1)	3.0 (0.48)	42 (1)
Ni (mg/kg)	0.89 (0.20)	10 (2)	4 (0.2)	6 (2)	2.4 (0.03)	21 (1)

4.3.2 Composts and lime

We used four commercially available composts, made from contrasting raw materials (Table 4.1): municipal green waste compost (MC), animal offal and sawdust compost (SD), mushroom industry residue compost (MS) and pig manure and sawdust compost (PG). The effect of

shredded corn stover (SC) and lime (LM) were also considered. The lab grade dry lime powder (calcium carbonate) was used (AnalaR NORMAPUR, VWR®, PROLABO®, Belgium).

4.3.3 Treatments

Soils were mixed with specific treatments: the composts and shredded corn stover at (w/w) application rates of 0% (control), 2.5% (1) and 5 % (2) and lime at a rate of 0.6% (1) and 1.3% (2). All treatments were replicated three times. Liming rates were chosen following Valentinuzzi et al. (2015), who demonstrated these rates effectively reduced the Cd uptake by lupin (*Lupinus albus* L.). The pots were placed in a greenhouse in a randomised block design, where the temperature range varied between 15.6-27.4°C over the growing period.

4.3.4 Pot trial

Seed potatoes (*Solanum tuberosum*, 'Nadine' variety) were purchased from a seed supplier (Morton and Smith DWE, Christchurch, NZ). After a seven day incubation in covered trays, the sprouted potatoes were planted on 18th August 2014. Water was supplied every day in the morning up to field capacity and weeds were removed manually. The potatoes were harvested when the plants were showing symptoms of shoot dieback. For the SC treated soils, this occurred 75 days after sowing. All other treatments were harvested 60 days after planting. No fertilisers were applied before or during the growth period.

Soil samples were collected from each pot at the time of harvesting potatoes. Care was taken to avoid scratching of potato tubers. The aboveground portions and the tubers were separated and washed three times with tap water followed by three washings with de-ionised water. Following drying with paper towels, the fresh weights of the tubers were obtained.

The potato skin (1-2 mm) was separated using a clean stainless steel knife and the potato was cut in to small pieces to facilitate grinding. The aboveground portions were separated in to shoots and leaves. All of plant parts were kept in labelled paper envelopes and left in an oven

at 70°C until a constant weight was obtained (approximately one week). Paper envelopes were immediately transferred in sealed polythene sacks to prevent absorption of moisture from the air. After weighing and grinding, samples were placed in sealed plastic vials and analyzed in the laboratory.

4.3.5 Chemical analysis

Soil pH was determined using 10 g of soil and 25 mL of deionised water (18.2 MΩ resistivity; Heal Force® SMART Series, SPW Ultra-pure Water system, Model-PWUV) at a solid/water ratio of 1:2.5 (1:10 for composts and shredded corn stover). The mixture was shaken, left to equilibrate for 24 hr before measurement and shaken again before determination with a pH meter (Mettler Toledo Seven Easy) (Blakemore, 1987). We measured the Cation Exchange Capacity (CEC) using the 0.01 M Silver Thiourea (AgTU) method (Blakemore, 1987). An Elementar Vario-Max CN Elementar analyser (Elementar ®, Germany) was used to analyse the total carbon and nitrogen content in the soil and compost samples.

The phytoavailable fraction of Cd in the soils was determined using a modified 0.05 M $\text{Ca}(\text{NO}_3)_2$ extraction based on Black et al. (2012), Gray et al. (1999c) and Gray et al. (1999b). Briefly, in a centrifuge tube, 5 g of soil was mixed with 30 mL of extractant using a vortex mixer and a suspension was formed. The centrifuge tube was agitated for 2 hours using an end-over-end shaker and then centrifuged at 3000 rpm for 15 minutes. The supernatant was filtered through a Whatman no. 52 filter paper and frozen until analysis.

Pseudo-total elemental analyses of plants, were carried out using microwave digestion (MARSXPRESS, CEM Corporation, USA) of 0.5 g of plant sample in 8 mL of Aristar™ nitric acid ($\pm 69\%$) and filtered by means of Whatman no. 52 filter paper (pore size 7 µm) after dilution with milliQ water to a volume of 10 mL. For soils, a Block Digest method was used following the procedure of Kovács et al. (2000). Certified Reference Materials (CRMs) for soil

(International Soil analytical Exchange - ISE 921) and plant (International Plant analytical Exchange IPE 100) from Wageningen University, the Netherlands, samples were also digested.

Concentrations of Cd, Ca, Mg, K, S, B, Cu, P, Pb, Zn, Cr, Ni and Zn were determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES Varian 720 ES - USA) in soils (Kovács et al., 2000) and in plants (Simmler et al., 2013; Valentinuzzi et al., 2015). Extraction and digestion solution and method blanks were analysed in triplicate as part of standard quality control procedure for the analysis and were below the ICP-OES's detection limit for all metals. Recoverable concentrations of the CRMs were within 93% - 110% of the certified values.

4.3.6 Statistical analysis

We used Minitab® 17 (Minitab Inc, State College, Pennsylvania, USA) and Microsoft Excel 2013 to analyse data. The ANOVA with Fisher's Least-Significance-Difference post-hoc test was used to assess the effects of different treatments. The significance level for all statistical analyses was $P < 0.05$.

4.4 Results

4.4.1 Effect of amendments on the Cd concentration in peeled potato tubers

The Cd concentration in the peeled tubers ranged from 0.01-0.04 mg/kg dry weight (d.w.) (Figure 4.1), which is at the lower end of the range 0.01-1.50 mg/kg d.w. reported in the literature (Kabata-Pendias and Mukherjee, 2007; McLaughlin et al., 1994a; McLaughlin et al., 1994b). The moisture content in our potatoes was 82% (w/w). Therefore, the fresh weight Cd concentrations of the tubers ranged from 0.002 – 0.008 mg/kg. This Cd concentration is well below the World Health Organisation's and Food Standards of Australia and New Zealand's

limit for Cd in vegetables of 0.1 mg/kg (f.w.) (Bigdeli and Seilsepour, 2008b; FSANZ, 2015) and the Codex limit of 0.1 mg/kg f.w. for potatoes (Codex, 2011; Codex, 2015).

All the composts significantly decreased ($P < 0.05$) the concentration of Cd in peeled tubers (29-73%) compared to the control (Figure 4.1). The greatest reduction in the Cd concentration compared to the control was achieved by the SC treatment (71%). Potatoes grown in PG, MS, SD and MC treated soils accumulated less Cd (58-66%, 46-63%, 52-53% and 29-49%, respectively) in the potato flesh compared to the control. The 0.6% and 1.3% lime treatments decreased Cd concentration in the peeled tubers (by 43% - 54%) as well as the $\text{Ca}(\text{NO}_3)_2$ -extractable Cd (by 23-85%).

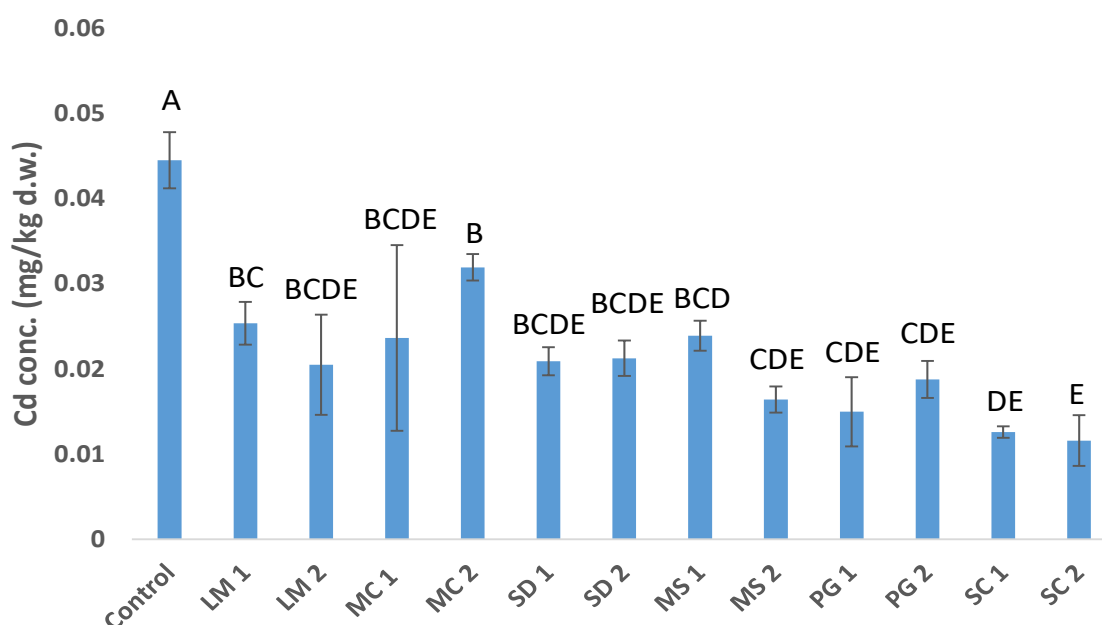


Figure 4.1 The cadmium concentration in potato tubers (dry weight basis). The error bars represent the standard error of the mean ($n = 3$). Values with the same letters are not significantly different. (Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.)

4.4.2 Cadmium in potato skins and shoots

The Cd concentration in potato skins varied from 0.02 to 0.09 mg/kg d.w. (Figure 4.2). All treatments in soil significantly decreased the concentration of Cd in potato skins except the potato skins grown in MC1 and PG2 treated soils (Figure 4.2). The greatest reduction (85%) in the potato skin Cd concentration was observed in SC2 treated soils followed by SC1 (70% reduction), SD2 (63% reduction) and L1 (62% reduction) treated soils. No significant difference was observed in the concentration of Cd in potato skin grown in the two rates of soil amendments except MC treated soils where potato skins of potato grown in MC2 treated soils had significantly less Cd concentration than that of MC1 treated soils.

The Cd concentrations in the potato stems ranged from 0.18 – 0.94 mg/kg d.w. (Table S1). Both the rates of MC, SD and 2.5 % rate of PG significantly reduced the concentration of Cd in potato stem (by 62%, 66%, 62%, 67% and 66%, respectively). The Cd concentrations in the potato leaves ranged from 0.11 – 0.27 mg/kg d.w. (Table S2). Both the rates of SC and LM 1 significantly decreased the concentration of Cd in potato leaves by 52%, 56% and 51%, respectively.

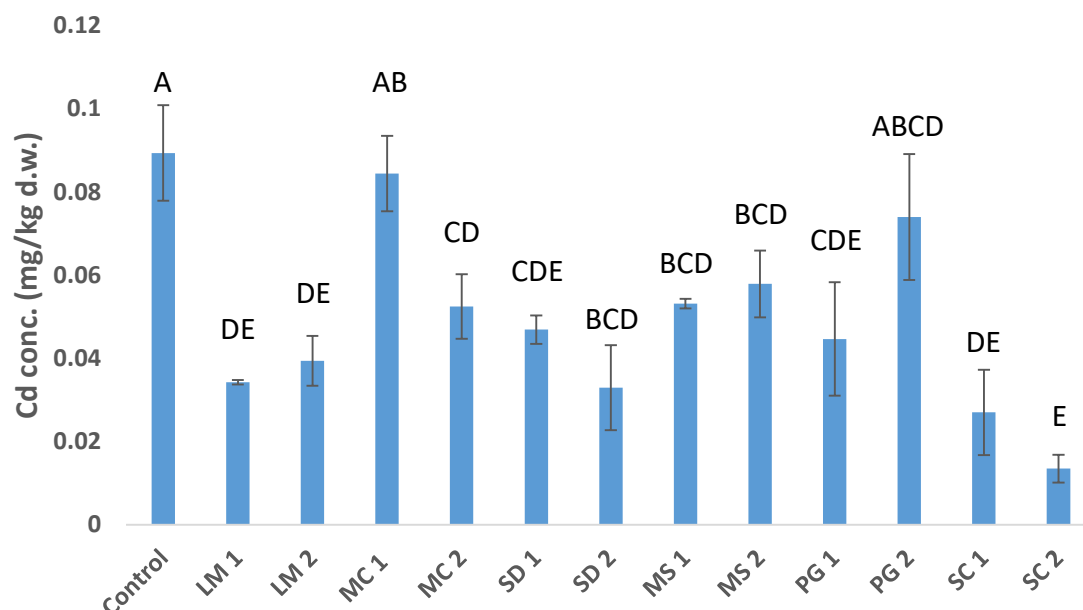


Figure 4.2 The cadmium concentration in potato skins (dry weight). Bars represent the standard error of the mean (n=3). Values with the same letters are not significantly different. Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

4.4.3 Concentrations of other elements

Unlike Cd, the treatments had no consistent effect on the other elements in either the tubers, peel, stems or leaves (Table 4.2-4.5, Table S1 4.1 and 4.2). The concentration of B decreased in potato tubers grown in soils treated with both the rates of LM and SC (Table 4.3). The Zn concentration in potato tubers ranged from 16.7 to 23.0 mg/kg and no consistent differences were observed for Zn accumulation in potato tuber compared to control. There were no significant differences in the concentration of P in either the potato tubers, skins, and stems.

Phosphorous in potato leaves increased in the SC treatments. All the treatments reduced the Zn and Fe concentrations in potato skins.

Table 4.2 Elemental composition (macronutrients) of peeled potato tubers (mg/kg). Standard errors are given in brackets (n=3). Values in the same column with the same letters are not significantly different

Treatment	% C	%N	Ca	K	Mg	P*ns	S
Control	40.59 (0.193) ^{AB}	0.83 (0.075) ^B	419 (65) ^{ABC}	20811 (424) ^{BCD}	1268 (72) ^{BCD}	3356 (179)	1248 (71) ^{EF}
LM 1	40.34 (0.189) ^{ABC}	0.85 (0.034) ^B	436 (42) ^{AB}	19428 (526) ^{CD}	1134 (29) ^D	3118 (116)	1338 (60) ^{CDEF}
LM 2	40.70 (0.197) ^A	0.96 (0.062) ^B	518 (66) ^A	18791 (867) ^D	1137 (28) ^D	3088 (170)	1366 (56) ^{CDEF}
MC 1	40.24 (0.257) ^{ABC}	0.91 (0.022) ^B	289 (15) ^{CD}	21565 (705) ^{ABC}	1253 (39) ^{BCD}	3245 (60)	1214 (37) ^F
MC 2	39.98 (0.099) ^C	0.98 (0.034) ^B	258 (22) ^D	21640 (123) ^{ABC}	1217 (19) ^{CD}	3163 (111)	1275 (38) ^{DEF}
SD 1	40.07 (0.099) ^C	0.86 (0.065) ^B	307 (18) ^{BCD}	20414 (694) ^{BCD}	1227 (17) ^{CD}	3284 (21)	1295 (60) ^{DEF}
SD 2	40.33 (0.046) ^{ABC}	0.93 (0.040) ^B	308 (53) ^{BCD}	21229 (11081) ^{ABC}	1330 (37) ^{ABC}	3264 (267)	1405 (48) ^{CDEF}
MS 1	40.19 (0.157) ^{BC}	0.88 (0.108) ^B	418 (55) ^{ABC}	20011 (185) ^{CD}	1201 (60) ^{CD}	3026 (88)	1539 (83) ^{BCD}
MS 2	40.25 (0.083) ^{ABC}	0.85 (0.031) ^B	320 (23) ^{BCD}	21600 (1476) ^{ABC}	1294 (34) ^{BC}	3014 (43)	1593 (53) ^{BC}
PG 1	40.63 (0.109) ^{AB}	0.95 (0.035) ^B	298 (33) ^{CD}	22611 (757) ^{AB}	1473 (18) ^A	3397 (12)	1531 (24) ^{BCDE}
PG 2	40.65 (0.255) ^{AB}	1.01 (0.104) ^B	420 (57) ^{ABC}	20464 (414) ^{BCD}	1386 (69) ^{AB}	3082 (61)	1452 (100) ^{CDEF}
SC 1	39.37 (0.165) ^D	1.40 (0.152) ^A	326 (48) ^{BCD}	21622 (988) ^{ABC}	1143 (101) ^D	3134 (87)	1757 (209) ^{AB}
SC 2	39.44 (0.161) ^D	1.55 (0.292) ^A	376 (49) ^{BCD}	23203 (1039) ^A	1239 (36) ^{CD}	3327 (340)	1900 (206) ^A

*ns=no significant difference, Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

Table 4.3 Elemental composition (micro nutrients and others) of peeled potato tubers (mg/kg). Standard errors are given in brackets (n=3). Values in the same column with the same letters are not significantly different

Treatments	B	Cr	Cu	Fe	Mn	Mo	Na	Zn
Control	7.40 (0.04) ^A	0.624 (0.04) ^A	6.1 (0.3) ^{AB}	23 (2) ^{AB}	6.96 (0.7) ^{ABC}	0.6 (0.05) ^D	87 (16) ^{CD}	20 (2) ^{ABC}
LM 1	6.37 (0.2) ^{BC}	0.484 (0.2) ^{ABC}	5.9 (0.2) ^B	19 (0.8) ^B	6.04 (0.2) ^C	2.1 (0.1) ^A	110 (13) ^{ABCD}	18 (0.4) ^{BCD}
LM 2	6.43 (0.04) ^{BC}	0.463 (0.06) ^{ABC}	6.2 (0.4) ^{AB}	19 (1) ^B	5.95 (0.1) ^C	2.1 (0.2) ^A	83 (4) ^D	18 (0.8) ^{BCD}
MC 1	7.33 (0.3) ^A	0.266 (0.02) ^{BCD}	6.4 (0.4) ^{AB}	21 (0.2) ^B	6.7 (0.2) ^{ABC}	1.4 (0.2) ^B	153 (1) ^{ABC}	19 (1) ^{BCD}
MC 2	6.72 (0.3) ^{ABC}	0.469 (0.1) ^{ABC}	6.6 (0.3) ^{AB}	21 (0.1) ^{AB}	6.3 (0.1) ^C	1.3 (0.2) ^{BC}	173 (34) ^A	19 (0.6) ^{BCD}
SD 1	6.80 (0.1) ^{ABC}	0.467 (0.2) ^{ABC}	5.8 (0.2) ^B	20 (1) ^B	6.8 (0.2) ^{ABC}	0.63 (0.1) ^{CD}	98 (20) ^{BCD}	17 (0.3) ^{CD}
SD 2	6.89 (0.2) ^{AB}	0.495 (0.07) ^{AB}	6.6 (0.2) ^{AB}	23 (0.3) ^{AB}	7.5 (0.2) ^{AB}	1.2 (0.1) ^{BC}	152 (47) ^{ABC}	18 (1) ^{BCD}
MS 1	6.66 (0.4) ^{ABC}	0.212 (0.04) ^D	6.8 (0.5) ^{AB}	19 (0.7) ^B	6.4 (0.4) ^{BC}	0.6 (0.04) ^D	140 (31) ^{ABCD}	17 (0.4) ^{CD}
MS 2	6.61 (0.3) ^{ABC}	0.18 (0.1) ^D	6.3 (0.2) ^{AB}	18 (0.9) ^B	6.0 (0.2) ^C	0.57 (0.2) ^D	135 (25) ^{ABCD}	16 (0.5) ^D
PG 1	6.74 (0.1) ^{ABC}	0.169 (0.1) ^D	6.1 (0.1) ^{AB}	21 (0.6) ^B	7.0 (0.1) ^{ABC}	0.8 (0.07) ^{BCD}	110 (10) ^{ABCD}	18 (0.3) ^{CD}
PG 2	6.95 (0.3) ^{AB}	0.238 (0.03) ^{CD}	6.1 (0.4) ^{AB}	20 (0.7) ^B	6.4 (0.3) ^{BC}	0.9 (0.02) ^{BCD}	158 (21) ^{AB}	17 (1) ^{CD}
SC 1	5.99 (0.3) ^{CD}	0.105 (0.02) ^D	7.6 (0.5) ^A	21 (2.5) ^{AB}	6.7 (0.9) ^{ABC}	1.1 (0.5) ^{BCD}	89 (12) ^{CD}	22 (2) ^{AB}
SC 2	5.39 (0.4) ^D	0.241 (0.1) ^{CD}	7.4 (1.5) ^{AB}	27 (5) ^A	7.6 (0.6) ^A	1.4 (0.5) ^B	120 (14) ^{ABCD}	23 (3) ^A

Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

Table 4.4 Macro nutrient elements (mg/kg) of potato skin/peel grown under different treatments. Standard errors are given in brackets (n=3). Values in the same column with the same letters are not significantly different

Treatments	Ca	K	Mg	P*ns	S
Control	1286 (155) ^B	37687 (1278) ^A	2063 (146) ^{AB}	5327 (269)	1647 (150) ^{ABC}
LM 1	1690 (224) ^{AB}	27967 (921) ^E	1504 (72) ^B	4540 (176)	1394 (55) ^C
LM 2	1909 (19) ^{AB}	30785 (1623) ^{CDE}	1733 (61) ^B	5000 (209)	1607 (82) ^{BC}
MC 1	925 (114) ^B	35960 (1956) ^{AB}	1811 (46) ^B	5269 (327)	1388 (14) ^C
MC 2	859 (17) ^B	35257 (614) ^{ABC}	1750 (74) ^B	5058 (96)	1452 (76) ^C
SD 1	1018 (166) ^B	33589 (1071) ^{ABCD}	1711 (115) ^B	5298 (373)	1482 (101) ^C
SD 2	1232 (46) ^B	31632 (2983) ^{BCDE}	2039 (98) ^{AB}	5075 (565)	1676 (64) ^{ABC}
MS 1	1252 (79) ^B	32001 (1101) ^{BCDE}	1801 (52) ^B	4972 (128)	2129 (25) ^A
MS 2	1084 (75) ^B	32503 (1229) ^{BCDE}	1601 (50) ^B	4594 (109)	1809 (39) ^{ABC}
PG 1	890 (79) ^B	32041 (1624) ^{BCDE}	1784 (89) ^B	5177 (172)	1435 (113) ^C
PG 2	3540 (23) ^A	34002 (1104) ^{ABCD}	2534 (730) ^A	4946 (195)	2045 (474) ^{AB}
SC 1	840 (37) ^B	34760 (1914) ^{ABCD}	1498 (226) ^B	4496 (522)	1546 (238) ^C
SC 2	931 (79) ^B	30190 (2899) ^{DE}	1463 (72) ^B	4401 (723)	1789 (175) ^{ABC}

*ns=no significant difference, Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

Table 4.5 Micro nutrient elements (mg/kg) and Cr of potato skin (peel) grown under different treatments. Standard errors are given in brackets (n=3). Values in the same column with the same letters are not significantly different

Treatments	B	Cr	Cu	Fe	Mn	Mo	Zn
Control	15.3 (1) ^A	0.4 (0.1) ^A	7.5 (0.4) ^{BC}	353 (115) ^A	20 (5) ^A	0.6 (0.1) ^{CD}	42 (10) ^A
LM 1	9.8 (0) ^{DE}	0.1 (0.03) ^C	7.0 (0.1) ^C	77 (18) ^B	7 (0.1) ^B	1.9 (0.1) ^A	22 (2) ^B
LM 2	11.6 (1) ^{BCDE}	0.2 (0.02) ^B	7.9 (0.6) ^{BC}	53 (3) ^B	8 (0.4) ^B	1.9 (0.1) ^A	24 (1) ^B
MC 1	13 (1) ^{ABC}	0.1 (0.03) ^C	8.8 (0.5) ^{ABC}	119 (33) ^B	9 (1.4) ^B	1.1 (0.1) ^{BC}	25 (3) ^B
MC 2	12.6 (0) ^{BC}	0.1 (0.02) ^C	9.5 (0.3) ^{AB}	98 (32) ^B	9 (1.3) ^B	1.1 (0.1) ^{BC}	25 (2) ^B
SD 1	12.7 (1) ^{BC}	0.1 (0.02) ^C	8.2 (0.7) ^{BC}	98 (22) ^B	10 (0.8) ^B	0.5 (0.1) ^{CD}	22 (2) ^B
SD 2	12.1 (1) ^{BCD}	0.2 (0.03) ^B	8.5 (0.5) ^{ABC}	109 (11) ^B	10 (1.5) ^B	1.1 (0.1) ^{BC}	22 (3) ^B
MS 1	11.9 (1) ^{BCDE}	0.1 (0.03) ^C	9.3 (0.4) ^{ABC}	133 (42) ^B	10 (1) ^B	0.5 (0.1) ^{CD}	20 (0) ^B
MS 2	10.8 (1) ^{CDE}	0.1 (0.01) ^C	8.8 (0.5) ^{ABC}	50 (8) ^B	7 (0.8) ^B	0.4 (0.1) ^D	19 (0) ^B
PG 1	11.1 (0) ^{BCDE}	0.1 (0.02) ^C	8.6 (0.1) ^{ABC}	67 (9) ^B	7 (0.1) ^B	0.7 (0.1) ^{CD}	20 (1) ^B
PG 2	13.5 (0) ^{AB}	0.2 (0.08) ^{BC}	9.6 (1.1) ^{AB}	161 (73) ^B	12 (2.2) ^B	0.8 (0.2) ^{BCD}	24 (3) ^B
SC 1	11.5 (2) ^{BCDE}	0.1 (0.01) ^C	9 (1.4) ^{ABC}	49 (11) ^B	8 (3) ^B	1.1 (0.4) ^{BC}	28 (5) ^B
SC 2	9.6 (1) ^E	0.1 (0.01) ^C	10.7 (1.9) ^A	40 (12) ^B	9 (0.3) ^B	1.4 (0.5) ^{AB}	24 (3) ^B

Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

4.4.4 Effect of treatments on potato growth

The Figure 4.3 and Figure 4.4 show that composts significantly increased the growth of both tubers and shoots. The LM treatments significantly increased the tuber growth but decreased the shoot growth. SC decreased potato tuber and shoot growth. An unpleasant odour emanated from the SC soil, indicating that it may have turned anaerobic after approximately three weeks, which may explain the poor yield. The highest tuber growth was observed in MC2 treated soils (168% increase) followed by PG1 (112% increase), MS2 (109% increase), MC1 (106% increase), MS1 (102%), PG2 (67%), SD2 (63%), SD1 (47%), LM1 (45%) and LM2 (33%)

treated soils. The addition of SC1 and SC2 decreased potato growth by 50% and 60%, respectively.

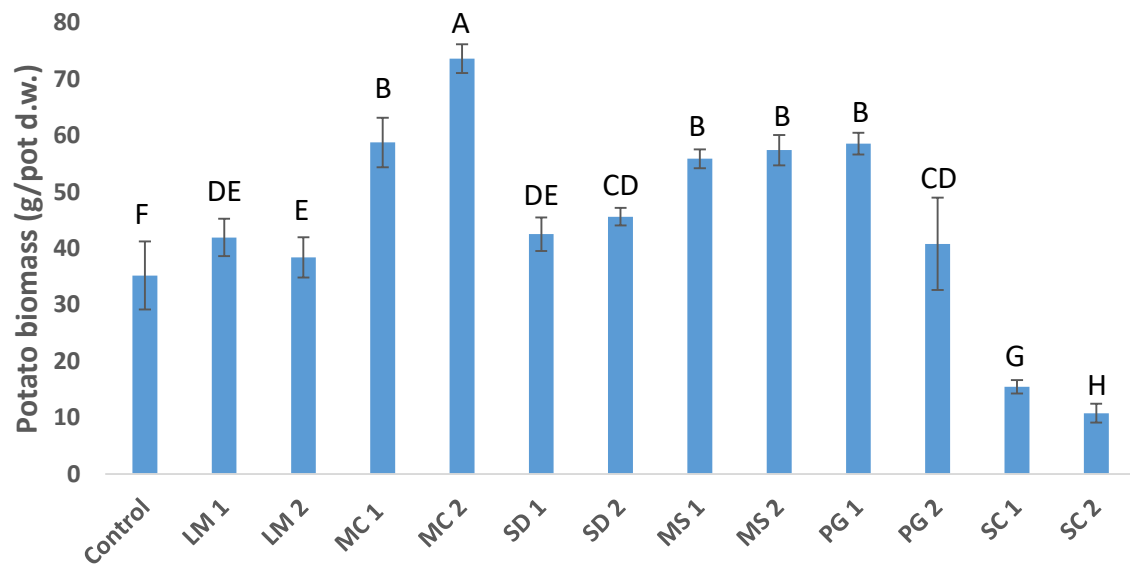


Figure 4.3 Tuber biomass (including skins). Bars represent the standard error of the mean (n=3). Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

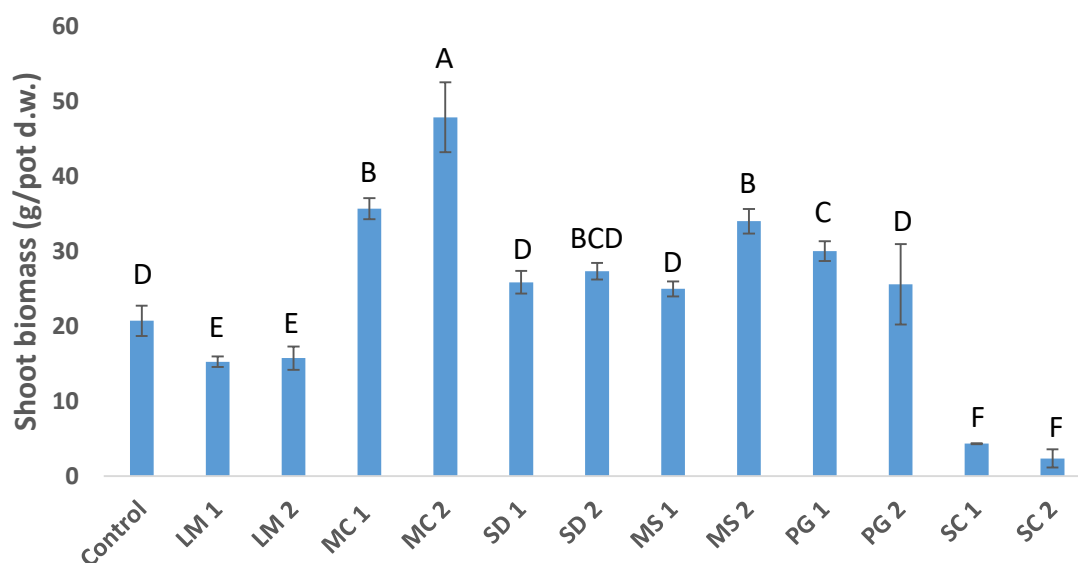


Figure 4.4 Shoot biomass (d.w.). Bars represent the standard error of the mean (n=3). Values with the same letters are not significantly different. Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

4.4.5 Effect of treatments on soil properties

The Table 4.6 shows that all treatments increased pH except SD1, SD2, PG2, and SC1, which had no significant effect on pH. The LM treatments resulted in by far the largest pH increase by 1.0 – 1.2 pH units respectively, whereas the composts either had no effect or result in a slight increase (<0.4 pH units). All the composts significantly increased C & N with a small increase in the C: N ratio in all treatments.

All of the organic amendments reduced $\text{Ca}(\text{NO}_3)_2$ -extractable Cd in the soil, except PG2 (Table 4.7). The effect of the composts on the $\text{Ca}(\text{NO}_3)_2$ -extractable concentrations of other elements

was variable, with the changes reflecting the composition of the composts (Table 4.1). The LM treatments caused an approximately 10-fold decrease in $\text{Ca}(\text{NO}_3)_2$ -extractable Zn, whereas the effect of the composts was smaller and in many cases not significant (Table 4.7)

Table 4.6 Soil pH, total C and N (%), and 0.05 M $\text{Ca}(\text{NO}_3)_2$ extracted macro nutrient elements (mg/kg). Standard errors are given in brackets (n=3). Values in the same column with the same letters are not significantly different

Treatments	pH	% C	%N	C/N	K	Mg	P	S
Control	6.04 (0.02) ^{GH}	2.29 (0.02) ^G	0.212 (0.003) ^{FG}	10.84 (0.021) ^{EF}	258 (13) ^H	426 (18) ^E	3.85 (0.3) ^{FG}	219 (57) ^D
LM 1	7.03 (0.58) ^B	2.28 (0.13) ^G	0.206 (0.002) ^{FG}	11.06 (0.046) ^{DEF}	271 (5) ^{GH}	291 (1) ^F	3.99 (0.01) ^{FG}	231 (23) ^D
LM 2	7.28 (0.03) ^A	2.29 (0.03) ^G	0.185 (0.009) ^G	12.47 (0.540) ^{BC}	244 (6) ^H	247 (2) ^G	4.01 (0.14) ^{FG}	200 (16) ^D
MC 1	6.26 (0.02) ^E	3.00 (0.08) ^{EF}	0.285 (0.007) ^{BC}	10.53 (0.128) ^{FG}	305 (3) ^{FG}	493 (4) ^{CD}	4.27 (0.03) ^{DEF}	184 (11) ^D
MC 2	6.37 (0.03) ^{CD}	4.07 (0.16) ^A	0.403 (0.018) ^A	10.12 (0.070) ^G	408 (5) ^{CD}	569 (13) ^{AB}	4.88 (0.1) ^{BC}	155 (7) ^D
SD 1	6.09(0.01) ^{FG} ^H	3.21 (0.04) ^{DE}	0.269 (0.006) ^{CD}	11.93 (0.257) ^{CD}	267 (4) ^H	431 (7) ^E	4.10 (0.2) ^{EFG}	146 (12) ^D
SD 2	6.13 (0.05) ^{FG}	4.12 (0.08) ^A	0.309 (0.009) ^B	13.34 (0.172) ^{AB}	258 (20) ^H	452 (6) ^{DE}	4.54 (0.3) ^{CDE}	135 (9) ^D
MS 1	6.28 (0.03) ^{DE}	3.84 (0.02) ^{AB}	0.247 (0.002) ^{DE}	11.84 (0.007) ^{CD}	374 (14) ^{DE}	535 (8) ^{BC}	4.79 (0.1) ^{BC}	1064 (53) ^B
MS 2	6.43 (0.01) ^C	2.93 (0.10) ^{EF}	0.302 (0.007) ^B	12.70 (0.071) ^{BC}	422 (2) ^C	612 (6) ^A	5.70 (0.1) ^A	1521 (54) ^A
PG 1	6.30 (0.05) ^{DE}	2.86 (0.04) ^F	0.231 (0.015) ^{EF}	12.43 (0.690) ^{BC}	573 (24) ^B	430 (9) ^E	3.73 (0.1) ^G	47 (4) ^D
PG 2	6.10 (0.03) ^{FGH}	3.67 (0.11) ^{BC}	0.264 (0.008) ^{CD}	13.90 (0.532) ^A	769 (9) ^A	504 (21) ^C	4.67 (0.1) ^{BCD}	96 (8) ^D
SC 1	6.01 (0.01) ^H	2.92 (0.11) ^F	0.255 (0.007) ^{DE}	11.46 (0.128) ^{DE}	313 (5) ^F	452 (8) ^{DE}	4.87 (0.1) ^{BC}	287 (37) ^D
SC 2	6.14 (0.04) ^F	3.45 (0.22) ^{CD}	0.306 (0.020) ^B	11.27 (0.187) ^{DEF}	372 (16) ^E	502 (15) ^C	5.02 (0.1) ^B	559 (88) ^C

Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

Table 4.7 The 0.05 M $\text{Ca}(\text{NO}_3)_2$ extracted Cd, Na and micro nutrient elements (mg/kg) of the soils. Standard errors are given in brackets (n=3). Values in the same column with the same letters are not significantly different

Treatments	Cd	Cu	Fe	Mn	Na	Zn
Control	0.011 (0.003) ^A	0.16 (0.014) ^{DEF}	0.20 (0.04) ^C	23 (2) ^{DE}	118 (9) ^{EF}	0.419 (0.03) ^A
LM 1	0.002 (0.001) ^{DE}	0.21 (0.005) ^{AB}	0.34 (0.15) ^{BC}	6 (2) ^{FG}	92 (0.2) ^G	0.032 (0.01) ^E
LM 2	0.009 (0.000) ^E	0.20 (0.004) ^{BC}	0.41 (0.1) ^{ABC}	3 (0.6) ^G	89 (1) ^G	0.055 (0.02) ^E
MC 1	0.002 (0.000) ^{DE}	0.17 (0.015) ^{DE}	0.34 (0.11) ^{BC}	14 (0.2) ^{EF}	200 (4) ^B	0.322 (0.04) ^{ABC}
MC 2	0.001 (0.000) ^E	0.17 (0.018) ^{CDE}	0.43 (0.13) ^{ABC}	14 (2) ^{EFG}	245 (3) ^A	0.215 (0.04) ^{CD}
SD 1	0.006 (0.000) ^B	0.15 (0.015) ^{EFG}	0.19 (0.02) ^C	23 (4) ^{DE}	114 (5) ^F	0.323 (0.01) ^{ABC}
SD 2	0.003 (0.000) ^{CDE}	0.13 (0.013) ^{FG}	0.14 (0.06) ^C	23 (2) ^{DE}	123 (4) ^{EF}	0.251 (0.03) ^{BCD}
MS 1	0.004 (0.000) ^{CD}	0.24 (0.006) ^A	0.17 (0.1) ^C	33 (7) ^{CD}	146 (4) ^D	0.175 (0.03) ^{CDE}
MS 2	0.001 (0.000) ^E	0.24 (0.001) ^A	0.30 (0.01) ^{BC}	17 (0.3) ^E	179 (4) ^C	0.148 (0.08) ^{DE}
PG 1	0.006 (0.001) ^B	0.13 (0.001) ^G	0.43 (0.01) ^{ABC}	44 (2) ^{AB}	89 (4) ^G	0.457 (0.11) ^A
PG 2	0.009 (0.002) ^A	0.15 (0.003) ^{DEFG}	0.53 (0.2) ^{AB}	49 (8) ^A	127 (6) ^{EF}	0.419 (0.09) ^A
SC 1	0.005 (0.001) ^{BC}	0.19 (0.003) ^{BCD}	0.38 (0.03) ^{ABC}	38 (3) ^{BC}	135 (6) ^{DE}	0.475 (0.06) ^A
SC 2	0.001 (0.000) ^E	0.17 (0.001) ^{CDE}	0.69 (0.02) ^A	29 (0.4) ^{CD}	173 (3) ^C	0.403 (0.05) ^{AB}

Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

4.5 Discussion

The low Cd concentrations in the potato tubers was not anticipated because the soil Cd concentration (1.48 mg/kg) is within the top 5% of NZ soils (Reiser et al., 2014). In contrast to the tubers, the Cd concentrations in the stems and leaves of potato were with the range (0.2 – 0.9 mg/kg) of concentrations reported for the aerial parts of spinach, lettuce and onion grown in the same soil under similar conditions (Al Mamun et al., 2016). This indicates that the low concentration of Cd in the tubers is the result of plant physiological process rather than low-

Cd phytoavailability in the soil. Given that Cd is relatively phloem-immobile (Uraguchi et al., 2009), one would not expect high Cd concentrations in the tubers, which receive most of their nutrients via the phloem (Dunbar et al., 2003).

The lower tuber Cd concentrations in our study compared to those reported by other authors (Kabata-Pendias and Mukherjee, 2007; Kim, 2008; McLaughlin et al., 1994a; McLaughlin et al., 1994b) may be due to differences in variety, although McLaughlin et al. (1994a) reported only small differences in Cd uptake between varieties.

The concentration ratios of the potato flesh: skin/peel: shoots was 2:5:29, with little variation between treatments. This is similar to other experiments with potato (Corguinha et al., 2012; Reid et al., 2003). Some of Cd in potato skins may arise from the incorporation of soil particles into the skin that could not be removed even after washing.

All amendments significantly reduced Cd uptake by the potato tubers and most amendments reduced uptake into the shoots. The reduction in Cd uptake may be partially explained by the reduction in the phytoavailable Cd (estimated in our experiments using a 0.05 M $\text{Ca}(\text{NO}_3)_2$ extraction), which occurred in all of the treatments. Black et al. (2012), Gray et al. (1999c) and Gray et al. (1999b) reported a strong positive correlation between plant Cd and $\text{Ca}(\text{NO}_3)_2$ -extractable Cd in a single soil type.

For the MC, MS, and PG1 treatments, the reduced Cd concentration in the tubers may be partly explained by the small increase in pH of the amended soils (Table 4.2). However, most of the decrease in tuber Cd may be attributed to the increase in Cd-binding sites on the composts, which is indicated by their high CEC values (Table 4.1). The CEC of the composts in this study was similar to those reported in other composts and organic amendments (Pusz, 2007; Simmler et al., 2013). For all treatments except the SC, the increased growth of the tuber may have resulted in a lower-Cd concentration due to a “dilution effect” (Robinson et al., 2009). This

effect may also explain the increased shoot Cd in the SC1 treatment where the shoot growth was significantly reduced.

The reduction of Cd concentration in potato flesh grown in LM treatments was anticipated as these two rates of lime were selected from a previous study using the same soil, where the effects of seven rates of lime were tested on the Cd solubility and uptake by white lupin (Valentinuzzi et al., 2015). Lime treatments in soil have been reported to both increase and decrease the uptake of Cd by plants. Lime significantly increased soil pH (Table 4.6), which has been associated with decreasing the accumulation of Cd in plants in almost all studies (Hong et al., 2007; Kabata-Pendias and Mukherjee, 2007; Simmler et al., 2013) through increasing the availability of exchangeable sites (Brady and Weil, 2008) that may bind Cd. Our results stand in contrast to other studies that reported an increased uptake of Cd by plants due to lime application, which was attributed to competition between Cd and Ca for sorbing sites in soil (Chaney et al., 2009; Maier et al., 2002; McLaughlin et al., 1997; Merian, 1991).

A positive growth response to compost addition has also been shown by other authors (Barkoczi et al., 2008; Khan et al., 2007; Muhammad et al., 2007). The composts used in this study contained high P content compared to the soil and thus no fertilizer was used, which eliminated the risk of further addition of Cd input in these soils. Moreover, these composts probably improved the physical properties of soils by improving soil porosity, aggregate stability, nutrient and water holding capacity, temperature insulation and decreasing apparent soil density (Sarwar et al., 2008; Shiralipour et al., 1992), and soil nutrient content (Shiralipour et al., 1992). The reduced shoot growth in the lime treatment may have been due to the imbalance of nutrient elements in soil due to the pH increase (Maier et al., 2002).

4.6 Conclusions

Composts with contrasting provenances all decreased the concentration of Cd in potato tubers and skins as well as decreasing the $\text{Ca}(\text{NO}_3)_2$ -extractable concentrations of Cd in soil. Most of this effect was attributed to the increased number of binding sites for Cd in compost-amended soil. In addition, the increase in fertility associated with compost-addition may have reduced potato Cd concentrations by increasing the biomass, thereby resulting in a ‘dilution by growth’ effect. All composts and lime significantly increased tuber growth except SC, which significantly reduced growth. That all the composts in this study reduced Cd uptake does not imply that every compost will do so. Further work is warranted to identify the key components of composts that result in reduced Cd uptake by plants and increased biomass of potato. Potentially, composts may be a low-cost means of ensuring that crop Cd concentrations remain within Food Safety Standards by reducing plant uptake and offsetting the need to apply Cd-contaminated phosphate fertilizers.

Supplementary Information

Table S1 4.1 Elemental composition of potato stem grown under different treatments. Standard errors are given in brackets (n=3). Values in the same column with the same letters are not significantly different

Treatments	B (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	K (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Mo (mg/kg)	P*ns (mg/kg)	S (mg/kg)	Zn (mg/kg)
Control	25.0 (2) ^{BCD}	13562 (1444) ^{DEF}	0.527 (0.02) ^{BC}	0.26 (0.1) ^B	6.2 (0.4) ^{BCD}	26.1 (1) ^B	59335 (1638) ^A	1257 (154) ^{CDEFG}	25 (1) ^C	0.37 (0.05) ^C	3327 (530)	4832 (281) ^A	62 (12) ^{CD}
LM 1	26.5 (0.5) ^{BC}	19345 (341) ^{BC}	0.318 (0.04) ^{CD}	0.22 (0.1) ^B	9.9 (0.4) ^{BC}	24.0 (4) ^B	51355 (1219) ^{AB}	790 (88) ^{FG}	8 (2) ^C	3.5 (0.4) ^B	2685 (443)	5497 (208) ^A	53 (3) ^{CD}
LM 2	25.0 (1) ^{BCD}	18848 (704) ^C	0.508 (0.09) ^{BC}	0.33 (0.2) ^B	8.5 (1) ^{BCD}	32.0 (9) ^B	46787 (2643) ^{BC}	975 (230) ^{DEFG}	11 (3) ^C	3.4 (0.01) ^B	3203 (415)	5045 (388) ^A	54 (9) ^{CD}
MC 1	22.2 (4) ^{CD}	11756 (3368) ^{EF}	0.200 (0.02) ^D	0.05 (0.01) ^B	3.9 (0.8) ^D	45.8 (6) ^B	55091 (4539) ^{AB}	1754 (360) ^{CDEF}	19 (8) ^C	0.85 (0.09) ^C	2669 (386)	2761 (250) ^{CD}	41 (7) ^D
MC 2	23.0 (1) ^{BCD}	10856 (1547) ^F	0.181 (0.006) ^D	0.09 (0.0) ^B	4.6 (0.6) ^D	26.0 (2) ^B	61238 (4856) ^A	1887 (435) ^{CDE}	12 (3) ^C	1.23 (0.03) ^C	2304 (110)	2497 (112) ^D	49 (7) ^D
SD 1	22.0 (2) ^{CD}	11260 (1313) ^F	0.200 (0.01) ^D	0.12 (0.0) ^B	5.2 (0.5) ^{CD}	21.3 (1) ^B	50335 (19780) ^{AB}	659 (95) ^G	13 (1) ^C	0.41 (0.07) ^C	2828 (457)	3415 (117) ^{BC}	42 (4) ^D
SD 2	23.5 (1) ^{BCD}	12242 (1191) ^{EF}	0.171 (0.0) ^D	0.14 (0.0) ^B	5.6 (0.5) ^{BCD}	25.2 (4) ^B	56519 (4399) ^{AB}	704 (336) ^{FG}	13 (4) ^C	1.01 (0.18) ^C	3019 (661)	3570 (210) ^B	45 (3) ^D
MS 1	27.1 (1) ^B	16477 (840) ^{CD}	0.370 (0.01) ^{CD}	0.10 (0.0) ^B	10.0 (1) ^{BC}	34.1 (7) ^B	50416 (1012) ^{AB}	2034 (263) ^C	20 (1) ^C	0.32 (0.1) ^C	3235 (287)	4892 (413) ^A	85 (5) ^C
MS 2	25.2 (0.3) ^B	15784 (602) ^{CDE}	0.278 (0.003) ^{CD}	0.06 (0) ^B	10.7 (1.4) ^B	29.5 (1) ^B	55170 (2192) ^{AB}	2130 (179) ^C	20 (1) ^C	0.33 (0.12) ^C	2619 (201)	5137 (223) ^A	72 (6) ^{CD}
PG 1	24.5 (2) ^{BCD}	12765 (427) ^{DEF}	0.178 (0.01) ^D	0.09 (0.0) ^B	8.1 (0.5) ^{BCD}	21.2 (3) ^B	56237 (4165) ^{AB}	935 (160) ^{EFG}	8 (2) ^C	0.67 (0.1) ^C	2808 (416)	3969 (248) ^B	47 (2) ^D
PG 2	20.7 (2) ^D	11066 (1411) ^F	0.241 (0.03) ^{CD}	0.18 (0.0) ^B	5.1 (0.3) ^{CD}	23.5 (3) ^B	54360 (2128) ^{AB}	2019 (630) ^{CD}	21 (5) ^C	0.63 (0.1) ^C	2723 (115)	3257 (262) ^{BCD}	51 (6) ^D
SC 1	51.2 (2) ^A	24834 (1098) ^A	0.943 (0.1) ^A	0.06 (0.0) ^B	25.4 (5.3) ^A	47.8 (3) ^B	37885 (6260) ^C	9374 (763) ^A	184 (33) ^B	1.22 (0.7) ^C	3458 (307)	4932 (238) ^A	269 (30) ^A
SC2	52.3 (0.017) ^A	23707 (1155) ^{AB}	0.752 () (0.29) ^{AB}	9.88 (7.95) ^A	19.74 (3.23) ^A	81.1 (42) ^A	36319 (8759) ^C	6088 (172) ^B	268 (73) ^A	6.80 (1.8) ^A	3226 (822)	3542 (417) ^{BC}	222 (16.10) ^B

Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

Table SI 4.2 Elemental composition of potato leaf grown under different treatments. Standard errors are given in brackets (n=3). Values in the same column with the same letters are not significantly different

Treatments	B (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	K (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Mo (mg/kg)	P (mg/kg)	S (mg/kg)	Zn (mg/kg)
Control	66.1 (4) ^{CDE}	26124 (1395) ^{CDE}	0.258 (0.005) ^{AB}	0.19 (0.02) ^{BC}	8.3 (1) ^{CDE}	125 (9) ^A	37096 (1547) ^{ABC}	2806 (231) ^E	79 (5) ^B	1 (0.2) ^C	2590 (35) ^B	5432 (258) ^{DEFG}	30 (2) ^{BC}
LM 1	72.9 (1) ^{ABC}	27815 (1074) ^{BC}	0.114 (0.003) ^C	0.15 (0.06) ^{BCD}	9.0 (1) ^C	108 (10) ^{ABC}	33144 (1160) ^{BC}	2020 (175) ^F	53 (2) ^{CD}	6 (1) ^B	2398 (127) ^B	7184 (763) ^{BC}	23 (1) ^{CD}
LM 2	69.3 (2) ^{ABCD}	27352 (1083) ^{BCD}	0.201 (0.01) ^{ABC}	0.13 (0.05) ^{CD}	7.9 (0) ^{CDE}	85 (4) ^C	30145 (1823) ^C	1950 (136) ^F	57 (2) ^{CD}	6 (1) ^B	2292 (174) ^B	5829 (480) ^{CDEF}	18 (1) ^D
MC 1	58.3 (3) ^{DEF}	25332 (1963) ^{CDEF}	0.265 (0.05) ^{AB}	0.10 (0.05) ^{CD}	6.5 (0) ^E	114 (14) ^{AB}	35957 (3953) ^{ABC}	4578 (201) ^{BC}	66 (7) ^{BCD}	1 (0.1) ^C	2522 (300) ^B	4289 (563) ^{GH}	27 (3) ^C
MC 2	63.6 (5) ^{CDEF}	22713 (1187) ^F	0.236 (0.06) ^{AB}	0.11 (0.02) ^{CD}	6.7 (0) ^{DE}	101 (7) ^{BC}	41615 (3921) ^A	4339 (276) ^C	58 (5) ^{CD}	1 (0.2) ^C	2212 (92) ^B	3294 (178) ^H	28 (3) ^{BC}
SD 1	55.7 (3) ^{EF}	22888 (759) ^{EF}	0.170 (0.1) ^{BC}	0.13 (0.07) ^{CD}	7.4 (1) ^{CDE}	109 (8) ^{ABC}	32459 (1224) ^{BC}	2704 (24) ^E	63 (3) ^{CD}	1 (0) ^C	2359 (91) ^B	5038 (85) ^{EFG}	29 (2) ^{BC}
SD 2	56.7 (2) ^{EF}	24297 (1659) ^{DEF}	0.173 (0.01) ^{BC}	0.12 (0.02) ^{CD}	7.0 (1) ^{CDE}	117 (8) ^{AB}	35388 (3285) ^{ABC}	2829 (21) ^E	65 (4) ^{BCD}	1 (0.2) ^C	2479 (282) ^B	4189 (359) ^{GH}	25 (1) ^{CD}
MS 1	66.2 (7) ^{CDE}	27748 (752) ^{BC}	0.254 (0.04) ^{AB}	0.10 (0.04) ^{CD}	8.8 (1) ^{CD}	102 (9) ^{ABC}	35401 (1422) ^{ABC}	2653 (254) ^E	66 (2) ^{BCD}	1 (0.1) ^C	1917 (120) ^B	7493 (236) ^{AB}	27 (4) ^C
MS 2	69.2 (5) ^{ABCD}	28422 (680) ^{BC}	0.214 (0.01) ^{ABC}	0.12 (0.03) ^{CD}	8.0 (1) ^{CDE}	106 (4) ^{ABC}	38320 (4342) ^{AB}	3092 (183) ^{DE}	68 (4) ^{BC}	0.9 (0.1) ^C	2011 (223) ^B	8782 (980) ^A	23 (2) ^{CD}
PG 1	68.7 (3) ^{BCD}	23903 (94) ^{EF}	0.195 (0.03) ^{BC}	0.10 (0.04) ^{CD}	7.8 (0) ^{CDE}	112 (3) ^{AB}	37052 (1674) ^{ABC}	3651 (101) ^D	64(2) ^{CD}	1 (0.1) ^C	2378 (133) ^B	5957 (181) ^{CDE}	25 (1) ^{CD}
PG 2	52.5 (4) ^F	27460 (820) ^{BCD}	0.296 (0.03) ^A	0.06 (0.01) ^D	8.0 (1) ^{CDE}	101 (4) ^{BC}	38362 (1982) ^{AB}	4941 (241) ^{BC}	72 (4) ^{BC}	1 (1) ^C	2456 (47) ^B	4557 (547) ^{FGH}	37 (5) ^B
SC 1	80.4 (5) ^A	34853 (862) ^A	0.126 (0.02) ^C	0.34 (0.03) ^A	16.6 (1) ^A	122 (12) ^{AB}	36391 (1425) ^{ABC}	6617 (216) ^A	158 (10) ^A	5 (3) ^{BC}	6684 (927) ^A	7191 (309) ^{BC}	29 (4) ^{BC}
SC 2	79.3 (5) ^{AB}	30580 (1151) ^B	0.123 (0.03) ^C	0.26 (0.02) ^{AB}	13.8 (1) ^B	107 (5) ^{ABC}	39282 (1167) ^{AB}	5100 (498) ^B	169 (8) ^A	15 (5) ^A	6898 (1847) ^A	6849 (255) ^{BCD}	47 (2) ^A

Control, no treatment in soil; LM 1 and LM 2, lime 0.6 and 1.3%, respectively; MC 1 and MC 2: municipal green waste compost 2.5 and 5%, respectively; MS 1 and MS 2, mushroom industry residue compost 2.5 and 5%, respectively; PG 1 and PG 2, pig manure composted with sawdust 2.5 and 5%, respectively; SC 1 and SC 2, shredded corn stover 2.5 and 5%, respectively; SD 1 and SD 2, sawdust composted with animal offal 2.5 and 5%, respectively.

Chapter 5 Temporal changes of Cd sorption in compost amended soils

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My contribution to the article: I designed and setup the experiments with the help of my co-authors. I collated and interpreted the data and wrote the article in collaboration with my co-authors.

5.1 Abstract

The application of Cd-contaminated phosphate fertilizer has elevated concentrations of this non-essential element in many agricultural soils. Consequently, some agricultural products exceed food safety standards. Composts can reduce the transfer of Cd from soil to plants. However, it is unclear how long this beneficial effect endures. We aimed to determine temporal changes of phytoavailable Cd, as estimated by a 0.05 M $\text{Ca}(\text{NO}_3)_2$ extraction, in two soils (Pukekohe as Allophanic Orthic Granular Soil and Levin as Silt Loam), each amended with either municipal green waste compost or sawdust & animal waste compost. There were three incubation regimes at 20 °C, 30 °C with or without added N (0.6 g urea / kg soil added over one year). We grew potatoes in the Pukekohe soil freshly amended with municipal compost and the same soil aged for one year. The C content of the soil – compost mixtures decreased over the year, with the greatest decreases occurring in the soils incubated at 30 °C with added

N. Unexpectedly, the concentration of extractable Cd in the compost-amended soils did not increase over time and in some cases even decreased. The potato Cd concentration was lower by 50% in both the freshly amended soil and the amended soil aged for one year than the potatoes grown in control soils. Our results indicate that while the organic matter degraded, Cd and other elements may have been occluded by Fe and Al moieties brought into suspension / solution by the mechanical disturbance. The role of soil disturbance on the phytoavailability of soil Cd is a fertile area for future research.

Key words: phytoavailable Cd; extractable Cd; incubation; potato; organic amendment;

5.2 Introduction

Cadmium is a non-essential trace element that is present at elevated concentrations in many agricultural soils (Bolan et al., 2003a; Kabata-Pendias and Mukherjee, 2007). Soil-borne Cd is readily taken up by plants (Bolan et al., 2003a; Nan et al., 2002; Simmler et al., 2013; Valentinuzzi et al., 2015) and animals through plant consumption (Alloway et al., 1990; Arcella et al., 2012; Berkelaar and Hale, 2003; EFSA, 2012; Lopez-Chuken and Young, 2010; McLaughlin et al., 1998). Exceedances of food safety standards have been reported in vegetables worldwide (Kim, 2008; McLaughlin et al., 1997; Zheng et al., 2007; Zhuang et al., 2009).

Most Cd in soil is attached to the soil colloids, with relatively low concentrations present in soil solution (Christensen and Haug, 1999a). Soils K_d (sorbed / solution Cd quotient) (Simmler et al., 2013) values for silt loam soils range from 50-200 from pH 5 to 6.5 (Al Mamun et al., 2016), which indicates that most of the Cd in soil is sorbed by soils. The accumulation of Cd in plants depends on the soluble fraction of Cd in soils, which is a function of the total concentration as well as physicochemical and biological properties of the soils (Kabata-Pendias and Mukherjee, 2007). In most soils, some 55-90% of Cd in soil solution is present as free metal ion Cd^{2+} (Taylor and Percival, 2001). It may occur as cationic species: $CdCl^+$, $CdOH^+$, $CdHCO_3^+$, $CdHS^+$ or as an anionic species: $CdCl_3^-$, $Cd(OH)_3$, $Cd(OH)_4^{2-}$, $Cd(HS)_4^{2-}$ (Kabata-Pendias and Mukherjee, 2007). Sposito and Page (1984) reported that Cd^{2+} , $CdSO_4^0$ and $CdCl^+$ are phytoavailable in acidic solution and Cd, $CdCl^+$, $CdSO_4^0$ and $CdHCO_3^+$ are most phytoavailable in alkaline solution (Kabata-Pendias and Mukherjee, 2007). Cadmium also forms several types of organic chelates (Kabata-Pendias and Mukherjee, 2007).

The solubility and speciation of Cd is sensitive to pH, salinity, total Cd concentration, CEC, clay, Fe and Mn oxides, macronutrients (especially Ca), micro nutrients (especially Zn), aeration and chloride ion (Cl^-) (Kabata-Pendias and Mukherjee, 2007; McLaughlin et al.,

1994b). Most studies report increased binding of Cd with soil colloids at increased soil pH, leading to less accumulation by plants (Kabata-Pendias and Mukherjee, 2007; Loganathan et al., 2003; McLaughlin et al., 1996). However, some studies showed the increased uptake of Cd in plants at high pH even though the Cd concentration was low in soil solution which was attributed to the Zn deficiency in plants (Smolders and McLaughlin, 1996). Soil salinity increased the CdCl^- species activity in soil and therefore increased the Cd concentration in Wheat (*Triticum aestivum* cv. Halberd) and Swiss chard (*Beta vulgaris* cv. Foodhook Giant) (Weggler-Beaton et al., 2000) (Ghallab and Usman, 2007; Smolders and McLaughlin, 1996). Many authors reported that the elevated Cd in soil was associated with increased Cd concentration in plants (Dziubanek et al., 2015; Fekete et al., 2001; Krauss and Diez, 1997; Maclean, 1976; McLaughlin et al., 1997; Pérez and Anderson, 2009; Rai et al., 2015; Weggler-Beaton et al., 2000). Increased CEC, clay, Fe and Mn oxides and aeration were reported decreasing the uptake of Cd by plants whereas decreased Zn increased Cd uptake. Increased CEC, clay, Fe and Mn oxides and aeration were observed decreasing the uptake of Cd by plants whereas decreased Zn increased Cd uptake. Depending on environmental conditions, macronutrients may either increase or decrease the Cd uptake by plants (Adriano, 2001; Kabata-Pendias and Mukherjee, 2007).

Many authors reported that organic matter reduces Cd uptake by plants (Basta et al., 2001; Bjerre and Schierup, 1985; Bolan et al., 2003a; Chen et al., 2000; Lee et al., 2004; Li et al., 2001) through Cd sorption leading to less available Cd in soil solution (Lee et al., 2004; Simmler et al., 2013; Vaca-Paulin et al., 2006). Compost made from mixtures of food waste, lawn clippings and tree pruning's and composts from sawdust and animal offals effectively reduced solution Cd in batch sorption experiment and Cd-uptake by onion, spinach and lettuce by up to 60% (Al Mamun et al., 2016). Al Mamun et al. (2016) attributed the reduction in plant-Cd uptake is due to the decrease in the dissolved Cd in soil solution. Shuman et al. (2002)

reported that larger surface area of humified organic matter adsorb significant amount of Cd from soil solution making the Cd less available to Corn (*Zea mays L.*). The Cd uptake reduction in plants in the incubated soils may be due to the higher humification of organic matter as has been observed by (Tapia et al., 2010).

Karaca (2004) showed, using a six-month incubation experiment at 25 °C, that soils amended with mushroom compost and grape mark added at 2%, 4%, and 8% retained their ability to bind Cd for at least six months. Lee et al. (2004) reported that the reduction in DTPA-extractable Cd resulting from hog-manure application also persisted for at least six months. Neither of these studies measured the temporal release of Cd from the incubated soil.

We hypothesize that the sorbed Cd in composts will be released into soil solution as the compost decomposes. Depending on environmental conditions, compost manufactures recommend that compost be added every 2-3 years to maintain the soil's organic matter content (Ouattara et al., 2007). Therefore, most Cd that is bound to the compost is likely to be released over this timeframe.

We aimed to determine the temporal changes in extractable Cd in two soils amended with composts of different provenances under contrasting incubation regimes over one year. We also sought to measure the transfer of Cd from soil to potato in a pot trial using freshly amended compost and a compost-amended soil aged for one year.

5.3 Materials and Methods

5.3.1 Soil sample collection

We used two distinct soils from market gardens in New Zealand, namely Pukekohe (37°13'18.92"S 174°52'5.94"E) and Levin (40°38'17.49"S 175°14'23.61"E) in the North Island of New Zealand. Ploughed soils were collected from within the plough zone (top 0.25 m) and were dried, ground, passed through a 7 mm sieve, and homogenised. The particle size analysis of Levin soil and Pukekohe soil were conducted following the method of Bouyoucos (1962). In Levin soil there were 10% sand, 70% silt and 20% clay and in Pukekohe soil, there were 15% sand, 60% silt and 25% clay.

One year before the experiment, the soils were spiked with Cd to increase their Cd concentration by 1 mg / kg. A solution containing 100 mg/L Cd (as the sulphate) was mixed with the soil using a concrete mixer. Spiking the compost increased contamination of soils (currently, Cd loading in cultivated soils continues to increase) enabling the accurate quantification of Cd after extractions. Prior to spiking, the Pukekohe soil had Cd concentration of 1.45 mg / kg soil and Levin soil had a Cd concentration of 0.47 mg/kg. After Cd spiking the Pukekohe soil and Levin soil had a Cd concentration of 2.08 (\pm 0.09) mg / kg and 0.99 (\pm 0.05) mg / kg, respectively. After spiking, the moist soils were stored for one year to allow the added Cd to equilibrate. Table 5.1 and Table 5.2 show the chemical and physical properties of the soils.

Table 5.1 Properties and macronutrient concentrations (total) of the materials used in the experiments

Properties	Municipal compost (Living Earth compost)	Sawdust compost (Parkhouse compost)	Pukekohe soil	Levin soil
pH (H ₂ O)	7.4	7.0	6.0	6.5
CEC (Cmolc/kg)	45 (0)	47 (0)	22*	15*
C (%)	21	21	2.1*	1.2*
N (%)	2.3	1.6	0.23*	0.13
P (mg/kg)	4178 (37)	5159 (227)	3414 (26)	2247 (20)
S (mg/kg)	2644 (27)	3610 (70)	491 (6)	296 (1)
Ca (mg/kg)	24903 (588)	37416 (1456)	4147 (117)	7008 (99)
Mg (mg/kg)	4177 (16)	2186 (34)	2400 (95)	2873 (43)
K (mg/kg)	14938 (33)	5412 (67)	1951 (59)	2242 (54)

* data from Hill Laboratories, NZ. Standard errors are given in brackets (n=3).

Table 5.2 Trace element (total) concentrations (mg/kg) of the materials used in these experiments (Al Mamun et al., 2016). Standard errors are given in brackets (n=3)

Properties	Living Earth Compost	Parkhouse compost	Pukekohe soil	Levin soil
B ⁺	20*	<1	33 (0)	9 (0)
Cd	0.70 (0.10)	0.45 (0.10)	1.5 (0.03)	0.47 (0.01)
Cu	59 (1)	25 (1)	65 (1)	20 (0.2)
Zn	310 (11)	34 (2)	173 (1)	67 (1)
Cr	28 (1)	37 (1)	40 (2)	15 (0.3)
Ni	9.3 (1)	5.2 (0.1)	25 (1)	7.4 (0.5)

* data from Hill Laboratories, NZ.

5.3.2 Collection of composts

We collected municipal compost from Living Earth Ltd. (Christchurch branch, NZ). The source materials for this compost are mostly lawn clippings, tree prunings and food waste. Hereafter, this compost will be referred to as municipal compost.

A compost manufactured from sawdust and animal residues (manure and carcasses) was obtained from Parkhouse Garden Supplies (Christchurch, New Zealand). Hereafter, this compost will be referred to as sawdust compost.

5.3.3 Incubation experiment

Municipal compost and Sawdust compost were mixed with soils at a rate of 2.5% w/w (20 gram of composts was added with 800-gram soil and each soil and compost mixture was mixed manually in two buckets transferring them from one to another more than 10 times). The 2.5% value corresponds to a rate of 50 t / ha (2000 t/ha furrow slice, considering soil depth 15 cm and bulk density 1.3 gm/cm³) and this rate was used by other authors (Horrocks et al., 2016). There was also a control treatment where no compost was applied. There were three replicates for each treatment. At the start of the experiment, 800 grams of soil or/and soil-compost mixture were introduced into plastic 2 liter boxes.

The experiment was started on 11th March 2014. Urea (NH₂CONH₂) was applied in T2 experimental units (Table 5.3) at the start of the experiment, after 4 weeks and 31 weeks as a source of N for microorganisms to enhance the microbial activity in soils. Urea used in this experiment was from LabServ™, analytical grade, Biolab (Aust) Ltd. A total of 413 mg of urea (dissolved in 10 mL of water) was added to the N treatments in the three separate applications. The rate of N addition is equivalent to 200 kg/ha, assuming a soil depth of 0.15m and a dry bulk density of 1.3 g/cm³. The treatment layout is given in (Table 5.3).

Table 5.3 Treatment layout

No.	Treatment (compost)
1	Levin soil control (no compost)
2	Levin soil + 2.5% municipal compost
3	Levin soil + 2.5% sawdust compost
4	Pukekohe soil control (no compost)
5	Pukekohe soil + 2.5% municipal compost
6	Pukekohe soil + 2.5% sawdust compost
T0= treatments 1-6 with no added Urea-N, incubated at 19°C	
T1= treatments 1-6 with no added Urea-N, incubated at 30°C	
T2= treatments 1-6 with added Urea-N and incubated at 30°C	

The soils and soil mixtures in the boxes were mixed with a glass rod twice a week (on days 4 and 7 of each week). We added deionized water to maintain the boxes at a constant weight by providing 25% moisture content of the oven dry weight of the soils. Sampling occurred after 1, 5, 9, 13, 21, 31 and 49 weeks. At each sampling, 40 g soil or compost-amended soil was collected from each box.

Samples were dried in an oven at 70°C temperature for 5 days until a constant weight was obtained. The dried samples were passed through a 2 mm Nylon sieve and the pH, %C, %N and extractable Cd were determined as described below.

5.3.4 Pot trial

Unspiked Pukekohe soil was mixed with the municipal compost using a concrete mixer to give 2.7% (w/w) compost (henceforth 2.5% compost). Unamended and amended soils were transferred into 5kg plastic pots. There was a total of 12 pots (six for freshly compost amended soils and control and 6 for the compost amended aged soil and control, including replications).

The pots were placed in a randomised block design in the Plant Growth Unit at Lincoln University. Seed potato (*Solanum tuberosum*) '**Nadine**' variety, was obtained from Morton and Smith DWE, Halswell. Seed potatoes were sprouted in moist trays covered with black polythene. After one week, the potatoes were transferred to the pots and grown for nine weeks

whereupon the tubers had formed and the shoots were showing signs of chlorosis. The tubers were gently removed from the soil to avoid scratching and hence soil contamination. Tubers were washed thrice with tap water. Excess moisture was removed using a paper towel. The fresh weight of potato tuber was taken. The tubers were washed thrice with reverse osmosis water and thrice with deionized water. The peel (1-2 mm) was separated with a clean stainless steel knife. Peeled tubers were placed in paper bags and dried in an oven at 70°C until a constant weight was obtained. The dry weights were taken and the tubers were ground using a Retch ZM200 grinder and stored in sealed plastic vials.

5.3.5 pH

The pH was measured by adding 25 ml of deionized water to 10.0 g soil (1:2.5) (Blakemore et al., 1987). The samples were then shaken for 5 minutes and then allowed to stand for 24 hours before being measured. The pH meter (Mettler Toledo, Netherlands) was calibrated after every 9 samples to avoid a drift.

5.3.6 Extractable Cd

The 0.05 M $\text{Ca}(\text{NO}_3)_2$ extractable Cd was used to estimate Cd phytoavailability as several authors have reported good correlations between the extract and plant uptake (Black et al., 2012; Gray et al., 1999b; Gray et al., 1999c). We prepared a 0.05 M $\text{Ca}(\text{NO}_3)_2$ solution using $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$, BDH AnalaR salt crystals according to Black et al. (2012). Five grams of soil sample was taken in a 50 mL centrifuge tube. The mixture was agitated using a vortex mixer for 3 minutes, shaken on an end-over-end shaker for two hours, and centrifuged at 3000 rpm (Hettich Universal 30 RF) for 10 minutes. The supernatant was filtered through a Whatman no. 52 filter paper in to 30 mL vials and analysed using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer) (Blakemore, 1987).

Total C and N were analysed in soil and compost samples using an Elementar Vario-Max CN Elementar analyser (Elementar ®, Germany). Pseudo-total elemental analyses of soil and plant samples were carried out using microwave digestion in 8 mL of Aristar™ nitric acid ($\pm 69\%$), diluted with milliQ water to a volume of 25 mL and filtered using Whatman no. 52 filter paper (pore size 7 μm), and concentrations of B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mo, Mn, Na, P, S, and Zn were determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES Varian 720 ES – USA) for plants (Gray et al., 1999a).

The Reference materials (soil and plant material (International Soil analytical Exchange – ISE 921 and International Plant analytical Exchange IPE 100)) were acquired from Wageningen University, the Netherlands, which were analysed for the quality assurance. Recoverable concentrations of the CRM (WEPAL) were within 74% - 114% of the certified values.

The data was analysed using Minitab® 17 (Minitab Inc, State College, Pennsylvania, USA) and Microsoft Excel 2013. The level of significance was 0.05. We used percentage (%), standard error, a correlation analysis and ANOVA with a post-hoc Fisher's test in the incubation section to determine the changes in extractable Cd and other elements in treated soils compared to control soils with time. We used ANOVA with a post-hoc Fisher's test and standard error to determine the changes in Cd and other elements concentration in potato grown in control soils, freshly compost amended soils and compost amended aged soils.

5.4 Results

5.4.1 Changes in total C with time

The addition of municipal compost and sawdust compost at 2.5% w/w increased the total C concentration in the Levin soil and Pukekohe soil by 0.65 and 0.75 percentage points respectively (Figure 5.1). The total C in soil and soil / compost mixtures was lower in all treatments (control, municipal compost and sawdust compost) in week 49 compared to week 1

in both the Levin and Pukekohe soils (Figure 5.1(A-F)). In general, the magnitude of decrease followed the order $T0 < T1 < T2$, indicating that the degradation of the organic matter was more rapid at higher temperatures and with added nitrogen. Some treatments had a small but significant increase in total C during weeks 5-13 (Figure 5.1 and Table SI 5.12), which is consistent with the rapid degradation of low-carbon moieties in the composts, such as carbohydrates and low-molecular weight carboxylic acids.

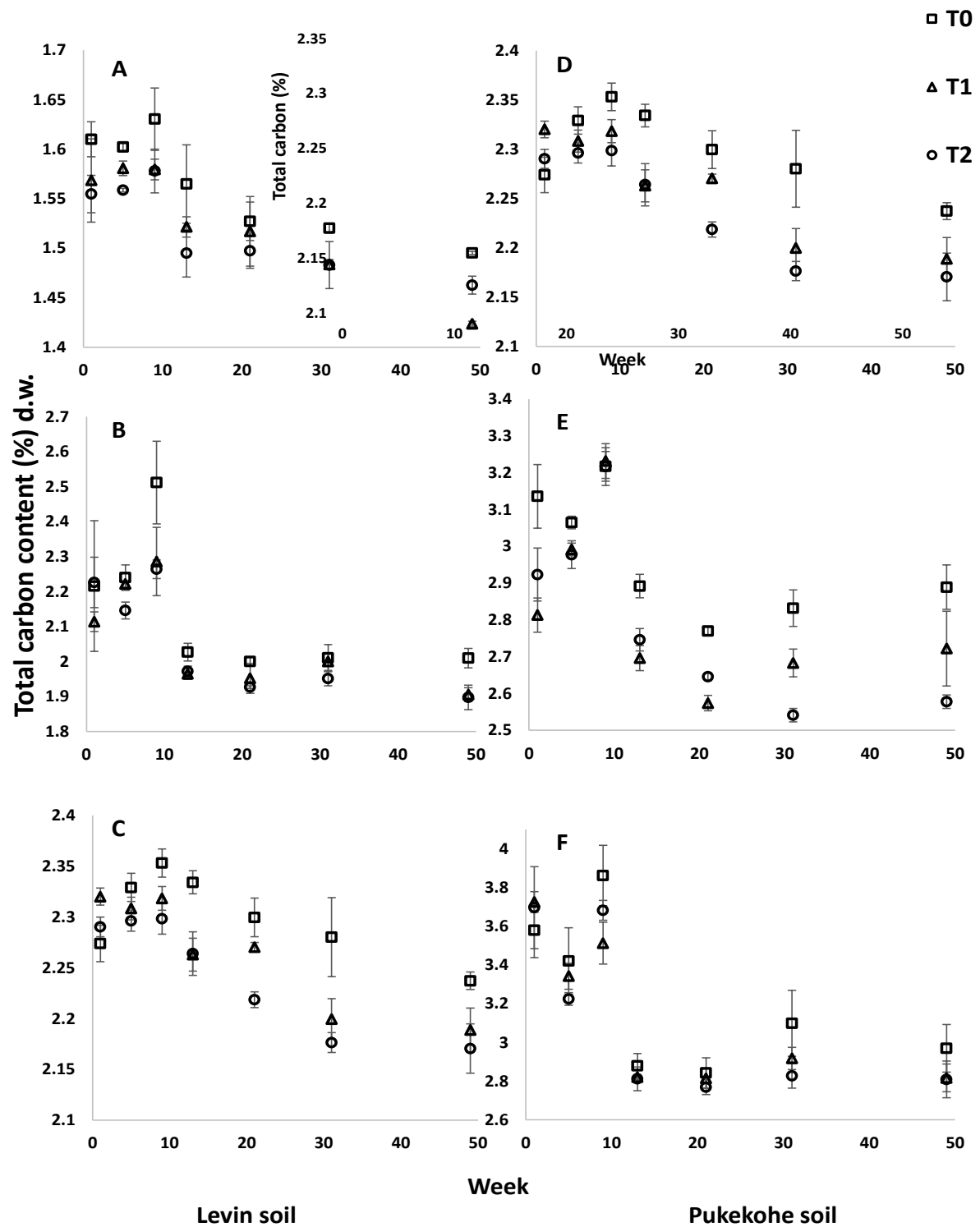


Figure 5.1 (A-F). Changes of total C in soils with time (week) at T0, T1 and T2 conditions (A. Levin soil control soil, B. Levin soil municipal compost applied, C. Levin soil sawdust compost applied, D. Pukekohe soil control, E. Pukekohe soil municipal compost applied, F. Pukekohe soil sawdust compost applied).

5.4.2 Effect of composts on extractable Cd and other elements

The application of both the municipal compost and sawdust compost in Levin soil and Pukekohe soil decreased the concentration of extractable Cd in soils compared to the control (no compost added) soils throughout the experiment (Figure 5.2 and Table 5.2). Comparing week one with week 49, the magnitude of extractable Cd reduction in the compost treatments relative to the controls was either unchanged or greater after 49 weeks (Table 5.4). The reduction in extractable Cd in the compost treated soils compared to controls occurred for all incubation treatments (T0, T1, & T2) except sawdust treated soils sampled at week 9 which may be due to unwanted handling error of the sample. The extractable Cd as a percentage of control ranged from 10% to 89% for all the soils / mixtures except a single outlying measurement in the Levin soil at week 5. The extractable Cd in the controls also decreased during the experimental period in all treatments (Table SI 5.13).

In contrast to Cd, the composts had little effect on the extractable Cu, Mg, Mn and P, while there were significant increases in extractable K, Na, and S (Table SI 5.3, 5.55, 5.6, 5.7, 5.8, 5.9 and 5.10). Both composts increased the extractable Zn in the Levin soil but not the Pukekohe soil (Table SI 5.11).

Regarding the temporal changes in the $\text{Ca}(\text{NO}_3)_2$ -extractable elements, the concentrations of Cu, K, Mn, Na, P, S, and Zn followed a similar pattern to Cd in that they either remained unchanged or significantly decreased during the experimental period. In contrast, concentrations of Fe significantly increased (Table SI 5.4). Aluminium mostly remained unchanged or significantly increased in the Pukekohe soil (Table SI 5.2). Magnesium remained unchanged throughout the experiment (Table SI 5.6). The urea application to the soils and soil-compost mixtures decreased the pH of soils by ca. 0.4 pH units (Table SI 5.1).

Table 5.4 0.05 M Ca(NO₃)₂ extractable Cd in the compost amended incubated Levin and Pukekohe soils as a % of control (no compost added) soils with time (Week)

Week	Extractable Cd as a % of control treatments (No compost)					
	Municipal compost amended soils			Sawdust compost amended soils		
	T0*	T1*	T2*	T0*	T1*	T2*
Levin soil						
1	66	56	54	56	56	42
5	59	69	56	77	155	73
9	54	56	49	48	47	39
13	10	31	48	13	37	43
21	58	63	58	47	28	57
31	39	67	77	56	53	52
49	58	35	43	60	23	37
Week	Pukekohe soil					
1	52	53	59	46	42	47
5	61	59	56	53	51	51
9	58	64	60	52	48	47
13	87	63	58	53	55	53
21	66	77	68	39	56	48
31	78	57	87	38	58	55
49	57	89	48	63	52	36

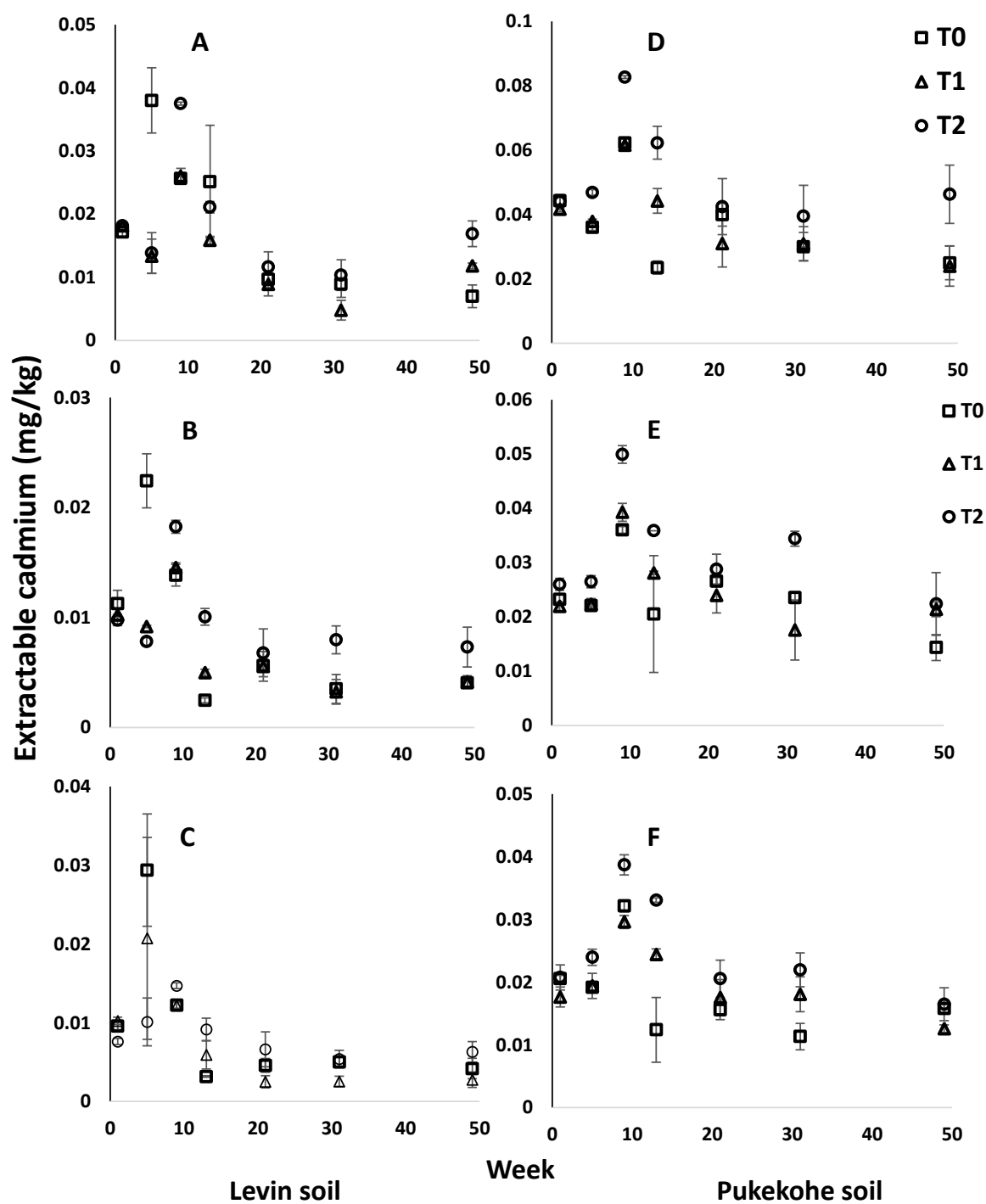


Figure 5.2 (A-F). Extractable Cd (mg/kg) with time (week) at T0, T1 and T2 conditions. Error bars represent the standard error of the mean (n=3). (A. Levin soil control soil, B. Levin soil municipal compost applied, C. Levin soil sawdust compost applied, D. Pukekohe soil control, E. Pukekohe soil municipal compost applied, F. Pukekohe soil sawdust compost applied).

5.4.3 Accumulation of Cd and other elements by Potato grown in incubated soils

Table 5.5 shows that the Cd uptake by potatoes grown in the Pukekohe soil amended with municipal compost was 50% of the control soils for both the freshly-amended soil and the amended soil that had been incubated for one year. The concentration of Cd in the peeled potato tubers ranged from 0.011- 0.044 mg/kg dry weight (d.w.), which was well below food safety standards for potato of 0.1 mg/kg f.w., equivalent to (0.002-0.008 mg/kg fresh weight).

Comparing the concentration of other (except Cd) elements in potatoes grown in freshly compost amended soils and aged compost amended soils with the control soils, there was a significant decrease in Mn concentration in compost amended aged soils compared to controls and freshly amended soils. The concentration of Mo increased in both the compost treated soils compared to control soils. No significant changes observed in the concentration of Cu and Zn.

Table 5.5 Elemental concentrations (mg/kg) in the peeled tubers grown in freshly amended compost treated soil and compost amended soil aged for 1 year, and total % C and extractable Cd in soils

Treatments	Cd	Extractable Cd in soil	Total % C in soil	B*	Ca	Cu*	Fe	K	Mg*	Mn	Mo	Na	P*	S	Zn*
Freshly amended compost															
Control	0.04 (0.003) ^A	0.011 (0.003) ^A	2.29 (0.02) ^C	7.40 (0.04) ^A	419 (65) ^A	6.1 (0.3)	23 (2) ^A	20811 (424) ^A	1268 (72) ^B	6.7 (0.7) ^A	0.6 (0.05) ^B	87 (16) ^B	3356 (179) ^{AB}	1248 (71) ^{BC}	20 (2)
Municipal compost	0.02 (0.011) ^B	0.002 (0.000) ^B	3.0 (0.01) ^A	7.33 (0.3) ^A	289 (15) ^B	6.4 (0.4)	21 (0.2) ^{AB}	21565 (705) ^A	1253 (39) ^B	6.7 (0.2) ^A	1.4 (0.2) ^A	153 (1) ^A	3245 (60) ^B	1214 (37) ^B	19 (1)
Compost amended soil aged for 1 year															
Control	0.02 (0.001) ^B	ND	2.0 (0.01) ^D	5 (0.5) ^B	247 (11) ^B	5.7 (0.5)	19 (1) ^{AB}	21833 (408) ^A	1465 (46) ^A	6.2 (0.3) ^A	0.8 (0.2) ^B	75 (8) ^B	3521 (106) ^A	1606 (68) ^A	17 (0.3)
Municipal compost	0.01 (0.001) ^C	ND	2.4 (0.01) ^B	6 (0.2) ^B	357 (40) ^{AB}	5.5 (0.1)	18 (1) ^B	20256 (544) ^B	1244 (103) ^B	4.8 (0.4) ^B	1.5 (0.1) ^A	163 (19) ^A	3351 (26) ^{AB}	1336 (84) ^{BC}	16 (0.5)
ND-Not done, * No significant difference															

5.5 Discussion

There was a decrease in the C-content of all the soils and soil-compost mixtures. This indicates that soil organic matter is being oxidised. The greater decrease at higher temperature and with added N was expected due to the likely increase of microbial activity (not measured) under these conditions. The decrease in organic matter would likely reduce the number of binding sites for cations on the soil colloids as the CEC of compost and soil organic matter is 50 Cmolc/kg compared to other components of the soil (<5 Cmolc/kg), except clay depending on pH (Helling et al., 1964). Unfortunately, the CEC of the soils at the conclusion of the experiment was not measured.

Helling et al. (1964) have shown that decreasing SOM leads to a decrease in CEC, which results in increased solubility of cations. Our finding that the solubility of Cd and other elements either remained unchanged or even decreased during the experiment was unexpected and falsifies our hypothesis that the degradation of SOM will lead to increased Cd solubility.

Our results indicate that the decreases in extractable elements over time are not the result of increased CEC, because the concentrations of extractable P and S, which occur as anions in soils (Brady and Weil, 2013), also decreased. Moreover, there were significant increases in extractable Fe (Lavado et al., 1999) and Al, which are usually cations at this pH (Brady and Weil, 2013). Potentially, the significant decrease in extractable Cd, Cu, K, Na, P, S, and Zn may have been due to occlusion on the soil colloids by Fe and Al plaques. This may, in part, be an artefact of the experimental conditions. The regular mechanical disturbance of the moist soils will have disrupted soil aggregates (Bissonnais, 1996; Brady and Weil, 2013; Watts et al., 1996) leading to increased surface area and higher concentrations of colloidal Fe and Al (Lavado et al., 1999) that may have occluded surface-bound elements. This same process may occur following repeated ploughing. The role of ploughing on the solubility and phytoavailability of elements in soil has been studied by Lavado et al. (1999), Düring et al.

(2002) and Düring et al. (2003). Lavado et al. (1999) observed in a field trial that the DTPA extractable Cd were not changed due to the mechanical disturbances whereas Düring et al. (2002) Observed that the EDTA extractable Cd decreased due to the mechanical disturbance in soils in laboratory trials although Düring et al. (2003) in the field condition, soils with no mechanical disturbance had less soluble Cd and less Cd uptake by plants than mechanically disturbed soils.

The extractable Fe and Al moieties would have interacted with the organic matter present. Several authors (Baldock and Skjemstad, 2000; Deng and Dixon, 2002; Huang et al., 2005) have reported that SOM can be stabilised by interacting with clay minerals and oxides.

Urea application in soil has generally decreased the pH of soils (Table SI 5.1) which is consistent with Maier et al. (1996) who observed, in a glass house experiment, that the application of urea in soil decreased soil pH. The pH decrease in urea-N treated soils is suggested to be the release of NO_3^- from urea that caused the pH decrease that has been reported by Heilman (1975) and Bouman et al. (1995).

The uptake of elements into potato tubers reflected the results from the extractions both in terms of the reduction in Cd when compost was added and the reduction over time for both the controls and the compost amended soils. In both the pot trial and the incubation experiment, there was increased mechanical disturbance in the aged compost, which may have led to high concentrations of extractable Fe (Lavado et al., 1999) and Al.

Contrary to our initial hypothesis, our results indicate that, in two contrasting soil types, the degradation of SOM is not accompanied by an increase in extractable Cd or plant-available Cd as measured in the pot trial. Were our results indicative of the field situation, then a single application of compost is likely to reduce crop Cd uptake for several years because in our one-year experiment, the degradation of the incubated, mechanically disturbed and N-augmented soils was likely to have been higher than what would occur in the field. However, the mechanic

disturbance in our system may have resulted in increased occlusion of Cd, thereby artificially reducing the extractable and plant-available Cd concentrations.

5.6 Conclusion

In artificially incubated soils, extractable Cd concentrations and plant uptake of Cd remained either unchanged or decreased over a one-year incubation period, despite significant decreases in soil C. Part of the effect is likely due to the experimental conditions, which included regular mechanical disturbance, potentially occluding Cd and other elements attached to the surfaces of soil colloids. If these results are translatable to the field, then it is likely that the beneficial effect of compost addition will last for several years before reapplication is required. Future work should focus on the role of mechanical disturbance on Cd phytoavailability using field trials to confirm the longevity of compost-bound Cd in agricultural soils.

Table SI 5.1 pH with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	pH																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	6.6	0.01	6.6	0.01	6.6	0.01	6.5	0.01	6.5	0.01	6.5	0.03	6.7	0.01	6.4	0.01	6.3	0.02
5	6.7	0.00	6.7	0.02	6.6	0.01	6.7	0.01	6.8	0.00	6.7	0.03	6.7	0.03	6.6	0.02	6.6	0.02
9	6.4	0.00	6.5	0.02	6.2	0.01	6.5	0.01	6.5	0.01	6.2	0.01	6.4	0.03	6.7	0.01	6.7	0.01
13	6.5	0.00	6.4	0.01	6.1	0.01	6.5	0.00	6.5	0.00	6.1	0.01	6.5	0.00	6.5	0.01	6.1	0.02
21	6.5	0.02	6.5	0.01	6.2	0.03	6.6	0.02	6.5	0.02	6.4	0.07	6.5	0.03	6.4	0.02	6.1	0.03
31	6.6	0.01	6.5	0.03	6.3	0.01	6.6	0.01	6.5	0.01	6.4	0.01	6.6	0.02	6.5	0.02	6.2	0.02
49	6.6	0.01	6.5	0.01	6.2	0.01	6.6	0.02	6.5	0.02	6.2	0.01	6.6	0.01	6.5	0.02	6.3	0.02
Pukekohe soil																		
1	6.4	0.02	6.4	0.02	6.4	0.00	6.5	0.02	6.5	0.01	6.5	0.02	6.2	0.06	6.1	0.04	6.0	0.04
5	6.4	0.01	6.4	0.04	6.3	0.02	6.5	0.02	6.4	0.03	6.4	0.03	6.5	0.04	6.4	0.03	6.4	0.02
9	6.2	0.01	5.9	0.01	5.8	0.01	6.2	0.01	6.0	0.02	5.8	0.01	6.2	0.04	5.9	0.02	5.7	0.02
13	5.9	0.01	5.9	0.01	5.8	0.05	6.1	0.01	6.0	0.01	5.7	0.02	6.0	0.02	5.9	0.02	5.6	0.02
21	5.9	0.02	5.9	0.02	5.7	0.03	6.0	0.02	6.0	0.02	5.7	0.02	5.9	0.02	5.9	0.01	5.7	0.02
31	6.0	0.00	5.9	0.01	5.7	0.01	6.1	0.01	5.9	0.00	5.8	0.01	6.0	0.02	5.9	0.03	5.7	0.01
49	6.0	0.02	5.9	0.03	5.6	0.02	6.1	0.01	5.9	0.00	5.7	0.03	6.0	0.01	5.9	0.02	5.6	0.01

*no significant difference

Table SI 5.2 Extractable Al (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable Al (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	0.4	0.007	0.4	0.012	0.4	0.003	0.5	0.022	0.5	0.015	0.5	0.015	0.4	0.016	0.5	0.012	0.4	0.009
5	0.3	0.004	0.3	0.018	0.3	0.014	0.3	0.005	0.3	0.026	0.4	0.019	0.3	0.011	0.3	0.024	0.4	0.019
9	0.2	0.006	0.3	0.004	0.3	0.010	0.2	0.011	0.2	0.006	0.3	0.006	0.2	0.002	0.3	0.010	0.3	0.038
13	0.8	0.131	1.5	0.464	1.2	0.088	1.4	0.059	1.4	0.182	1.4	0.199	1.4	0.059	1.4	0.159	1.3	0.209
21	1.1	0.413	0.5	0.009	0.4	0.020	0.5	0.028	0.7	0.028	0.9	0.299	0.7	0.190	0.4	0.079	0.9	0.072
31	1.2	0.174	0.8	0.059	1.3	0.274	2.0	0.235	1.4	0.427	0.8	0.278	1.6	0.167	1.1	0.139	1.4	0.177
49	0.4	0.058	0.7	0.043	0.6	0.089	0.5	0.055	0.5	0.060	0.6	0.030	0.4	0.092	0.7	0.182	0.7	0.105
Pukekohe soil																		
1	0.4	0.022	0.4	0.021	0.4	0.030	0.5	0.043	0.4	0.029	0.5	0.030	0.5	0.052	0.5	0.036	0.6	0.050
5	0.3	0.021	0.4	0.011	0.4	0.013	0.4	0.026	0.4	0.021	0.7	0.237	0.5	0.029	0.5	0.017	0.5	0.028
9	0.2	0.022	0.2	0.004	0.3	0.022	0.2	0.058	0.3	0.033	0.2	0.040	0.3	0.011	0.3	0.012	0.4	0.015
13	0.9	0.166	0.9	0.129	1.1	0.058	0.8	0.109	1.7	0.172	1.5	0.200	1.2	0.261	1.3	0.215	1.6	0.273
21	0.8	0.157	0.7	0.074	1.0	0.224	0.7	0.312	0.7	0.078	1.7	0.404	1.3	0.296	1.1	0.210	0.9	0.147
31	1.4	0.469	1.1	0.207	1.2	0.255	2.3	0.393	1.1	0.166	1.2	0.271	1.7	0.208	1.4	0.193	1.2	0.340
49	0.9	0.283	1.3	0.469	0.8	0.085	1.0	0.321	0.8	0.029	1.2	0.096	0.8	0.117	0.8	0.152	0.8	0.069

*no significant difference

Table SI 5.3 Extractable Cu (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable Cu (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	0.2	0.012	0.2	0.006	0.2	0.010	0.2	0.025	0.2	0.011	0.2	0.004	0.2	0.035	0.2	0.008	0.2	0.007
5	0.1	0.001	0.1	0.003	0.1	0.000	0.1	0.004	0.1	0.003	0.1	0.003	0.1	0.004	0.1	0.005	0.1	0.006
9	0.1	0.002	0.1	0.001	0.1	0.002	0.1	0.006	0.1	0.001	0.1	0.003	0.1	0.003	0.1	0.005	0.1	0.002
13	0.1	0.003	0.1	0.001	0.1	0.005	0.1	0.012	0.1	0.001	0.1	0.002	0.1	0.012	0.1	0.002	0.1	0.005
21	0.1	0.008	0.1	0.015	0.1	0.012	0.1	0.000	0.1	0.009	0.1	0.009	0.1	0.010	0.1	0.014	0.1	0.014
31	0.1	0.006	0.0	0.011	0.1	0.008	0.1	0.003	0.0	0.003	0.0	0.011	0.1	0.011	0.0	0.009	0.0	0.013
49	0.1	0.004	0.0	0.011	0.1	0.014	0.1	0.012	0.0	0.007	0.1	0.009	0.0	0.013	0.1	0.001	0.1	0.005
Pukekohe soil																		
1	0.2	0.008	0.1	0.007	0.2	0.006	0.2	0.011	0.2	0.013	0.2	0.003	0.2	0.020	0.1	0.003	0.2	0.014
5	0.1	0.002	0.1	0.003	0.1	0.002	0.1	0.003	0.1	0.006	0.1	0.015	0.1	0.011	0.1	0.006	0.1	0.004
9	0.1	0.001	0.1	0.004	0.1	0.006	0.1	0.005	0.1	0.015	0.1	0.001	0.1	0.006	0.1	0.010	0.1	0.003
13	0.1	0.009	0.1	0.003	0.1	0.003	0.1	0.003	0.1	0.001	0.1	0.001	0.1	0.003	0.1	0.002	0.1	0.009
21	0.1	0.009	0.1	0.009	0.1	0.010	0.1	0.003	0.1	0.007	0.1	0.008	0.1	0.009	0.1	0.010	0.1	0.016
31	0.1	0.002	0.0	0.016	0.1	0.001	0.0	0.007	0.0	0.005	0.1	0.004	0.1	0.007	0.0	0.009	0.1	0.013
49	0.0	0.008	0.1	0.003	0.0	0.015	0.1	0.007	0.0	0.005	0.0	0.007	0.1	0.013	0.0	0.011	0.1	0.012

*no significant difference

Table SI 5.4 Extractable Fe (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable Fe (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	0.2	0.012	0.2	0.006	0.2	0.006	0.2	0.012	0.2	0.004	0.2	0.006	0.2	0.024	0.2	0.007	0.2	0.009
5	0.1	0.002	0.2	0.009	0.2	0.007	0.2	0.005	0.2	0.015	0.2	0.009	0.1	0.003	0.2	0.004	0.2	0.015
9	0.1	0.002	0.1	0.001	0.1	0.008	0.1	0.007	0.1	0.002	0.1	0.002	0.1	0.004	0.1	0.008	0.1	0.010
13	0.4	0.041	0.7	0.235	0.5	0.036	0.6	0.035	0.7	0.087	0.6	0.118	0.6	0.035	0.7	0.116	0.6	0.096
21	0.9	0.153	0.6	0.046	0.5	0.040	0.6	0.013	0.6	0.036	0.7	0.135	0.7	0.085	0.5	0.051	0.6	0.051
31	0.9	0.107	0.7	0.050	1.0	0.122	1.3	0.111	0.9	0.222	0.7	0.144	1.0	0.129	0.7	0.099	0.9	0.064
49	0.6	0.043	0.7	0.045	0.7	0.075	0.6	0.076	0.5	0.050	0.7	0.027	0.5	0.077	0.7	0.062	0.7	0.033
Pukekohe soil																		
1	0.1	0.008	0.1	0.014	0.2	0.008	0.1	0.015	0.2	0.027	0.2	0.005	0.1	0.007	0.1	0.017	0.2	0.018
5	0.1	0.009	0.2	0.010	0.1	0.009	0.1	0.010	0.2	0.012	0.3	0.101	0.2	0.016	0.1	0.010	0.2	0.005
9	0.1	0.003	0.1	0.001	0.1	0.006	0.0	0.005	0.1	0.022	0.1	0.003	0.1	0.004	0.1	0.001	0.1	0.002
13	0.4	0.076	0.4	0.056	0.4	0.020	0.3	0.037	0.6	0.071	0.6	0.098	0.5	0.097	0.5	0.080	0.5	0.097
21	0.7	0.044	0.7	0.036	0.7	0.045	0.6	0.071	0.6	0.049	0.9	0.104	0.8	0.071	0.7	0.050	0.6	0.007
31	0.9	0.145	0.8	0.105	0.9	0.070	1.1	0.136	0.8	0.055	0.8	0.079	1.0	0.081	0.9	0.086	0.8	0.081
49	0.7	0.048	0.9	0.165	0.7	0.059	0.8	0.126	0.6	0.018	0.7	0.056	0.7	0.075	0.6	0.081	0.6	0.032

*no significant difference

Table SI 5.5 Extractable K (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable K (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	324	33	308	10	344	10	217	13	221	6	220	2	182	3	180	3	179	1
5	276	2	268	2	269	3	204	0	201	2	209	2	180	2	176	1	180	1
9	303	1	297	1	263	34	195	2	223	0	224	4	246	3	229	33	191	1
13	327	4	325	2	332	7	194	8	227	3	232	6	194	8	189	3	202	3
21	251	22	282	46	235	43	219	6	185	30	131	15	169	17	174	27	133	28
31	258	36	249	51	283	32	242	1	149	12	182	40	169	31	107	23	137	35
49	278	26	254	37	277	57	183	40	134	23	210	28	133	32	196	2	188	12
Week	Pukekohe soil (mg/kg)																	
1	460	16	419	9	396	5	330	2	335	4	335	10	281	2	281	1	277	0
5	376	1	380	3	401	2	305	2	309	4	306	7	285	3	284	1	303	2
9	415	1	412	1	416	2	342	4	334	2	334	2	307	1	308	1	315	1
13	473	2	478	4	481	1	390	2	384	4	395	1	352	3	349	2	361	2
21	450	12	412	43	396	40	274	24	304	36	269	28	340	20	272	50	268	47
31	452	4	319	71	467	2	216	25	310	33	290	29	276	37	274	38	252	55
49	321	52	436	14	337	61	346	15	245	11	237	33	277	52	242	53	299	52

*no significant difference

Table SI 5.6 Extractable Mg (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable Mg (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	165	4	164	1	166	1	151	3	152	1	153	2	146	1	145	0	143	1
5	172	1	168	2	168	1	161	1	154	1	160	3	146	0	146	0	150	1
9	128	1	126	1	121	5	113	0	120	1	121	2	130	2	113	5	108	2
13	262	2	267	3	287	6	216	6	241	3	261	6	216	6	224	6	244	2
21	170	12	183	20	170	19	173	5	160	15	142	11	154	13	167	19	143	23
31	166	16	167	20	195	12	179	1	138	8	163	24	159	21	115	19	147	25
49	185	9	171	15	190	26	156	25	129	16	186	13	133	24	177	1	181	5
Pukekohe soil																		
Week																		
1	194	1	190	1	187	1	184	1	183	1	181	1	176	1	178	2	175	1
5	191	1	192	1	200	1	184	1	186	1	186	2	176	1	176	1	186	0
9	144	1	149	1	150	1	141	1	143	1	146	1	134	1	137	1	138	0
13	358	3	360	4	379	2	331	1	330	6	342	2	313	4	321	1	335	2
21	240	5	234	20	230	17	182	9	206	16	193	12	216	11	195	23	196	22
31	245	2	200	29	265	1	156	9	212	18	202	13	194	14	194	15	187	26
49	192	22	244	6	206	23	217	9	182	3	176	14	192	23	182	23	213	23

*no significant difference

Table SI 5.7 Extractable Mn (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable Mn (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	5.0	0.132	4.9	0.061	5.4	0.205	5.7	0.298	5.5	0.062	5.9	0.212	5.2	0.049	5.0	0.084	5.1	0.097
5	3.3	0.089	3.2	0.014	3.2	0.083	3.3	0.095	3.4	0.154	3.5	0.087	3.3	0.028	3.4	0.089	3.5	0.127
9	5.0	0.101	5.7	0.033	6.5	0.025	4.6	0.225	5.1	0.236	6.0	0.269	5.3	0.067	5.5	0.428	6.4	0.525
13	3.6	0.018	3.4	0.241	5.0	0.262	3.4	0.240	3.3	0.496	5.2	0.447	3.4	0.240	3.2	0.125	4.9	0.191
21	4.5	0.256	5.1	1.707	6.3	1.187	5.4	0.135	3.8	0.593	4.7	0.664	5.2	0.457	4.2	0.735	6.0	1.113
31	2.5	0.276	1.9	0.330	2.9	0.433	3.5	0.264	2.1	0.179	2.9	0.497	2.5	0.138	1.5	0.291	2.4	0.457
49	1.6	0.122	1.8	0.251	2.6	0.455	1.8	0.406	1.5	0.244	3.1	0.333	1.4	0.310	2.4	0.061	3.1	0.224
Pukekohe soil																		
1	19	1	15	0	17	1	20	1	16	0	19	1	25	4	19	1	23	2
5	11	0	12	0	13	0	11	0	12	0	13	1	13	1	15	0	17	0
9	25	0	21	0	25	0	22	1	20	1	20	1	25	2	21	1	28	1
13	18	0	14	0	18	1	16	1	13	0	20	1	19	1	16	1	22	0
21	38	2	26	3	40	4	27	1	22	2	39	5	44	2	25	4	47	10
31	16	0	11	3	19	0	9	1	13	1	15	1	14	1	14	2	18	4
49	7	1	9	0	10	2	9	0	7	0	10	1	9	2	9	2	15	2

*no significant difference

Table SI 5.8 Extractable Na (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable Na (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	113	13	105	5	120	5	72	5	73	3	73	0	54	1	53	2	56	0
5	108	2	100	4	101	2	71	1	67	2	74	3	55	2	53	1	58	2
9	76	0	73	0	62	11	43	0	52	1	53	2	61	1	51	9	41	1
13	90	1	92	1	90	1	45	1	59	1	65	3	45	1	49	2	48	1
21	57	4	60	9	52	9	42	2	35	5	27	3	30	3	32	5	25	5
31	57	8	55	10	62	7	47	1	30	2	36	7	30	5	21	4	26	7
49	61	5	57	7	64	11	38	7	29	4	45	5	24	5	39	0	39	2
Pukekohe soil																		
1	168	8	145	4	137	4	113	3	113	3	114	4	92	3	88	1	90	2
5	130	1	128	2	136	1	98	2	101	1	99	3	91	2	92	1	98	2
9	96	2	95	1	96	1	81	1	76	1	76	1	69	1	68	1	69	1
13	120	4	111	2	115	2	98	3	97	2	99	1	85	1	89	1	87	1
21	77	2	71	7	68	7	47	4	55	7	47	5	63	5	48	9	46	8
31	90	1	64	13	96	2	46	4	60	6	58	5	54	7	55	4	50	10
49	66	10	86	3	69	11	69	3	52	2	50	7	55	10	50	11	62	10

*no significant difference

Table SI 5.9 Extractable P (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable P (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	7.3	0.2	7.0	0.1	7.4	0.2	7.0	0.4	6.9	0.1	7.0	0.0	6.6	0.0	6.6	0.0	6.6	0.1
5	6.7	0.1	6.8	0.0	6.9	0.1	6.2	0.0	6.4	0.1	6.7	0.0	6.3	0.0	6.6	0.1	6.7	0.1
9	6.1	0.1	6.9	0.0	7.0	0.2	5.8	0.2	6.0	0.1	6.4	0.1	5.6	0.0	6.6	0.3	6.6	0.1
13	6.3	0.0	6.7	0.1	7.2	0.2	5.7	0.1	6.0	0.1	6.8	0.0	5.7	0.1	6.3	0.2	6.7	0.2
21	5.5	0.3	5.3	0.8	5.4	1.0	6.4	0.1	4.7	0.7	4.0	0.5	5.8	0.6	4.8	0.8	4.7	0.9
31	5.3	0.7	5.2	1.0	6.0	0.7	6.5	0.2	4.3	0.4	5.2	1.0	5.1	0.7	3.3	0.7	4.2	0.9
49	5.2	0.4	5.4	0.7	6.2	1.2	4.5	0.9	3.8	0.7	6.3	0.8	3.9	0.8	6.0	0.1	6.2	0.3
Week	Pukekohe soil																	
1	4.0	0.1	3.6	0.0	3.8	0.1	3.8	0.2	3.6	0.0	4.1	0.1	3.6	0.3	3.3	0.1	3.7	0.2
5	3.1	0.0	3.5	0.1	3.5	0.0	3.0	0.0	3.3	0.1	3.3	0.2	2.9	0.0	3.1	0.1	3.1	0.0
9	2.9	0.3	3.1	0.1	3.3	0.0	2.9	0.2	3.0	0.1	3.0	0.3	2.8	0.1	2.7	0.1	2.8	0.1
13	3.1	0.1	3.2	0.1	3.3	0.2	3.1	0.0	3.0	0.1	3.3	0.0	2.8	0.1	2.9	0.1	2.9	0.1
21	3.3	0.2	2.4	0.3	2.5	0.3	2.5	0.2	2.3	0.3	2.0	0.2	3.2	0.2	1.9	0.3	2.1	0.4
31	3.1	0.1	2.0	0.5	3.0	0.0	1.7	0.1	2.4	0.3	2.3	0.2	2.1	0.3	2.0	0.3	1.9	0.4
49	1.9	0.4	2.7	0.1	2.0	0.4	2.6	0.1	1.8	0.1	1.8	0.3	2.0	0.4	1.7	0.4	2.2	0.4

*no significant difference

Table SI 5.10 Extractable S (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable S (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	31.6	3.7	28.1	0.8	32.6	1.6	37.2	3.7	36.4	2.4	39.0	1.9	22.8	0.7	20.8	0.3	21.8	0.4
5	30.1	0.8	31.2	1.3	30.3	0.2	34.6	1.0	37.6	1.6	39.0	1.6	19.3	0.4	21.1	0.6	21.5	0.3
9	22.7	0.2	28.0	0.2	22.5	3.2	14.6	0.6	32.5	0.8	30.8	1.0	31.7	1.2	20.5	2.0	17.2	0.3
13	23.8	0.4	29.3	0.7	29.1	0.3	15.9	0.9	34.1	0.8	35.6	0.6	15.9	0.9	19.9	0.5	18.5	0.4
21	21.8	2.1	26.1	5.1	24.2	4.9	34.2	0.8	29.4	4.7	22.7	2.2	18.7	2.0	17.4	3.4	15.7	3.8
31	20.1	3.1	24.2	5.1	27.2	4.2	32.2	0.7	25.1	2.3	27.8	6.2	12.6	2.0	10.6	3.0	12.1	3.6
49	22.2	2.3	27.7	3.9	29.1	6.7	25.9	6.4	24.9	4.7	37.6	5.0	10.4	3.1	24.9	1.5	19.5	1.4
Week	Pukekohe soil																	
1	60.7	1.7	53.6	0.4	56.5	1.9	68.1	3.3	69.3	2.0	75.6	1.6	54.3	4.8	50.7	1.8	55.7	3.8
5	46.4	0.1	50.6	0.9	50.0	0.3	51.8	0.9	55.2	1.1	55.3	1.5	43.5	1.0	46.6	0.9	46.2	0.1
9	47.3	0.9	45.3	0.4	44.5	0.2	49.1	0.9	49.8	1.0	49.1	0.4	39.2	1.3	36.8	1.0	37.9	0.5
13	45.9	1.0	50.4	0.4	48.4	0.6	51.9	0.9	55.7	0.6	57.5	0.6	40.2	0.8	41.5	0.5	41.2	0.2
21	57.6	1.6	44.1	5.4	46.2	6.2	44.8	3.0	46.3	6.3	42.3	3.9	52.0	2.9	31.3	5.9	35.2	6.8
31	46.2	0.7	34.7	9.2	52.0	0.4	28.6	3.1	48.4	5.9	43.2	4.4	30.7	4.3	32.0	4.8	29.3	6.8
49	30.8	6.0	51.3	2.0	33.8	7.2	48.3	2.5	38.3	2.0	35.0	5.3	30.1	6.3	29.1	7.1	34.5	6.5

*no significant difference

Table SI 5.11 Extractable Zn (mg/kg) with time (week) at T0, T1 and T2 conditions in Levin soil and Pukekohe soil amended with different composts. SE is the standard error of the mean (n=3)

Week	Extractable Zn (mg/kg)																	
	Municipal compost amended soils						Sawdust compost amended soils						No organic matter added soils					
	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE	T0*	SE	T1*	SE	T2*	SE
Levin soil																		
1	0.258	0.01	0.151	0.01	0.178	0.02	0.179	0.04	0.183	0.03	0.099	0.01	0.149	0.03	0.018	0.00	0.165	0.02
5	0.065	0.00	0.069	0.01	0.071	0.00	0.052	0.00	0.064	0.01	0.060	0.00	0.066	0.00	0.013	0.00	0.060	0.01
9	0.066	0.01	0.069	0.00	0.090	0.00	0.061	0.01	0.052	0.01	0.900	0.00	0.012	0.00	0.026	0.00	0.090	0.00
13	0.161	0.05	0.178	0.02	0.305	0.05	0.172	0.05	0.244	0.06	0.143	0.03	0.156	0.02	0.016	0.00	0.272	0.06
21	0.130	0.06	0.150	0.00	0.059	0.00	0.109	0.02	0.100	0.05	0.006	0.00	0.133	0.10	0.009	0.00	0.041	0.03
31	0.277	0.12	0.129	0.03	0.062	0.02	0.254	0.06	0.151	0.06	0.038	0.02	0.050	0.00	0.005	0.00	0.030	0.01
49	0.038	0.01	0.008	0.00	0.010	0.00	0.002	0.00	0.015	0.00	0.060	0.00	0.022	0.01	0.012	0.00	0.026	0.01
Pukekohe soil																		
1	0.31	0.01	0.25	0.01	0.30	0.01	0.32	0.01	0.29	0.05	0.26	0.01	0.37	0.04	0.31	0.02	0.34	0.02
5	0.24	0.00	0.24	0.01	0.30	0.01	0.21	0.01	0.23	0.02	0.27	0.03	0.29	0.03	0.28	0.02	0.32	0.01
9	0.23	0.00	0.29	0.02	0.37	0.01	0.25	0.06	0.24	0.03	0.25	0.03	0.26	0.01	0.26	0.01	0.37	0.00
13	0.56	0.03	0.54	0.02	0.80	0.14	0.44	0.03	0.45	0.01	0.48	0.03	0.49	0.05	0.65	0.07	0.63	0.05
21	0.33	0.03	0.29	0.05	0.54	0.16	0.28	0.06	0.21	0.04	0.29	0.06	0.36	0.01	0.30	0.03	0.31	0.06
31	0.42	0.02	0.26	0.07	0.51	0.04	0.17	0.02	0.32	0.01	0.31	0.04	0.31	0.04	0.34	0.07	0.37	0.05
49	0.17	0.03	0.26	0.01	0.32	0.08	0.20	0.03	0.15	0.02	0.21	0.03	0.19	0.05	0.17	0.05	0.40	0.08

*no significant difference

Table SI 5.12 Fisher's post hoc test of the data (Total C) used in Figure 5.1 (A-F). Same capital letters in the rows are not significantly different. Same small letters in the columns are not significantly different. * no significant difference among T0, T1 and T2

Treatment				Week			
For Figure 1A							
	1*	5	9*	13*	21*	31*	49
T0	A	Aa	A	AB	BC	BC	Ca
T1	A	Ab	A	AB	AB	BC	Cb
T2	A	Ac	A	B	B	B	Bc
For Figure 1B				Week			
	1*	5	9*	13*	21*	31*	49
T0	A	Ba	B	B	B	B	Ba
T1	BC	ABab	A	D	D	CD	Db
T2	AB	Bb	A	C	C	C	Cb
For Figure 1C				Week			
	1*	5*	9	13*	21	31	49
T0	B	BC	Aa	CD	Da	Da	Da
T1	BC	AB	Ab	CD	Db	Dab	Db
T2	AB	B	Aab	C	Cab	Cb	Cab
For Figure 1D				Week			
	1	5*	9	13	21	31	49*
T0	BCb	AB	Aa	ABa	Aba	BCa	C
T1	Aa	AB	Aab	Cb	BCa	Dab	D
T2	Aab	A	Ab	ABb	BCb	CDb	D
For Figure 1E				Week			
	1	5*	9*	13	21	31	49
T0	ABa	B	A	Ca	Ca	Ca	Ca
T1	Cb	B	A	CDb	Dc	CDb	CDab
T2	Bab	B	A	Cb	CDb	Dc	Db
For Figure 1F				Week			
	1*	5*	9*	13*	21*	31*	49*
T0	AB	BC	A	D	D	CD	D
T1	A	B	B	C	C	C	C
T2	A	B	A	C	C	C	C

Table SI 5.13 Fisher's post hoc test of the data (extractable Cd) used in Figure 2 (A-F). Same capital letters in the rows are not significantly different. Same small letters in the columns are not significantly different. * no significant difference among T0, T1 and T2

Treatment				Week						
For Figure 2A				1*	5	9	13	21*	31	49*
T0				BC	Aa	Bb	B	CD	CD	Db
T1				B	CDB	Ab	BC	DE	E	CDab
T2				BC	CDEb	Aa	B	DE	E	BCDa
For Figure 2B				Week						
				1*	5	9	13	21*	31	49*
T0				B	Aa	Bb	Cc	C	Cb	C
T1				B	Bb	Ab	CDB	C	Db	CD
T2				B	Bb	Aa	Ba	B	Ba	B
For Figure 2C				Week						
Treatment				1	5*	9	13	21*	31*	49*
T0				BCa	A	Bb	Cb	BC	BC	BC
T1				ABa	A	ABb	ABab	B	B	B
T2				Bb	AB	Aa	Ba	B	B	B
For Figure 2D				Week						
				1*	5	9	13	21*	31*	49*
T0				B	BCb	Ab	Dc	B	CD	D
T1				B	Bb	Ab	Bb	BC	BC	C
T2				BC	BCa	Aa	Ba	C	C	BC
For Figure 2E				Week						
				1*	5	9	13*	21*	31	49*
T0				AB	Bb	Ab	B	AB	ABab	B
T1				BC	BCb	Ab	B	BC	Cb	BC
T2				D	CDa	Aa	B	BCD	BCa	D
For Figure 2F				Week						
				1*	5*	9	13	21*	31	49*
T0				B	BC	Ab	CDB	BCD	Db	BCD
T1				CD	BC	Ab	ABa	CD	CDab	D
T2				BC	B	Aa	Aa	BC	BCa	C

Chapter 6 Effect of calcite lime on the transfer of Cadmium from soil to vegetables and perennial rye grass

This chapter may, eventually, be submitted for publication. It is intended to show the contrasting effects of lime compared to the organic amendments tested in the previous chapters.

My contribution to the article: I designed and setup the experiments with the help of my co-authors. I collated and interpreted the data and wrote the article in collaboration with my co-authors.

6.1 Abstract

Cadmium (Cd) is a non-essential biological trace element accumulated in agricultural lands through the Cd contaminated phosphate fertilizer application in soils or industrial effluent application in soils. The Cd concentration has been observed to be elevated in many countries throughout the world and some plants were observed having Cd concentration exceeding the food guideline value. Previous research has shown that lime reduced the accumulation of Cd in plants although the opposite was also reported by other scientists. We wanted to observe the effect of lime on the concentration of Cd in lettuce (*Lactuca sativa*), silver beet (*Beta vulgaris* V.), spinach (*Spinacia oleracea* L.) and perennial rye grass (*Lolium perenne* L.). We applied four rates of lime T2 (0.3%), T3 (0.6%), T4 (1.2%) and T5 (2.5%) in soils. There was also a control (T1) treatment. Lime application in soil significantly decreased ($p < 0.05$) the concentration of Cd in silver beet and perennial rye grass by up to 83% whereas no significant difference was observed in the concentration of Cd in spinach due to different rates of lime treatment. Only the T4 treatment in soil increased the concentration of Cd in lettuce whereas

the lower rates of lime had no significant effect. Future work is warranted to elucidate the contrasting effects of lime on the Cd-uptake by various plant species.

6.2 Introduction

Cadmium is a toxic heavy metal that can enter in the food chain directly through plant uptake (Adriano, 2001; Kabata-Pendias and Mukherjee, 2007). The concentration of Cd in some agricultural soils has increased due to the continuous application of Cd containing phosphate fertilizers (Roberts et al., 1994; Taylor, 1997; Williams and David, 1976). In many parts of the world health experts are concerned about the effect of Cd on environmental and human health and its potential impact on international trade (Adriano, 2001). The accumulation of Cd in grazing animals liver and kidneys makes the liver and kidneys unsuitable for human consumption and imperils their use even in pet foods (Roberts et al., 1994). Accumulation of Cd in rice and wheat affected animal and human health following implications in local and international marketing (Nogawa and Kido, 1996). Because of the broader potential negative impact of Cd on human health and economy of a country, there are many studies conducted to reduce the availability of Cd in soil solution therefore reducing the accumulation of Cd in plants. Organic matter (Basta et al., 2001; Bolan et al., 2003a; Chen et al., 2000; Karaca, 2004; Lee et al., 2004; Li et al., 2001; Shuman et al., 2002; Simmler et al., 2013; Tapia et al., 2010), liming material (Table SI 1), and inorganic soil amendments (Chen et al., 2016) have been tried to increase the sorption of Cd in soil leading to less Cd accumulation in plants.

There is a contradictory effect of lime on Cd accumulation in plants. Most studies (Table SI 1) show that addition of lime in soil increases the sorption of Cd in soils reducing the accumulation of Cd in plants whereas Maier et al. (1997) reported that when calcite lime was added in field conditions, liming of the soil did not reduce the concentration of Cd in potato tubers although the pH of soil increased by 2 units than control soils, rather increased the accumulation of Cd

in plants. The increases in Cd accumulation in plants have been attributed to: ineffective mixing of lime throughout the whole root zone, inadequate time of reaction of lime with soil, competitive desorption of Cd^{2+} by Ca^{2+} and low soil moisture inhibiting lime dissolution under field conditions (Maier et al., 1997). In another study, it was observed that liming the soil decreased the phytoavailable and exchangeable Cd in soil but increased the concentration of Cd in plants (Shaheen and Rinklebe, 2015). The increase in Cd uptake may be due to competition between Ca and Cd for the cation exchange sites in soil (Bolan et al., 2003a; Maier et al., 1997) or due to an induced Zn deficiency at high soil pH, which influences the plant to generate additional root Zn transport proteins to gain sufficient soil Zn to check the Zn insufficiency stress (Chaney et al., 2009). As the Zn transport proteins also accrue Cd, so increased Zn transporting protein production by plants may result in even greater Cd accumulation during Zn deficiency stress in plants (Hart et al., 2002). Moreover, because of little soil solution Zn activity, there will be low competition with Cd^{2+} for uptake by the root Zn transporter (Chaney et al., 2009) leading to high accumulation of Cd in plants.

Lime is used in acidic soils to improve plant production through ameliorating the toxic effect of aluminium. In acidic soils, the Cd is more available to plants (phytoavailable), thus liming is used to reduce Cd availability in acidic soils. In soil, lime addition increases negative charge (cation exchange capacity) in variable charge soils and forms strongly bound hydroxyl metal species, enhances precipitation of metals as metal hydroxides and immobilization of metals thorough enhanced microbial activity (Bolan et al., 1999). However, what is not known is whether the effect of different rates of lime on the concentration of Cd in plants is similar for all plants or varies between plants. Keeping all these views in mind we designed an experiment to find out the effect of four rates of calcite lime on accumulation of Cd in some common vegetables in New Zealand and in perennial rye grass (*Lolium Perenne*) from an agricultural soil that had elevated Cd due to continuous application of Cd containing P fertilizers.

6.3 Methods and materials

6.3.1 Soil and lime collection

We collected soils for this experiment from a commercial vegetable growing area in Pukekohe (37°13'18.92"S 174°52'5.94"E) in the North Island of New Zealand. The top 0.25 m soils were collected and brought in to the glasshouse area at Lincoln University, New Zealand. Large stones and roots were removed from the soil. The soils were then air dried, ground and passed through a 7 mm sieve and homogenised. Three 500g sub samples were collected from the bulk soil, ground and passed through a 2mm Nylon mesh. The physical and chemical properties of the soil are given in Table 6.1. I conducted the particle size analysis of Levin soil and Pukekohe soil, following the method of Bouyoucos (1962). In Levin soil there were 10% sand, 70% silt and 20% clay and in Pukekohe soil, there were 15% sand, 60% silt and 25% clay.

This soil had a total concentration of Cd (1.45 mg/kg). We used the lab grade dry lime powder (calcium carbonate, AnalaR NORMAPUR, VWR®, PROLABO®, Belgium) in this experiment.

Table 6.1 Properties of Pukekohe soil (Chapter 1). Standard errors are given in brackets (n=3)

Properties	Pukekohe soil
pH (H ₂ O)	6.0
CEC (Cmolc/kg)	22
C (%)	2.1
N (%)	0.23
P (mg/kg)	3414 (26)
S (mg/kg)	491 (6)
Ca (mg/kg)	4147 (117)
Mg (mg/kg)	2400 (95)
K (mg/kg)	1951 (59)
B (mg/kg)	33 (0)
Cd (mg/kg)	1.5 (0.03)
Cu (mg/kg)	65 (1)
Zn (mg/kg)	173 (1)
Cr (mg/kg)	40 (2)
Ni (mg/kg)	25 (1)

6.3.2 Sample analysis

pH

We determined the pH of the sieved soils in high purity water (18.2 MΩ resistivity; Heal Force® SMART Series, SPW Ultra-pure Water system, Model-PWUV) using a Mettler Toledo pH meter. We added 25 ml of water to 10 grams of air dry soil (soil and water ratio of 1:2.5) from each sample and mixed the mixture well by hand shaking. The mixtures were left to equilibrate for 24 hr before measurement (Blakemore, 1987).

The Cation Exchange Capacity (CEC)

We used 0.01 M Silver Thiourea (AgTU) to measure the CEC of soils (Blakemore, 1987). Then, 35 mL of 0.01 M AgTU was added to 0.70 g of dry sample in a 50 mL centrifuge tube, agitated in an end-over-end shaker for 16 hours, centrifuged at 2000 rpm for 10 minutes and the supernatant was filtered through a Whatman no. 40 filter paper. We analysed the extractants

using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Varian 720 ES - USA). An Elementar Vario-Max CN Elementar analyser (Elementar ®, Germany) were used to measure the total carbon and nitrogen in soil and compost samples.

Elemental composition

Pseudo-total elemental analyses of plants and soils were carried out by means of microwave digestion in AristarTM nitric acid ($\pm 69\%$), diluted with milliQ water to a volume of 25 mL and filtered using Whatman no. 52 filter paper (pore size 7 μm). Inductively coupled plasma optical emission spectrometry (ICP-OES Varian 720 ES – USA) was used to determine the concentrations of B, Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, P, S and Zn in soils (Kovács et al., 2000) and plant samples (Gray et al., 1999a). Reference soil and plant material (International Soil analytical Exchange – ISE 921 and International Plant analytical Exchange IPE 100) from Wageningen University, the Netherlands, were analysed for quality assurance.

Pot trial

A pot experiment was conducted to reveal the effects of different rates of lime on the accumulation of Cd in lettuce, spinach, silver beet and perennial rye grass. Plastic pots of 2 kg size were filled with previously prepared soils (plant debris and big stones were removed). The soils were mixed with different rates (w/w) of lime namely, T1 (control), T2 (0.31%), T3 (0.63%), T4 (1.25%) and T5 (2.5%). The soils were mixed with lime and put in the plastic pots. They were watered daily two times up to field capacity for 2 weeks to allow lime to react with the soils. Then the seeds of lettuce, perennial rye grass, silver beet and spinach were sowed in the pots. Initially for lettuce, spinach and silver beet 3 seeds were sown. After germination, when the size of the seedlings was around 3 cm height, we kept one seedling removing the other two carefully. The plants were allowed to grow for 3 weeks, after which they were harvested. We collected the shoot 2 cm above the soil layer to avoid soil contamination in the plants.

For perennial rye grass we used 15-20 seeds in each pot and allowed those to grow for 3 weeks. Then the perennial rye grass was cut from 2 cm above the soil. The fresh weight of the plants was recorded. The plants were washed three times with tap water, three times with reverse osmosis water and three times with deionized water. Then the plants were placed in an oven for drying at 70°C temperature for 7 days until a constant weight was observed. They were then removed from the oven and plants were ground in a steel grinder. The ground samples were used for the chemical analyses stated above.

Data were analysed using Minitab® 17 (Minitab Inc, State College, Pennsylvania, USA) and Microsoft Excel 2013. The level of significance was 0.05. We used ANOVA with a post-hoc Fisher's test to determine the significant differences in the concentration of metals in plant, pH and extractable Cd in soil due to the addition of different rates of lime.

6.4 Results

6.4.1 Changes in soils due to the addition of lime

Table 6.2 shows that 0.05 M $\text{Ca}(\text{NO}_3)_2$ extractable Cd was decreased significantly ($p < 0.05$) due to the application of lime at 0.3 wt% (T2), 0.6 wt% (T3), 1.3 wt% (T4) and 2.5 wt% (T5) in soils compared to the control soil (T1). The concentration of Cd in the extractants was significantly lower in T3, T4 and T5 rates of lime treated soils than the T2 treatment, indicating that higher rates of lime are more effective in reducing the extractable Cd for this soil.

The T2, T3, T4, and T5 treatments increased soil pH by 0.5, 0.6, 0.7, and 0.8 units, respectively compared to control soil. The extractable concentration of Mg, Mn, Ni and Zn was higher due at higher rates of lime application whereas only the T5 treatment increased the extractable P in soils (Table 6.2).

Table 6.2 Ca(NO₃)₂-extractable metal fraction in rhizosphere soils treated with different lime application rates (T1: 0 wt%, T2: 0.3 wt%, T3: 0.6 wt%, T4: 1.3 wt%, T5: 2.5 wt%). Standard errors are given in brackets. Values with the same letters in columns are not significantly different

Pukekohe	pH	Cd (mg/kg)	Fe* (mg/kg)	P (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Mg (mg/kg)	K (mg/kg)
T1	5.98 ± 0.05 ^d	0.01 ± 0.0 ^a	0.16 ± 0.03	3.11 ± 0.04 ^b	0.15 ± 0.03 ^{ab}	21.75 ± 1.63 ^a	0.28 ± 0.02 ^a	0.088 ± 0.010 ^a	155.97 ± 1.35 ^a	160.63 ± 5.85 ^b
T2	6.37 ± 0.12 ^c	0.003 ± 0.0 ^b	0.12 ± 0.03	2.77 ± 0.02 ^c	0.13 ± 0.01 ^b	10.19 ± 1.88 ^b	0.11 ± 0.03 ^b	0.034 ± 0.010 ^b	153.57 ± 1.33 ^a	185.35 ± 23.88 ^{ab}
T3	6.93 ± 0.17 ^b	0.0001 ± 0.0 ^c	0.16 ± 0.05	2.97 ± 0.14 ^{bc}	0.11 ± 0.01 ^b	2.40 ± 0.85 ^c	0.03 ± 0.01 ^c	0.009 ± 0.003 ^c	143.34 ± 5.31 ^b	210.53 ± 20.76 ^a
T4	7.15 ± 0.03 ^b	0.0006 ± 0.0 ^c	0.15 ± 0.05	3.18 ± 0.19 ^b	0.16 ± 0.04 ^{ab}	1.52 ± 0.35 ^c	0.03 ± 0.01 ^c	0.008 ± 0.003 ^c	137.97 ± 1.47 ^b	219.25 ± 31.96 ^a
T5	7.42 ± 0.01 ^a	0.0006 ± 0.0 ^c	0.17 ± 0.03	3.56 ± 0.24 ^a	0.16 ± 0.03 ^{ab}	0.61 ± 0.03 ^c	0.02 ± 0.01 ^c	0.005 ± 0.003 ^c	127.16 ± 0.42 ^c	217.09 ± 6.58 ^a

*not significant

6.4.2 Concentration of Cd in plants

The concentration of Cd in silver beet ranged from 0.35 to 0.85 mg/kg (d.w.) and significantly differed from control and lime treatments. The T2, T3, T4 and T5 treatments significantly decreased ($p<0.05$) the concentration of Cd in silver beet by 51%, 61%, 70% and 83% respectively (Figure 6.1). In the case of perennial rye grass, the concentration of Cd was lower in lime treated soils compared to control soil. The T2, T3, T4 and T5 lime treatments significantly reduced the concentration of Cd in perennial rye grass by 32%, 58%, 61% and 74% respectively.

In the case of lettuce, there were no significant differences observed in the concentration of Cd among T1 (control), T2, T3 and T5 treatments. The T4 treatment significantly increased the concentration of Cd in lettuce by 77%. Among all the treatments, the Cd and Zn ratio is the highest in T4 treatment in lettuce (Table 6.3).

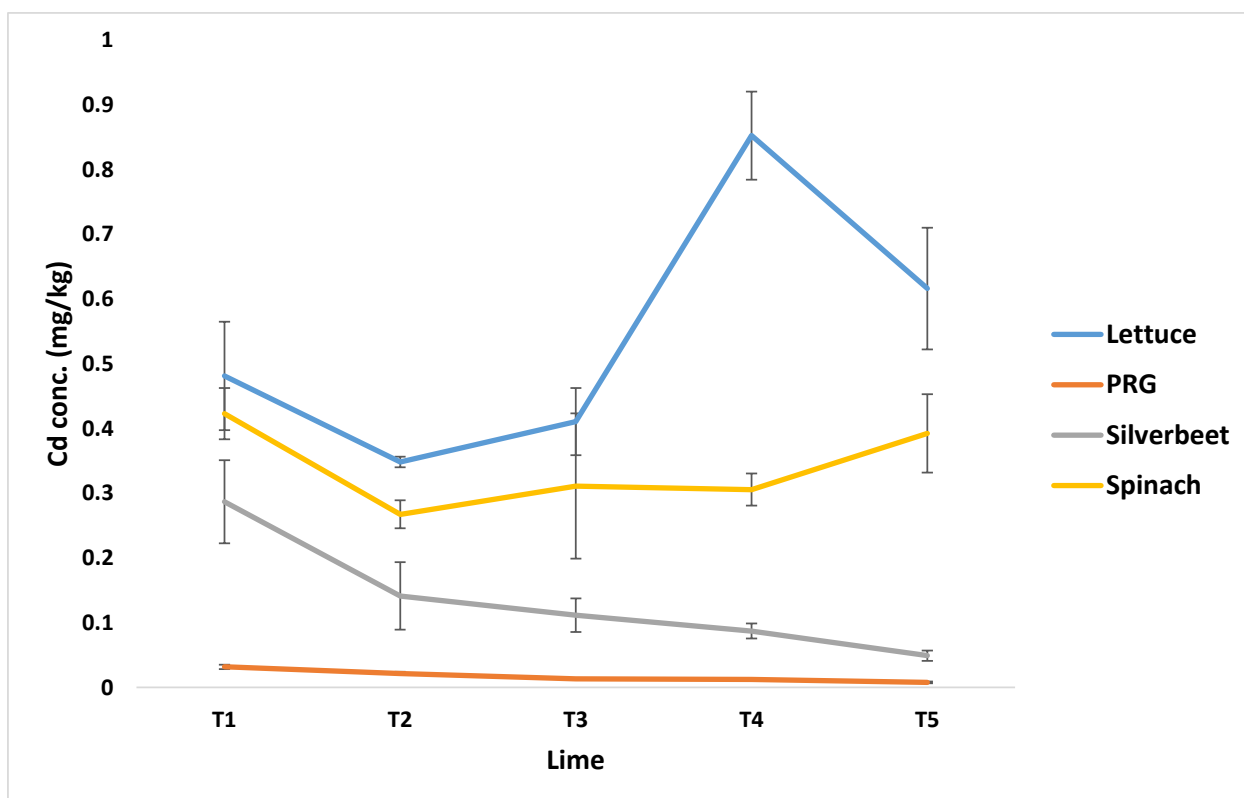


Figure 6.1 Concentration of Cd (mg/kg) in plants (dry weight basis) at different lime treatments. Significant differences are shown in Table 6.2-6.5.

Table 6.3 The Cd:Zn in lettuce, perennial rye grass, silver beet and spinach

Treatments	Lettuce	Perennial rye grass	Silver beet	Spinach
T1	0.0135	0.0003	0.0048	0.0035
T2	0.0100	0.0002	0.0052	0.0038
T3	0.0139	0.0002	0.0047	0.0037
T4	0.0238	0.0002	0.0049	0.0049
T5	0.0190	0.0001	0.0031	0.0069

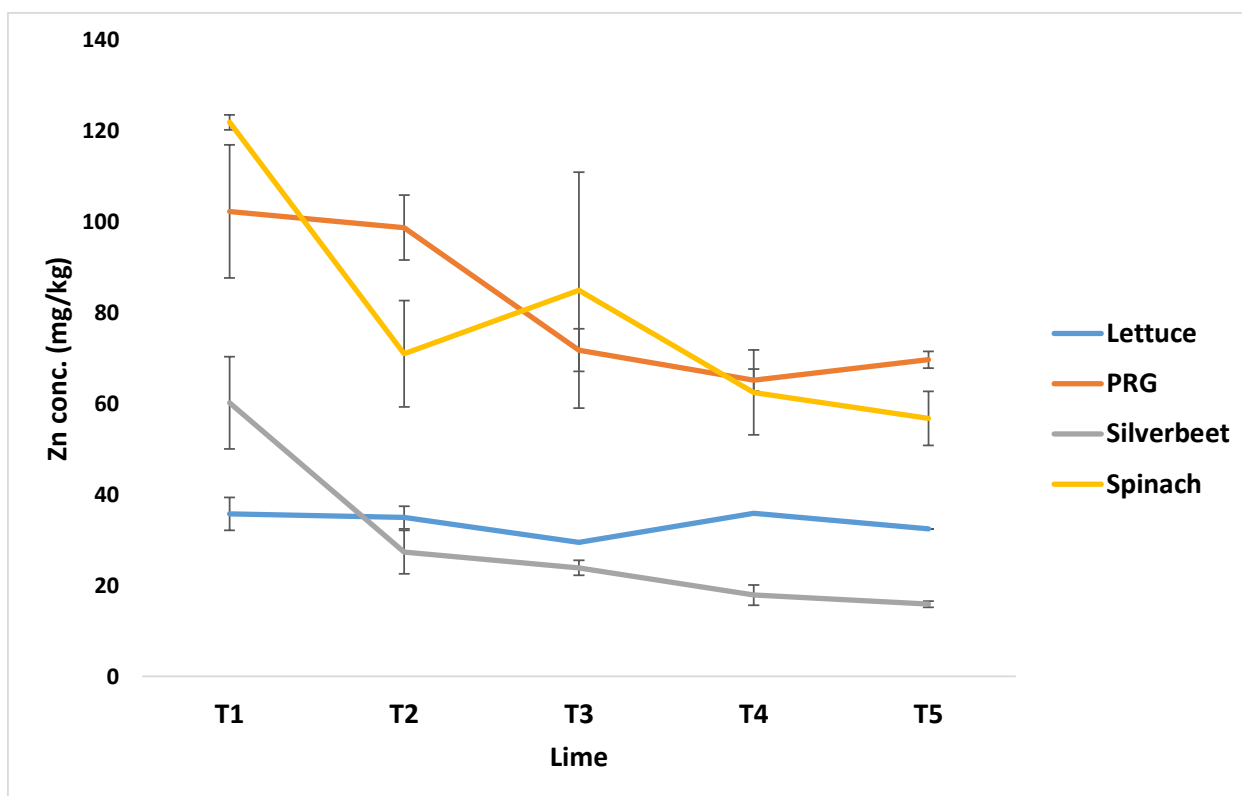


Figure 6.2 Concentration of Zn (mg/kg) in plants (dry weight basis) at different lime treatments. Significant differences are shown in Table 6.2-6.5.

6.4.3 Change in other elements in plants

Lime application in soil significantly reduced the concentration of Zn up to 50% in spinach, up to 70% in silver beet and up to 30% in perennial rye grass (Figure 6.2). No significant difference was observed in the concentration of Zn in lettuce between the different rates of lime treatment.

All the rates of lime application decreased the concentration of S, Na, Mg and increased the concentration of Ca and Mo in soil. There was no consistent difference observed in the concentration of Al, B, Cr, Cu, Fe, Mn, Ni and P in the studied plants in relation to the application of T2, T3, T4 and T5 treatments.

6.4.4 Changes in biomass

Different rates of lime application were observed to have a significant effect ($p < 0.05$) on the biomass production of plants (Table 6.4). The biomass production of Silver beet was higher ($p < 0.05$) in lime treatments compared to the control. The T2, T3, T4 and T5 treatments in soil increased the dry biomass of silver beet by 41%, 65%, 66% and 61% respectively. In spinach higher rates of lime (T4 and T5) significantly increased the biomass production (7% and 9%, respectively) whereas lower rates of lime (T2 and T3) showed no significant effect. No significant differences were observed in the biomass production of lettuce in relation to the application of different rates of lime. In the case of perennial rye grass lower rates (T2 and T3) did not show any effect on the biomass production although the higher rates of lime (T4 and T5) significantly reduced ($p < 0.05$) the biomass production up to 2% and 8%, respectively. No visual effect was observed in the growth of any of the plants due to the application of different rates of lime.

Table 6.4 Dry plant biomass (gram). Standard errors are given in brackets ($n=4$). Values in the same row with the same letters are not significantly different

Plants	Treatments				
	T1 (control)	T2	T3	T4	T5
Lettuce	6.2 (0.15) ^{AB}	5.8 (0.05) ^B	6.4 (0.2) ^A	5.9 (0.08) ^B	6.2 (0.2) ^{AB}
Perennial rye grass	6.5 (0.1) ^A	6.5 (0.1) ^{AB}	6.4 (0.1) ^{ABC}	6.1 (0.3) ^{BC}	6 (0.1) ^C
Silver beet	5 (0.2) ^C	7.1 (0.4) ^B	8.3 (0.3) ^A	8.3 (0.1) ^A	8.1 (0.1) ^A
Spinach	3.7 (0.1) ^B	3.8 (0.1) ^{AB}	4 (0.1) ^{AB}	4 (0.1) ^A	4 (0.1) ^A

6.5 Discussion

A decrease in the Cd concentration in ryegrass and silver beet (Figure 6.1) due to the lime treatment is consistent with other studies where lime application reduced the accumulation of

Cd (Basta and Sloan, 1999; Fernandes et al., 1999; He and Singh, 1993; John and Van Laerhoven, 1976; Kim et al., 2016; Maier et al., 2002; Singh et al., 1995). This can be attributed due to the decrease in the extractable concentration of Cd in soils (Table 6.2) (Dakora and Phillips, 2002; Hinsinger et al., 2003; Marschner, 1991). The application of lime increased the pH (Table 6.2), which subsequently increased the Cd sorption in soil (Comerford, 2005) leading to less available fraction to plants. Lime addition in soil increases the negative charge of soil that forms strongly bound hydroxyl Cd species resulting less soluble Cd (Bolan et al., 1999).

Even though extractable Cd was lower in all treatments, in lettuce, the T4 treatment increased the concentration of Cd compared to the control soil (Table SI 6.2). This Cd concentration increase in lettuce may also be due to an induced Zn deficiency at high soil pH, which causes the plant to produce additional root Zn transport proteins to have sufficient soil Zn to check the Zn insufficiency stress (Chaney et al., 2009). As the Zn transport proteins also transport Cd, so increased Zn transporting protein production by plants may result even greater Cd uptake at the time of Zn shortage stress in plants (Hart et al., 2002). From the Table 6.3, it is observed that lettuce grown in T4 treatment had the highest Cd and Zn ratio indicating that the plants probably were under stress from Zn deficiency. The different rates of lime application did not affect the concentration of Cd in spinach and partially to lettuce probably due to the response of plants to lime by producing more acidic root exudates.

Lettuce has accumulated more Cd compared to spinach (Table SI 6.2) in all treatments that have been also observed in our first experiment (Al Mamun et al., 2016). All the lime treatments in soil significantly reduced the accumulation of Zn in spinach (Figure 6.2), silver beet and perennial rye grass which has also been reported by other authors who observed the same effect of lime on other plants (Andersson and Siman, 1991; Merian, 1991). The

concentration of Zn was lower by up to 50% in spinach, up to 70% in silver beet and up to 30% in perennial rye grass. No significant difference was observed in the concentration of Zn in lettuce due to the different rates of lime treatment in soil.

6.6 Conclusion

Liming lead to lower Cd uptake in ryegrass and silverbeet but was ineffective or even increased Cd uptake by lettuce and spinach. Unlike composts, lime consistently reduced the uptake of Zn and other essential trace elements in all species. Future work should focus on the mechanisms behind the paradoxical increase in Cd uptake by some species growing in lime-amended soil.

Supplementary Information

Table SI 6.1 Selected references on the immobilization and phytoavailability of Cd by liming materials (adapted from Bolan et al. (2003a))

Liming material	Cadmium source	Observation	Reference
CaCO ₃	Fertilizer	Decreased Cd concentration in straw	(Andersson and Siman, 1991)
Ca(OH) ₂ (8, 15 and 22 Mg/ha)	Limed biosolids (spiked with Cd(NO ₃) ₂)	Decreased soil solution Cd and plant uptake of Cd	(Basta and Sloan, 1999)
CaCO ₃ (10 g/kg)	Cd-enriched sewage sludge	Decreased Cd-phytotoxicity in wheat	(Bingham et al., 1979)
Ca(OH) ₂ (8, 15 and 22 Mg/ha)	Sewage sludge	Decreased the solution Cd; increased residual fraction and plant uptake of Cd	(Brallier et al., 1996)
CaCO ₃ (2.1–45 Mg/ha)	Sewage sludge	Less movement of Cd than Cu and Zn in limed soil	(Brown et al., 1997)
Ca(OH) ₂ and CaCO ₃ (0–1120 kg/ha)	Sand	Reduced Cd phytotoxicity	(Chaney et al., 1977)
CaCO ₃ (0–4.5 g/kg)	CdSO ₄	Decreased CaCl ₂ and NH ₄ OAc extractable Cd in soil and plant tissue Cd	(Fernandes et al., 1999)
–	Limed soil	Increased Cd ²⁺ sorption	(Filius et al., 1998)
Ca(OH) ₂	Arable soil – fertilizer Cd	Decreased Cd in chemical extractants and plant tissue	(Gray et al., 1999a)
CaCO ₃ (0–20 g/kg)	Cd(NO ₃) ₂ (1.5 mg Cd /kg)	Decreased Cd concentration in plant tissue	(Han and Lee, 1996)
CaCO ₃ (0–5.226 g/kg)	Arable soil fertilizer Cd	Decreased Cd concentration in plant tissue	(He and Singh, 1993)
CaCO ₃ (to pH 7.4)	Arable soil/sewage sludge	Decreased Cd ²⁺ adsorption	(Hooda and Alloway, 1996)
CaCO ₃ (17.92 Mg/ha)	Sewage sludge and Milorganite	Decreased uptake of Cd by plants resulting in Cd attenuation	(John and Van Laerhoven, 1976)
CaCO ₃ (0–1000 mg/kg)	Arable soil	Increased plant Cd at low level of CaCO ₃ ; decreased at high levels	(John et al., 1972)
CaMgCO ₃ (4 Mg/ha)	Forest soil	Decreased Cd concentration in soil solution	(Kreutzer, 1995)
CaCO ₃ (0–10 g/kg)	Arable soil	Decreased Cd uptake by lettuce	(Lehoczky et al., 2000)
Limestone (83% CaCO ₃ and 12% MgCO ₃)	Arable soil	No effect on Cd uptake by sunflower plants	(Li et al., 1996)

CaCO ₃ (3000 kg/ha)	Arable soil	Decreased DTPA extractable Cd in soils and Cd in plant tissue	(Maclean, 1976)
CaCO ₃ (0–20 Mg/ha)	Arable soil	Increased Cd concentration in potato tuber	(Maier et al., 1996)
CaCO ₃ (0–2.5 Mg/ha)	Arable soil	Decreased Cd concentration in barley grain	(Oliver et al., 1996)
CaCO ₃	NPK fertilizer	Decreased DTPA and NH ₄ NO ₃ extractable Cd; increased plant tissue Cd	(Singh and Myhr, 1998)
CaCO ₃ (1–5 g/kg)	Arable soil	Decreased DTPA and NH ₄ NO ₃ extractable Cd, and plant tissue Cd	(Singh et al., 1995)
CaCO ₃	P fertilizer	No effect on Cd concentration of potato tuber	(Sparrow et al., 1993)
CaCO ₃	Pasture soil	Decreased Cd concentration in plant tissue	(Tyler and Olsson, 2001)
CaO	Limed sewage sludge	Less uptake of Cd by plants	(Vasseur et al., 1998)
CaCO ₃ , MgCO ₃ , CaSO ₄	Arable soil	Decreased Cd concentration with CaCO ₃ and MgCO ₃ , but increased with CaSO ₄	(Williams and David, 1976)
CaCO ₃	Arable soil	Decreased the accumulation of Cd in potato tubers	(Maier et al., 2002)
CaCO ₃	Arable soil	In glass house experiment cd accumulation was reduced, but in field condition either no effect or increased Cd accumulation in plants.	Maier et al. (1997)
Ca(OH) ₂	Cd (0–10 mg/kg soil) using Cd(NO ₃) ₂	Increased adsorption and Increased and decreased accumulation in plants, mustard (<i>Brassica juncea</i> L.).	(Bolan et al., 2003a)
Hydrated lime powder (85 % w/w) containing Ca(OH) ₂	Cd polluted soil from an adjacent smelting factory	Liming wetted and flooded soils decreased NH ₄ OAc extractable Cd and increased carbonates or Fe-Mn oxides bound fractions	(Chen et al., 2016)
CaCO ₃	Cd polluted soil from a mine	Decreased NaOAc extractable Cd	(Lim et al., 2013)

Table SI 6.2 Elemental composition of spinach on the dry weight basis (mg/kg). Standard errors are given in brackets (n=4). Values in the same row with the same letters are not significantly different. Zn and Cd data was used in graphs

Elements	Treatments				
	T1 (control)	T2	T3	T4	T5
Al*	525 (136)	662 (236)	1104 (425)	474 (76)	551 (187)
B	36 (2) ^A	33 (1) ^{AB}	27 (5) ^B	28 (1) ^B	31 (2) ^{AB}
Ca	8756 (607) ^C	11668 (1346) ^{BC}	13855 (1623) ^{AB}	15071 (764) ^A	14727 (267) ^A
Cd*	A	A	A	A	A
Co	0.51 (0.03) ^A	0.33 (0.06) ^{AB}	0.42 (0.03) ^{AB}	0.26 (0.06) ^{BC}	0.22 (0.02) ^C
Cr*	1.11 (0.1)	0.77 (0.2)	1.39 (0.8)	0.74 (0.1)	0.54 (0.1)
Cu*	7.3 (0.5)	5.7 (0.8)	6.2 (0.8)	6.2 (0.4)	5.8 (0.6)
Fe*	242 (57)	290 (95)	469 (172)	227 (28)	253 (78)
K	49460 (5339) ^{AB}	36209 (1422) ^B	48430 (9032) ^{AB}	53011 (5822) ^A	49625 (3381) ^{AB}
Mg*	3476 (517)	3250 (482)	2932 (393)	2922 (252)	2716 (67)
Mn	53 (6) ^A	30 (2) ^B	36 (4) ^B	33 (2) ^B	33 (4) ^B
Mo	0.75 (0.06) ^C	0.80 (0.15) ^{BC}	1.37 (0.25) ^{ABC}	1.45 (0.25) ^{AB}	1.57 (0.28) ^A
Na	2426 (163) ^A	2157 (525) ^{AB}	2143 (221) ^{AB}	1823 (198) ^{AB}	1631 (95) ^B
Ni	1.08 (0.07) ^A	0.86 (0.23) ^{AB}	1.13 (0.71) ^A	0.59 (0.08) ^B	0.60 (0.11) ^B
P*	5935 (752)	5059 (169)	4409 (850)	4284 (789)	4783 (470)
Pb	0.98 (0.2) ^A	0.55 (0.2) ^{AB}	0.63 (0.4) ^{AB}	0.54 (0.05) ^{AB}	0.30 (0.2) ^C
S	3229 (146) ^A	2279 (315) ^B	2605 (406) ^{AB}	2752 (115) ^{AB}	2292 (286) ^B
Zn	A	B	B	B	B

*no significant difference

Table SI 6.3 Elemental composition of lettuce on the dry weight basis (mg/kg). Standard errors are given in brackets (n=4). Values in the same row with the same letters are not significantly different. Zn and Cd data was used in graphs

Elements	Treatments (lettuce)				
	T1 (control)	T2	T3	T4	T5
Al	79 (26) ^{BC}	200 (60) ^A	28 (8) ^C	122 (16) ^{AB}	62 (6) ^{BC}
B	22 (6) ^{BC}	26 (3) ^{ABC}	16 (3) ^C	36 (1) ^A	28 (2) ^{AB}
Ca	10137 (1501) ^B	12458 (1332) ^{AB}	10207 (843) ^B	13964 (337) ^A	11515 (1131) ^{AB}
Cd	BC	C	BC	A	B
Cr	0.30 (0.08) ^A	0.30 (0.09) ^A	0.12 (0.05) ^B	0.16 (0.03) ^{AB}	0.10 (0.03) ^B
Cu	4 (0.6) ^{BC}	5 (0.4) ^{AB}	3 (0.2) ^C	5 (0.1) ^A	4 (0.5) ^{ABC}
Fe	88 (21) ^{BC}	152 (36) ^A	53 (3) ^C	117 (7) ^{AB}	68 (9) ^{BC}
K*	35068 (1525)	35321 (2488)	35072 (3796)	36964 (1780)	36836 (2337)
Li	0.19 (0.03) ^A	0.23 (0.06) ^A	0.13 (0.01) ^B	0.19 (0.03) ^A	0.12 (0.02) ^B
Mg*	1861 (195)	1775 (145)	1572 (154)	1949 (83)	1873 (140)
Mn	43 (8) ^B	41 (4) ^B	38 (5) ^B	68 (4) ^A	46 (4) ^B
Mo	0.26 (0.1) ^D	0.67 (0.1) ^C	0.72 (0.1) ^C	1.42 (0.1) ^A	1.05 (0.1) ^B
Na	1741 (226) ^A	1528 (222) ^{AB}	1133 (122) ^B	1463 (51) ^{AB}	1071 (123) ^B
P*	3953 (161)	3861 (261)	3771 (199)	3743 (176)	3847 (117)
Zn*	A	A	A	A	A

*=no significant difference

Table SI 6.4 Elemental composition of silver beet on the dry weight basis (mg/kg). Standard errors are given in brackets (n=4). Values in the same row with the same letters are not significantly different. Zn and Cd data was used in graphs

Elements	Treatments (silver beet)				
	T1 (control)	T2	T3	T4	T5
Al	310 (125) ^A	116 (66) ^{AB}	74 (11) ^B	34 (8) ^B	59 (24) ^B
B	40 (3) ^B	38 (5) ^B	43 (2) ^B	54 (3) ^A	46 (2) ^{AB}
Ca	11815 (785) ^B	10750 (865) ^B	16499 (2162) ^A	15143 (2025) ^{AB}	12690 (898) ^{AB}
Cd	A	B	B	B	B
Cr*	0.2 (0.06)	0.1 (0.03)	0.2 (0.03)	0.1 (0.02)	0.1 (0.01)
Cu	7 (0.4) ^A	6 (1.4) ^{AB}	5 (0.6) ^{AB}	4 (0.3) ^B	4 (0.2) ^B
Fe	181 (48) ^A	96 (35) ^B	68 (3) ^B	50 (5) ^B	59 (9) ^B
K	60450 (4405) ^A	50562 (11912) ^{AB}	45493 (1665) ^{AB}	41895 (5488) ^{AB}	40601 (951) ^B
Mg	6144 (450) ^A	4803 (893) ^{AB}	4470 (400) ^{BC}	4781 (325) ^{ABC}	3232 (264) ^C
Mn	66 (9) ^{AB}	34 (3) ^B	98 (16) ^A	92 (11) ^A	74 (12) ^A
Mo	0.5 (0.2) ^C	5.2 (0.8) ^{BC}	6.5 (1) ^B	16.6 (4) ^A	6.4 (0.4) ^{BC}
Na	15547 (643) ^A	14870 (3289) ^A	9895 (1181) ^B	9915 (588) ^B	8136 (694) ^B
P	5048 (564) ^{AB}	4220 (876) ^B	7181 (1146) ^A	5936 (549) ^{AB}	5465 (667) ^{AB}
S	3306 (178) ^A	2090 (508) ^B	1854 (124) ^B	1593 (160) ^B	1868 (201) ^B
Zn	A	B	B	B	B

*no significant difference

Table SI 6.5 Elemental composition of perennial rye grass on the dry weight basis (mg/kg). Standard errors are given in brackets (n=4). Values in the same row with the same letters are not significantly different. Zn and Cd data was used in graphs

Elements	Treatments (perennial rye grass)				
	T1 (control)	T2	T3	T4	T5
Al*	47 (5)	40 (4)	39 (3)	38 (4)	42 (3)
B	36 (5) ^A	16 (1) ^B	15 (1) ^B	19 (1) ^B	19 (1) ^B
Ca	7607 (277) ^{CD}	7439 (205) ^D	8029 (68) ^{BC}	8412 (67) ^{AB}	8613 (232) ^A
Cd	A	B	C	C	C
Co*	0.05 (0.01)	0.05 (0.01)	0.05 (0.01)	0.05 (0.01)	0.03 (0.01)
Cr*	0.16 (0.01)	0.34 (0.15)	0.15 (0.01)	0.13 (0.02)	0.18 (0.03)
Cu	13 (0.5) ^B	14 (0.1) ^{AB}	14 (0.3) ^A	14 (0.3) ^A	14 (0.2) ^A
Fe	61 (0.8) ^{AB}	63 (1.0) ^A	63 (1) ^A	60 (1) ^B	62 (0.3) ^{AB}
K	34582 (1490) ^C	39385 (657) ^A	38370 (737) ^{AB}	36103 (1123) ^{BC}	35838 (939) ^{BC}
Mg	3204 (53) ^A	2764 (45) ^B	2747 (97) ^B	2691 (39) ^B	2534 (121) ^B
Mn	37 (2) ^A	30 (1) ^B	37 (1) ^A	39 (1) ^A	40 (2) ^A
Mo	10 (0.5) ^C	27 (0.6) ^B	33 (1.2) ^{AB}	35 (3.9) ^A	33 (1.6) ^{AB}
Na	877 (33) ^A	806 (14) ^{AB}	780 (59) ^{AB}	725 (13) ^B	720 (32) ^B
Ni	0.77 (0.14) ^B	0.93 (0.02) ^A	0.81 (0.04) ^B	0.86 (0.20) ^{AB}	0.86 (0.05) ^{AB}
P	6139 (185) ^A	6072 (94) ^{AB}	5718 (147) ^{BC}	5466 (128) ^C	5627 (91) ^C
S	3795 (57) ^A	2392 (96) ^D	2796 (89) ^{CD}	3241 (222) ^B	3177 (182) ^{BC}
Zn	A	A	B	B	B

*no significant difference

Chapter 7 Summarizing conclusions

7.1 Potential of carbonaceous amendments to reduce the transfer of Cd from soils to plants

This thesis sought to determine the effects of various sources of organic matter in reducing the uptake of Cd in plants in agricultural soils where the concentration has been elevated due to continuous application of P fertilizers.

7.1.1 key findings related to the theoretical literature:

The Cd sorption by soils and composts followed the patterns expected for trace element cations. In the batch sorption experiment, the K_d values of all soils and soil amendments increased with increasing pH which is consistent with other batch sorption experiments conducted by Simmler et al. (2013) and Ulmanu et al. (2003). The increased K_d value indicates that at high pH more Cd will be sorbed by soil and soil amendments leading to less plant available Cd in soil solution and less uptake by plants (Loganathan et al., 2003; McLaughlin et al., 1996). The pH dependent charge increases in soil due to high pH as the H^+ ion leaves the exchangeable sites in soil leading to higher CEC (Brady and Weil, 2013). The high CEC of soils leads to binding of Cd through inner sphere and outer sphere binding leading to less phytoavailable Cd in soils and eventually less Cd concentration in plants (Brady and Weil, 2013). The batch sorption experiments revealed that lignite and composts had at least 50 times higher Cd sorption capability (K_d) than two soils delineating the capability of these amendments to sorb more Cd than soils which is consistent with Chami et al. (2013) who also observed that organic matter has the capability of modifying the phytoavailability of metals in soil.

Although biosolids showed higher Cd sorption capability compared to soils, we did not consider biosolids because the total analysis (Table 3.2) showed that biosolids had higher Cd concentrations than the other soil amendments, which might introduce Cd contamination in

agricultural soils (Islam et al., 2013; Nogueira et al., 2013; Ramachandran and D'Souza, 1999; Tsadilas and Shaheen, 2013). Biosolids are capable of both increasing (Moreno et al., 1999; Nogueira et al., 2013) and decreasing (Bolan et al., 2003b; Sato et al., 2010; Shuman et al., 2002; Tapia et al., 2010; Xu et al., 2012) Cd uptake by plants although some authors reported no effects of biosolids on Cd concentration in plants (Bartl et al., 1999; Krzywy et al., 1999). Pot trials with lignite and municipal composts showed that composts reduced the accumulation of Cd in onion (*Allium cepa* L.), spinach (*Spinacia oleracea* L.) and lettuce (*Lactuca sativa* L.) up to 60%. Lignite was not consistent in reducing the accumulation of Cd in the plants. A lower rate of lignite (1% w/w) was more effective than higher rate of lignite (2.5% w/w), which in some cases increased the accumulation of Cd. This was attributed to a reduction in soil pH, which brought more Cd into soil solution. Composts increased the sorption capacity (K_d) of soils leading to less plant available Cd in soil solution and less Cd accumulation by plants. The reduction in the concentration of Cd in plants may be partly because of a small pH increase in soils due to the application of composts in soil that has also been observed by Loganathan et al. (2003) and McLaughlin et al. (1996). Lignite also increased the K_d values (Simmler et al., 2013) but the pH decrease may have offset the effect of K_d value increase of lignite in amended soils. Municipal composts supplied significant amount of Zn in soils which might be responsible for less Cd accumulation by plants (Chaney et al., 2009; Grant et al., 1999b; Kabata-Pendias and Mukherjee, 2007; McKenna et al., 1992).

Another pot trial with potato (*Solanum tuberosum* L.) treated with lime, municipal composts, sawdust composted with animal wastes, pig manure composts, mushroom composts and shredded corn stover showed that all amendments decreased the concentration of Cd in potato. The dry mass production of potato was almost double in composts treated soils although shredded corn stover significantly decreased the dry mass production. The concentration of Cd in our potato tubers were in the lower range found in other experiments (Kabata-Pendias and

Mukherjee, 2007; Kim, 2008; McLaughlin et al., 1994a; McLaughlin et al., 1994b), which may be due to the variety difference (Grant et al., 1999a; Loganathan et al., 2003; Redjala et al., 2009; Welch and Norvell, 1999). Most of the decrease in the concentration of Cd in potato tuber may be attributed to the increase in Cd sorption capacity of soils due to composts application (Simmler et al., 2013) that I have also observed in the first experiment (Chapter 3). The increase in the growth of potato tubers may have resulted lower concentration of Cd due to a “dilution effect” (Robinson et al., 2009). Potato tubers had the lower concentrations of Cd than potato skin and potato stem, which indicates that the low Cd concentration in the potato tubers is the result of plant physiological process rather than low Cd availability in soils. The low tuber concentrations may be due to the fact that Cd is relatively phloem-immobile (Uraguchi et al., 2009) and high Cd in tubers would not be expected as it receives most of their nutrients via the phloem (Dunbar et al., 2003).

Lime significantly increased soil pH, that has been reported decreasing the accumulation of Cd in plants (Hong et al., 2007; Kabata-Pendias and Mukherjee, 2007; Simmler et al., 2013) through increasing the availability of exchangeable sites (Brady and Weil, 2008) for binding Cd. My experiment results stand in contrast to other studies that reported an increase in the concentration of Cd by plants due to lime application, which was attributed to the competition between Cd and Ca for sorbing sites in soil (Chaney et al., 2009; Maier et al., 2002; McLaughlin et al., 1997; Merian, 1991). An increase in the growth of potato has also been observed by other authors due to the application of composts in soil (Barkoczi et al., 2008; Khan et al., 2007; Muhammad et al., 2007), which may be due to the improvement of physical properties of soils by improving soil porosity, aggregate stability, nutrient and water holding capacity, temperature insulation and decreasing soil density (Sarwar et al., 2008; Shiralipour et al., 1992), and soil nutrient content (Shiralipour et al., 1992).

The reduced shoot growth in the lime treatment may have been due to the imbalance of nutrient elements in soil due to the pH increase (Maier et al., 2002). My experiments revealed that compost is a superior soil amendment to lime because compost invariably increased plant growth, decreased Cd uptake and did not perturb the plant uptake of other elements, especially Zn. In contrast, while lime reduced Cd uptake in some species (perennial rye grass (*Lolium perenne* L.), potato (*Solanum tuberosum* L.), and silver beet (*Beta vulgaris* V.), it either had no effect or increased Cd uptake by spinach (*Spinacia oleracea* L.) and lettuce (*Lactuca sativa*). Moreover, lime decreased plant uptake of Fe and Zn, inducing deficiencies and consequent biomass reduction in some species.

Although, lime decreased extractable Zn significantly, the paradoxical increase in plant Cd uptake caused by lime, may be due to upregulation of Zn transporters caused by induced Zn deficiency in some species (Chaney et al., 2009; Hart et al., 2002).

Most previous studies were conducted to determine the effects of composts in reducing the accumulation of Cd in plants grown in highly contaminated soils eg. 55 mg/kg (contaminated due to industrial activities or mining) (Kim et al., 2016) whereas my experiments were conducted with soils that have slightly elevated Cd concentrations (0.47 mg/kg and 1.45 mg/kg) due to the continuous application of Cd-rich P fertilizers over several decades (Syers et al., 1986). My experiments showed that composts are capable of reducing the concentration of Cd in plants from agricultural soils that has slightly elevated Cd concentrations due to agricultural activities.

An incubation experiment showed that compost-amended soils continued to sorb Cd even after significant degradation of the amended organic matter. The experimental units those received N treatment in the form of urea and 30°C temperature, the C content broke down in the fastest rate compared to the control and just urea added experimental units. The C content decomposition rate in the controlled experimental units was the slowest. The extractable Cd

concentration in the experimental units was decreasing slowly with time in all the experimental pots up to 1 year. The incubation experiment showed that the total C content in soil decreased with time in all soils up to 1 year, which indicates that soil organic matter was being oxidised. The greater break down at higher temperature and with added N was expected due to the likely increase of microbial activity (not measured) under higher temperature and added N. The reduction in organic matter would likely reduce the number of binding sites for cations on the soil colloids except clay depending on pH (Helling et al., 1964) as the CEC of compost and soil organic matter is significantly higher compared to other components of the soil (Brady and Weil, 2013).

Helling et al. (1964) have shown that decreasing soil organic matter leads to a decrease in CEC, which results in increased solubility of cations. Our finding that the solubility of Cd and other elements either remained unchanged or even decreased during the experiment. Our results indicated that the concentration of plant available Cd (0.05 M $\text{Ca}(\text{NO}_3)_2$ extractable Cd) was lower in all the experimental units in any weathering condition than the control soils in that weathering condition. Potentially, the decrease in extractable Cd, Cu, K, Na, P, S, and Zn may be, due to occlusion on the soil colloids by Fe and Al plaques. In part, this may be, an artefact of the conditions of the experiment. The regular mechanical disturbance probably would have disrupted soil aggregates of the moist soils (Bissonnais, 1996; Brady and Weil, 2013; Watts et al., 1996) leading to increased surface area and higher concentrations of colloidal Fe and Al (Lavado et al., 1999) which might have occluded surface-bound elements. This same process may happen following repeated ploughing. Lavado et al. (1999), Düring et al. (2002) and Düring et al. (2003) studied the role of ploughing on the solubility and phytoavailability of elements in soil. Lavado et al. (1999) observed in a field trial that the DTPA extractable Cd were not changed due to the mechanical disturbances whereas Düring et al. (2002) showed that

the EDTA extractable Cd decreased due to the mechanical disturbance of soils in laboratory trials.

The extractable Fe and Al moieties would have interacted with the organic matter present in soils. Several authors (Baldock and Skjemstad, 2000; Deng and Dixon, 2002; Huang et al., 2005) have reported that stabilisation of soil organic matter can occur by interacting with clay minerals and oxides. Generally, urea application in soil has decreased the soils pH which is consistent with Maier et al. (1996) who observed that, the application of urea in soil decreased soil pH in a glass house experiment. The pH decrease in urea-N treated soils may be associated due to be the release of NO_3^- from urea that caused the pH decrease (Bouman et al., 1995; Heilman, 1975). The Cd concentration in potato tubers reflected the results from the extractions both in terms of the reduction in Cd when compost was added and the reduction over time for both the controls and the compost amended soils. In both the pot trial and the incubation experiment, there was increased mechanical disturbance in the aged compost and this increased mechanical disturbance probably have led to high concentrations of extractable Fe (Lavado et al., 1999) and Al. The results indicated that, the degradation of soil organic matter is not accompanied by an increase in extractable Cd or plant-available Cd as measured in the pot trial. The persistency of composts in reducing the accumulation of Cd in potato grown in one year compost treated soil supported the incubation experiment indicating that composts will reduce the accumulation of Cd in plants at least for one year.

Were our results indicative of the field situation, then a single application of compost is likely to reduce crop Cd uptake for several years because in our one-year experiment, the degradation of the incubated, mechanically disturbed and N-augmented soils was likely to have been higher than what would occur in the field. However, the mechanical disturbance in our system probably have resulted in increased occlusion of Cd, thereby artificially reducing the concentrations of extractable and plant-available Cd.

7.1.2 Implications of the findings for soil management and food production:

In New Zealand, about 70,000 hectares of lands are exceeding the 1 mg/kg Cd in soil (Cadmium Working Group, 2008). Abraham et al. (2016) reported that there were agricultural soils (0.33% of 8835 soil samples taken between 2006 and 2015) in NZ that had a soil Cd concentration at or above the TFMS (Tiered Fertilizer Management System) Tier 4 threshold of 1.8 mg Cd/kg and the highest recorded soil cadmium concentration was 3.05 mg Cd/kg soil (Abraham et al., 2016). In Tier 4 Cd contaminated lands, the normal way of producing crops through applying P fertilizers is not be possible (Abraham et al., 2016), if the food safety standard (Chaney, 2012; FSANZ, 2015) is considered. It is more likely that the soils having Cd more than 1.8 mg/kg might cause more concentration of Cd in plants exceeding the WHO and FASANZ guideline values (Chaney, 2012; FSANZ, 2015). For these lands, compost might reduce the need for mineral P fertilizers thereby reducing the concentration of Cd in plants and reducing the accumulation of Cd in soil.

In the case of NZ soils, P fertilizers presently contain <280 mg Cd/kg P after a voluntary reduction in the concentration of Cd in P fertilizers (Abraham et al., 2016). This is still higher than many European countries P fertilizers (eg. In Sweden it was reported 16 mg Cd/kg P) (Oosterhuis et al., 2000). This high Cd containing P fertilizers will continue bringing Cd in agricultural soils. It is important for NZ agriculture to maintain soil fertility by supplying adequate amount of P. In NZ soils that has Cd concentration within the range of <0.6 mg/kg soil (Tier 1) and 0.6 to <1.0 mg Cd/kg soil (Tier 2) (Abraham et al., 2016; Rys, 2011), using composts might reduce the risk of Cd enrichment in soils, when composts will be applied as a source of P (Al Mamun et al., 2016).

Meharg et al. (2013) reported that in Bangladesh, there is a high Cd concentration (0.005-0.019 mg/kg) in rice grains (Meharg et al., 2013) and 80-90% of the diet is rice (Meharg et al., 2013). Meharg et al. (2013) thus showed that, there is a possibility that people might exceed the

monthly tolerable intakes of Cd (EFSA, 2012). The lands having high Cd concentration might be managed by using composts that sorb Cd and reduce the accumulation in rice. This requires experimentation to determine whether composts reduce Cd uptake by rice in wetland and dryland conditions. Rice cultivation is different than vegetables and potatoes. Before using composts as a Cd management tool, the effects of composts on the accumulation of Cd in rice grains should be determined. Bangladesh is a subtropical country with an annual rainfall of between 1600 mm to 3000 mm although in some areas the annual average rainfall is as high as 6400 mm (Banglapedia, 2015). The adequate temperature, rainfall and intensive cultivation of agricultural lands for feeding around 150 million people (BBS, 2013) is creating pressure on agricultural lands. The organic matter content in Bangladesh soils are typically from 0.5 to 1% (BBS, 2013) which is low compared to the typical value of organic matters in agricultural soils (Brady and Weil, 2013). Thus, by using composts in agricultural lands will not only reduce the import of Cd in agricultural lands from P fertilizers but also will increase the organic matter content in soils. Moreover, when the kitchen wastes and other organic wastes will be composted, less waste will be disposed on roadsides and into rivers, which contaminates waterways and reduces the aesthetic appeal of the countryside. There is currently no sorting of organic wastes. Sorting organic wastes properly, composting the organic wastes following standard techniques and finally using them in agricultural lands of Bangladesh will help to get rid of the present waste problem and reduce the need for expensive mineral fertilisers and may reduce Cd in the diet.

7.2 Practical considerations of using compost as a soil amendment

Composts supply a significant amount of organic C (Aranyos et al., 2016), N (Hopkins et al., 2017; Horrocks et al., 2016), P (Evanylo et al., 2008), S and Zn (Al Mamun et al., 2016) in soils. Application of composts will reduce the amount of N fertilizer application in soils specially in organic farming (Horrocks et al., 2016). The P in the composts are considered

100% plant available in the long term (Schröder et al., 2011) indicating that composts will reduce the amount of P fertilizers to be applied in soils. Compost application in soil will improve soil structure and water infiltration rates (Aranyos et al., 2016) reducing ponding and runoff, which are global environmental issues. In addition, composts may improve the water holding capacity and cation exchange capacity of the many sandy soils worldwide (Aranyos et al., 2016).

7.2.1 Rates of application

Composts can contain high concentrations of N, P, S, Cu and Zn depending on the source materials. Therefore, application rates need to be adjusted to minimise soil accumulation or toxicity from a particular element (Cu and Zn) as well as excess runoff (P) or leaching (N and S).

Composts have been applied at rates of 9, 18, 27, 25 50, 144 ton/ha dry weight in many studies (Evanylo et al., 2008; Hopkins et al., 2017; Horrocks et al., 2016). Evanylo et al. (2008) reported that lower rates of compost had little effect on the supply of N and P in soils whereas higher rates (144 ton/ha dry weight) had significant improvement in the supply (eg. 68% total N and 225% available P increase was observed when 144 ton/ha compost were used). Evanylo et al. (2008) also mentioned that lower rates (31 ton/ha d.w.) increase the concentration of nutrient element over long term application of composts in soils (Evanylo et al., 2008). In my thesis, no detrimental effects were observed at application rates of 50 ton/ha and 100 ton/ha.

The annual rates of application of composts will also vary from tropical to temperate climates. In the tropical countries, the composts will degrade fast requiring the input of large amount of compost every year whereas in temperate climates the yearly compost application rates may be lower due to lower microbial activity leading to less oxidation of composts in soils. For every climatic condition, the degradation rates of composts and subsequent nutrient release, should

be taken into consideration before applying composts in agricultural soils (Hargreaves et al., 2008).

The price of municipal compost is around \$12 per tonne whereas the price of composts from other companies might vary depending on the location of the company outlet, the transportation cost, the management process, the volume of the business, volume of purchase etc. The price of composts may also significantly vary from country to country. For example, in Bangladesh, around 10 million people live in the capital city, Dhaka. Every day a vast amount of kitchen wastes is generated which mainly goes for land filling causing a significant negative impact on air and water quality deteriorating the aesthetic views of the places where those are dumped. Composting of kitchen wastes together with other organic wastes will cause the price even cheaper as the city corporation of Dhaka collects Tax from the residents to pay for dumping of the wastes. Compared with mineral fertilizers, the price of compost is significantly lower for the equivalent nutrient value (Table 7.1).

Table 7.1 The monetary value of compost in comparison to mineral fertilizers

Fertilizer elements from composts applied at a 50 ton/ha d.w. (2.5 % d.w.)				
Fertilizer elements in composts	*N₂ (1-2%)	*P (4000-6000 mg/kg)	*K (5000-14000 mg/kg)	*S (2500-16000 mg/kg)
Total fertilizer elements (kg)	500-1000	200-300	250-800	125-800
Equivalent amount of mineral fertilizers required to replace the fertilizer elements in composts				
Mineral fertilizer	1100-2200 kg urea (46% N ₂)	2200-3300 kg super phosphate (9% P)	500-1600 kg potassium chloride (50% K)	130 kg-900 kg sulphur 90 (90% S)
Cost of replacing the fertilizer elements in composts by mineral fertilizers/ha of agricultural land				
NZD	350-700	700-1000	300-1100	80-500
Cost (NZD) of mineral fertilizers to replace the nutrient elements present in 50 ton of composts (\$12/ton)	1430-3300 NZD			

Unit price: urea- \$319/1000 kg (46% N), Superphosphate (9% P)- \$507/1000kg, Potassium chloride (50% K)- \$584/1000 kg, Sulphur 90 (90% S)- \$615 collected from Ravensdown.co.nz website on 26th February, 2017. * The nutrient elements in composts vary depending on sources and batches. I have considered the composts those I have used and considered here just 1 batch to have an idea. In the calculations values have been rounded, thus may slightly vary with other calculations.

Although their nutrient elemental composition is much lower than the commercial fertilizers, compost's long-term benefits (improving soil structure, water percolation rate, water holding capacity, microbial activity, buffering capacity etc.) and sustainability of crop production in agricultural lands amended with composts will compensate the initial costs.

7.2.2 Risks from composts

Some of the composts those are originated from industrial waste materials and biosolids may contain some heavy metals and pathogens (Sinha et al., 2010). Composts may contain high amount of Ni, Cu, Zn, Pb, Cr, Cd and Hg, and harmful microorganisms depending on the source material of composts (Déportes et al., 1995). Déportes et al. (1995) reported in his review paper that a temperature of 71°C for 50 minutes will kill all the pathogens in compost. In my study,

I have observed that biosolids contain high concentration of Cd (Chapter 4). As the biosolids are also used to produce composts in some places, thus the different heating techniques can be used to get rid of harmful pathogens from biosolid compost or the biosolids portion (depending on source and Cd content of biosolids) in composts (where biosolids are mixed with green wastes to make composts) should be kept in minimum ratio to reduce the Cd contamination in composts.

7.2.3 Present status of compost use

In New Zealand, annually about 726,000 tons of municipal garden and kitchen wastes are sent to landfills (Horrocks et al., 2016). By converting this large amount of organic wastes to composts and applying those in the agricultural lands would reduce the need of vast lands for land filling as well as the need of chemical fertilizers (N and P) would be reduced. In Austria, Germany, Norway, and United Kingdom in every year 164,000, 5,000,000, 112,000, 2,740,000 tons of composts are produced, respectively. This is just a part of organic wastes those are composted. Others are used for land filling (Möller, 2016). By using the above mentioned amount of composts, Austria, Germany, Norway, and United Kingdom are saving \$3 m, 100 m, \$2.2 m, \$55 m (considering saving of \$1000 from 50 ton/ha of compost application in agricultural land), respectively in each year by requiring less mineral fertilizers in agricultural lands. In urban areas, the organic waste production is around 100 kg per person. This data is for the countries in Europe (Möller, 2016). Although the costs may vary from continent to continent, nevertheless gives an indication of the amount of urban organic wastes produced which can be a good source of nutrient rich soil amendment.

7.3 Fertile areas of future research

All the composts tested in this study reduced Cd uptake by plants. It is unclear, however, which moieties in the compost have the strongest affinity for Cd. Identification of strongly Cd-sorbing components in compost may allow the eventual manufacture of superior composts for reducing plant Cd uptake.

The incubation experiment in this thesis indicated that compost-amended soil undergoing regular mechanical disturbance does not release Cd even after soil organic carbon is significantly reduced. This paradoxical result may be due to an experimental artefact (the regular mechanical disturbance) and therefore may not accurately portray the release of Cd from soil under field conditions. The long-term performance of composts should therefore be tested in field trials. Experiments investigating the occlusion of Cd and other elements following mechanical disturbance is also warranted.

Chapter 8 References

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Chapter 9 Appendix

The effect of lime on the rhizosphere processes and elemental uptake of white lupin

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My contribution to the article: I worked with Fabio Valentinuzzi to design the lime treatment experiment. Fabio and I grew the plants and conducted the chemical analysis. Fabio, Nik and I conducted the rhizobox experiments and Fabio oversaw the DGT and subsequent LA-ICPMS analysis in conjunction with Nik Lehto, Tanja Mimmo, Jacob Santner, and Christoph Hoefer. All co-authors contributed to the writing of the manuscript.

9.1 Abstract

Acid soils cover 30-40% of the world's arable land and represent one of the major constraints to agricultural production. Lime is routinely added to soil to improve fertility and to reduce the solubility of elements such as aluminium (Al) and cadmium (Cd). White lupin is cultivated globally, however, this is done mainly on acidic soils because of its calcifuge characteristics resulting from its limited ability to compartmentalize calcium (Ca). In abiotic stress conditions, lupins exude organic acids and flavonoids from cluster roots. This can increase the availability of essential soil nutrients to the plant but also exacerbate the uptake of contaminants (eg. Cd). We aimed to determine the effect of liming on the rhizosphere processes of white lupin plants in two high-fertility soils which were treated with seven levels of lime. Nutrient availability

and plant uptake was assessed with a pot experiment. Three lime levels have been chosen for a further rhizotron study. Diffusive gradient in thin layers (DGT) gels were applied on selected root zones and then analysed by laser ablation inductively-coupled plasma mass spectrometry (LA ICP-MS).

The results showed that lime affected the solubility of extractable elements and the plant uptake. In soils treated with different levels of lime, the uptake of nutrients was sufficient to avoid nutrient deficiency. However, analysis of the DGT gels only showed mobilization around the cluster root of the plant grown in the untreated soil. The results indicate that white lupin can be grown at pHs as high as 7.50 with 10 wt% lime without suffering from nutrient deficiencies.

Keywords: liming, white lupin, DGT, LA-ICP-MS, trace elements, iron, nutrients

9.2 Introduction

Soil pH is one of the most important chemical parameters influencing element sorption and dissolution processes in soil (Comerford, 2005) and thus the bioavailable fraction to plants. Many authors report that plant element uptake is highly correlated with pH (Dakora and Phillips, 2002; Hinsinger et al., 2003; Marschner, 1991). The bioavailability of trace elements cations such as copper (Cu), zinc (Zn), Nickel (Ni), cadmium (Cd) and lead (Pb) and their concentration in plants is significantly reduced at pH >7.0. Acid pH can favor the bioavailability of these elements, as well as essential plant micronutrients, such as iron (Fe), manganese (Mn) and boron (B). However, these benefits can be offset by increased bioavailability of phytotoxic elements such as aluminum (Al^{3+}). Acid soils, covering 30-40% of the world's arable land, represent one of the major constraints in agricultural production due to plant growth inhibition and yield reduction (Marschner, 1991). Several factors could further increase soil acidification, such as large inputs of inorganic fertilizers, high rainfall, acid deposition and greenhouse gases. In addition to toxic concentrations of Al^{3+} and protons (H^+), acid soils can provoke deficiencies in anionic plant nutrients such as molybdate (MoO_4^{2-}) and phosphate (PO_4^{3-}). The ongoing application of phosphate fertilizers to overcome P deficiency in acid soil, can lead to the accumulation of Cd (Williams and David, 1976), that exists naturally as an impurity in phosphate rocks, from which phosphate fertilisers are obtained. The entry of toxic metals, such as Cd, from soils and into the food chain through plant uptake is of primary concern in agricultural production systems because of the potential threats to food quality, crop growth, and environmental health (McLaughlin et al., 2000).

Liming (CaCO_3) is routinely used as long-term agricultural practice to improve soil quality by increasing nutrient availability, as well as improving soil structure and increasing rates of infiltration. In addition, liming has been demonstrated to be effective in reducing the solubility of cationic trace elements (eg. Cd^{2+} (Chen et al., 2016)) in soils by increasing the negative

charge on oxides, clays, and organic matter (Kirkham, 2006). However, excessive carbonate concentrations may lead to toxic effects besides reducing the plant-available fraction of essential macro- and micronutrients as phosphorus (P), iron (Fe), manganese (Mn) and zinc (Zn).

White lupin (*Lupinus albus* L.), is adapted to well drained, light to medium textured soil, can tolerate slightly alkaline soils (up to pH 8.0), provided that the free lime or Ca content of the soil is low (the accepted maximum soil level of CaCO_3 is 30-50 g/kg) (Jansen, 2006), since Lupin species are unable to regulate the Ca uptake (De Silva et al., 1994). Such typical calcifuge behavior may be related to an insufficient capacity for compartmentation and/or physiological inactivation of Ca (Hawkesford et al., 2012). In addition, an immobilization of P in the tissues of calcifuge plants may occur, since the excessive uptake of Ca may cause precipitation of Ca phosphate in plant tissues (Zohlen and Tyler, 2004). The concentration of carbonate (Brand et al., 2000) and especially the so-called free lime concentration as previously shown in *L. angustifolius* L. (Jessop et al., 1990) is the limiting factor for the plant growth. White lupin is known to cope with abiotic stresses by releasing organic compounds (organic acids and flavonoids) into the rhizosphere (Neumann et al., 1999). However, whether these substances can have beneficial effects increasing the availability of nutrients or might even counteract the liming effect by mobilizing toxic elements needs to be elucidated.

We aimed to determine the effect of different rates of lime on white lupin in two high-fertility soils. Specifically, we sought to measure the bioavailability of nutrients as well as heavy metals in selected root zones of the plants, where the release of root exudates is more pronounced. The final objective was to define a so-called “ideal [Ca]/pH zone” where lupin is still able to mobilize nutrients without suffering from Ca toxicity and trace elements such as Cd.

9.3 Materials and methods

9.3.1 Soils

We selected two high-fertility soils with contrasting chemical-physical characteristics (Table 9.1), hereafter called as “Pukekohe” and “Levin” soils.

Table 9.1 Physicochemical characteristics of Pukekohe and Levin soils; LOD= limit of detection.

Parameter	Pukekohe	Levin
pH (H ₂ O)	5.95 ± 0.04	6.46 ± 0.06
CEC (Cmolc/kg)	22.00	15
Base saturation [%]	70.00	88
C [%]	2.10	1
N [%]	0.23	0.13
Olsen P [Cmolc/kg]	290.00	229
N available [kg/ha]	50.00	53
P [mg/kg]	3414 ± 26	2247 ± 20
S [mg/kg]	491 ± 6	296.46 ± 1.32
Ca [mg/kg]	4147 ± 117	7008 ± 99
Mg [mg/kg]	2400 ± 95	2873 ± 43
K [mg/kg]	1951 ± 59	2242 ± 54
B [mg/kg]	<LOD	8.89 ± 0.15
Cd [mg/kg]	1.45 ± 0.03	0.47 ± 0.01
Cu [mg/kg]	65 ± 0.46	20 ± 0.20
Mo [mg/kg]	<LOD	<LOD
Mn [mg/kg]	1266 ± 12	387 ± 6
Zn [mg/kg]	173.21 ± 1.06	66.52 ± 0.72
Fe [mg/kg]	44606 ± 96	22729 ± 1527
Cd extractable [mg/kg]	0.015 ± 0.002	0.008 ± 0.002
Cu extractable [mg/kg]	0.13 ± 0.015	0.123 ± 0.006
Mn extractable [mg/kg]	39.75 ± 4.17	8.58 ± 0.25
Zn extractable [mg/kg]	0.37 ± 0.06	0.177 ± 0.017
Fe extractable [mg/kg]	0.654 ± 0.195	0.511 ± 0.036

Seven different lime (CaCO₃, Thermo Fischer Scientific NZ Ltd.) treatments (T1-T7) were applied to both soils, as follows T1: 0 wt%, T2: 0.31 wt%, T3: 0.61 wt%, T4: 1.25 wt%, T5: 2.50 wt%, T6: 5.00 wt%, T7: 10.00 wt%. Soils were well mixed in buckets and then transferred in to pots. For each treatment five replicates consisting of 250 g of soil were used. After that,

pots were moved to a greenhouse, watered to field capacity and left there for a week in order to allow the lime to react with soil.

9.3.2 Pot experiment

White lupin seeds (*Lupinus albus* L.), were soaked for 24 h in water and then transferred to the pots containing the different soil treatments. Subsequently, plants were watered every two days for 6 weeks and weeds were carefully removed every week. After 6 weeks, plants were harvested and the above ground biomass was assessed. The above-ground biomass of the plants was thereby cut 3 cm above the soil level and it was carefully washed with deionised water. Plants were dried at 60°C for one week until constant weight was reached and then ground for subsequent elemental analyses. Samples of rhizosphere soil were collected from each pot. These were oven dried, ground and sieved using a 2 mm sieve. All sample processing was carried out ensuring that there was minimal metal contamination.

9.3.3 Soil and plant analysis

Following microwave-assisted oven digestion (CEM MARS Xpress, CEM Corporation, NC, USA) of samples (0.3 g each) in concentrated HNO₃ and 30% hydrogen peroxide, the total concentrations of the elements in plants was determined by inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Varian 720-ES; Varian, Mulgrave, Australia). Wageningen Evaluating Programs for Analytical Labs (WEPAL) plant was used as reference material. The recoveries for Cd, Fe and Zn were 94%, 94.5% and 91.7% respectively. Soil pH was determined adding 25 ml of deionised water to 10 g of oven dried soil. Samples were stirred and left to stabilise overnight. Subsequently the pH was measured in the supernatant. The plant available element fraction was obtained by extracting soils with 0.05 M Ca(NO₃)₂ in a ratio of 1:6 (w/v) for 2 hours on an end-over-end shaker. Samples were then centrifuged at 3000 rpm for 10 min (Hettich Universal 30 RF) after which the supernatant from each extract

was filtered with Whatman paper No.52 and stored in a fridge at 6°C until further analysis of elemental concentrations by ICP-OES. Blank extracts representing 5% of the total number of extracts were prepared using the same batch of reagents with the same apparatus, and analysed at the same time and in the same way as soil extracts.

9.3.4 Rhizotron experiments

Rhizotrons were constructed from clear cast acrylic polymer according to a modified design to that described by (Göttlein et al., 1999). The internal dimensions of each rhizotron were 15 cm × 30 cm × 2.5 cm (w × h × d) and featured a removable front plate and a fixed back plate fitted with ten ports (in a 2 × 5 configuration at 5 cm intervals) to enable even watering of the soil inside the container. Rhizotron experiments were carried out only with Pukekohe soil because of its crumb structure that was more amenable to plant growth, water infiltration and aeration compared to the Levin soil. The results of the pot trial were used to select two lime treatments (T4 and T7) and a control (T1). The experimental soils were packed in layers into the rhizotrons to ensure a constant bulk density of 1.08 g cm⁻³ across the depth of the rhizotron. White lupin seedlings were transplanted four days after germination on moist tissue paper. The soils were moistened to 30% Maximum Water Holding Capacity (MWHC) before planting the lupin seedlings, after which the rhizotrons were evenly irrigated through the watering ports on the back of the rhizotrons. Moisture content was kept constant for the duration of the growth cycle. The rhizotrons were carefully covered with black plastic film below the level of the soil to limit photo-chemical reduction phenomena in the rhizosphere and biofilm formation on the front plate and were kept in a controlled environment growth chamber with a day/night cycle of 16/8 h and a day/night temperature of 24/16 °C, 70% relative humidity.

9.3.5 High-resolution Diffusive gradients in thin-films measurements (HR-DGT)

The diffusive gradients in thin-films (DGT) technique was used to measure the two-dimensional distribution of metal supply in the lupin rhizospheres in the three rhizotrons. The principles of this method are described in detail by Kreuzeder et al. (2013), Santner et al. (2012) and Williams et al. (2014). The chelating resin used in the DGT sensors here is a suspended particulate reagent–iminodiacetate (SPR–IDA)(CETAC Technologies Inc., USA) which has been previously identified as a suitable resin for high resolution 2D visualisation of metal supply owing to its capacity to bind trace metals and small resin bead size (Warnken et al., 2004). The SPR–IDA resin was supplied pre-cleaned as 10 mL of a 10 % (w/v) suspension. The 1.5 mL of the SPR–IDA resin suspension was mixed with 1.5 mL of a solution containing acrylamide (40%, Fisher Scientific, USA) and DGT cross-linker (DGT Research, Ltd., UK) in a ratio of 4:1.

To this 3 mL mixture, 21 μ L of ammonium persulfate (Merck, Germany) and 20 μ L of N,N,N,N-tetramethylethylenediamine (TEMED, ~99%, Sigma-Aldrich, USA) were added. The gel mixture was then immediately pipetted between two glass plates, where a 0.25 mm spacer was used to ensure that the solution polymerized into a gel sheet with a uniform thickness. The glass plate assembly was then placed in a 45°C oven for 1 h, after which the glass plates were separated and the resin gel was placed into 0.5 L of ultrapure water (filtered by Millipore, 18.2 M Ω) and allowed to fully hydrate for a minimum of 24 h. The hydrating solution was changed four times in the subsequent 72 h after which the resin gel was stored in 0.5 L of 0.05 M NaNO₃ solution. Before deployment, the resin gel sheet was cut down to suitably sized sections using PTFE-coated razor blades and then mounted between a 10 μ m-thick polycarbonate filter membrane (Nucleopore, Whatman, 0.4 μ m pore size) on one side and a sheet of cellulose acetate (OfficeMax New Zealand Ltd.) on the other to exclude solid particles from the soil and to help manipulate the gels. To minimize contamination, all

preparation and processing of gels was carried out using ultraclean trace metal techniques ensuring that all equipment were acid-washed and rinsed in double de-ionized water (DDI, 18.2 M Ω resistivity).

DGT sampling was performed after 6 weeks of plant growth, when the plants had fully developed cluster roots. For applying the DGT gels, the rhizotrons were laid horizontal with the removable front plate facing upwards. The root structures of interest were mapped onto a sheet of clear cellulose acetate which would then act as a template for the subsequent accurate location for the DGT gels on the root structures of interest. The soil in the rhizotrons was progressively saturated with water over 24 h by allowing water to gently infiltrate. Three hours after the beginning of the light cycle, the front plate was carefully removed and a small amount of water was added until an even thin film of water was visible at the soil surface. The cellulose acetate-DGT-filter assembly was taped on four sides onto the previously drawn template leaving a well-defined window of Nucleopore filter to allow diffusion of solute into the DGT. The DGT was then carefully applied on to exposed rhizosphere ensuring good and consistent contact between the soil and the measurement window across window area. The front plate was then placed over the measuring gels to provide gentle and even pressure. The DGT gels were deployed for 24 h starting at 3 h after the start of the light cycle. After the deployment, the DGT gel assembly was gently peeled off the rhizosphere interface and any soil particles attached to the assembly were removed using a combination of clean laboratory tissues and a steady stream of DDI water. The exposed areas of the deployed DGT gels were then cut away from the assembly using PTFE-coated razor blades, separated from the filter paper and stored horizontally in acid washed zip-lock polyethylene bags at 6°C for no longer than one week. The gels were then dried using the protocol described by (Stockdale et al., 2008) and mounted flat onto glass slides using double-sided tape.

9.3.6 Laser ablation ICP-MS

The standards for the laser ablation ICP-MS (LA-ICP-MS) analysis were the same standards as used by Hoefer et al. (2015). Preparation and analysis is described briefly here, for further details we refer the reader to Hoefer et al. (2015). Resin gel discs (2.5 cm diameter) were cut out of the SPR-IDA resin gel sheets and assembled with a 0.08 cm diffusion layers and a 0.45 μm pore size membrane filters (Supor 450, Pall Corporation, New York USA) within standard DGT polycarbonate housings (DGT Research Ltd., UK). These DGT units were immersed in triplicate into well-stirred solutions containing Mn, Cu, Zn, Cd and Pb at concentrations of 0.01-17.1 mg/L for 4, 8 and 20 h. The immersion solutions were prepared by dissolving *p.a.* grade nitrate and chloride salts of these elements in 3 L of DDI water containing 1 mmol/L NaNO_3 . The pHs of the immersion solutions were 5.6. After the probe specific deployment times, the samplers were retrieved, disassembled and the central resin gel area was cut out using a 20-mm diameter polypropylene stencil. The cut-away resin was cut into two even halves and each half was weighed to confirm the volume of the gel being eluted. One half of each gel replicate was eluted for 24 h in 2 mL 1 mol/L HNO_3 (*p.a.* grade, Sigma Aldrich, Vienna, Austria) and then analyzed using ICP-MS. The eluent concentration was used to calculate the mass of metal bound by per unit area of resin gel based on the metal-specific elution efficiencies reported in Warnken et al. (2004). The other half of each replicate was dried onto a 0.45- μm membrane filter for LA-ICP-MS analysis.

The mass of trace metals bound by the standard and the sample DGT gels was analyzed using laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) using a UP 193-FX (ESI, NWR Division, CA, US) laser ablation system coupled to a NexION 350D ICP-MS (Perkin-Elmer, MA, USA). Prior to analysis, the performance of the ICP-MS was confirmed by carrying out a standard performance test in solution mode confirming optimum sensitivity for ^{114}In and minimal formation of oxides and doubly charged ions in the plasma.

The LA-ICP-MS analysis was carried out in line scan mode with a laser beam diameter of 150 μm , scanning speed of 200 $\mu\text{m s}^{-1}$, laser pulse frequency of 20 Hz and a laser energy output of 40% (resulting in an approximate fluence of 4.35 J cm^{-2}). The ICP-MS was set to detect for the following analytes: ^{13}C , ^{58}Fe , ^{55}Mn , ^{63}Cu , ^{66}Zn , ^{111}Cd and ^{208}Pb . The dwell times of the analytes considered were adjusted to provide sufficient precision for a representative signal for each analyte, this resulted in an ICP-MS analysis time of 0.383 s per reading, giving an along-the-line resolution of 76.6 μm . ^{13}C is naturally part of the gel matrix and was used as the internal standard in line with previous laser ablation work involving DGT resin gels (Gao and Lehto, 2012; Lehto et al., 2012).

The standards were analyzed in line scan mode by ablating a single 1 mm line (total of 132 readings) in each of the seven standards. For every reading, the metal (M) signal was normalized to the internal standard (IS) signal. The mean normalized signals (M/IS), combined with the analyte mass determined in the eluted standard disc halves, were used to quantify the metal loading on the sample gels.

Following the calibration, specific areas of each sample gel were analysed using the same instrument settings as for the standards used in the calibration. The line scan was run using a 500 mm interval between the centres of adjacent lines (inter-line spacing of 350 mm). All signals were corrected with corresponding gas blank values. The mean normalized M/IS signals allow the analysis of relative differences in supply of metal to the DGT across the area of analysis (Williams et al., 2014). Where calibrated, the M/IS signals could be related to metal fluxes. Due to the difficulty in preparing Fe standards, we were unable to calibrate the signal to obtain a mass; however the M/IS relationship is directly proportional to the mass bound by the DGT resin (Williams et al., 2014). Data processing was done in MS Excel and the visualization was performed using an open source imaging software (ImageJ, National Institute of Health, Maryland, US. Available to download at <http://rsbweb.nih.gov/ij>).

9.3.7 Statistical analysis

The results are presented as means of at least three replicates \pm standard deviation (SD). Statistical analysis was performed using Statgraphics (Statpoint technologies, INC., Warrenton, VA, USA). Data were analysed by analysis of variance (ANOVA), and means were compared using the Student–Newman–Keuls (SNK) test at $P < 0.05$ to determine the significance of differences found.

Multivariate analyses were carried out by using STAT Graphic Centurion XV, version 15.1.02. The validity of the Principal Component Analysis (PCA) models were assessed by the cross-validation approach described by Bro et al. (2008).

9.4 Results

9.4.1 Pot experiment—Ca(NO₃)₂-extractions

Soil pH was measured at harvest after 6 weeks of plant growth (Table 9.2). Lime treatments significantly increased soil pH, from 5.98 in T1 to 7.50 in T7 in Pukekohe soil and from 6.62 to 7.18 in Levin soil. Unexpectedly, shoot biomass was not affected by lime treatments (Table 9.2).

Table 9.2 pH of the Pukekohe and Levin soils treated with increasing lime concentrations (T1-T7) measured at harvest and shoot dry biomass (d.w.) of lupin plants expressed in g; mean \pm SD (n=3).

Treatment	Pukekohe		Levin	
	pH ^{***}	Shoot d.w. ^{ns}	pH ^{***}	Shoot DW ^{ns}
T1	5.98 \pm 0.05 ^d	0.88 \pm 0.07	6.62 \pm 0.06 ^c	0.56 \pm 0.06
T2	6.37 \pm 0.12 ^c	0.71 \pm 0.17	6.96 \pm 0.01 ^b	0.67 \pm 0.20
T3	6.93 \pm 0.17 ^b	0.73 \pm 0.14	7.01 \pm 0.04 ^{ab}	0.58 \pm 0.05
T4	7.15 \pm 0.03 ^b	0.78 \pm 0.09	7.07 \pm 0.04 ^{ab}	0.35 \pm 0.26
T5	7.42 \pm 0.01 ^a	0.82 \pm 0.08	7.07 \pm 0.07 ^{ab}	0.59 \pm 0.32
T6	7.47 \pm 0.03 ^a	0.73 \pm 0.06	7.15 \pm 0.04 ^{ab}	0.46 \pm 0.18
T7	7.50 \pm 0.04 ^a	0.80 \pm 0.05	7.18 \pm 0.14 ^a	0.59 \pm 0.06

Ns = not significant, ***p<0.001

Plants grown on Pukekohe soil had almost 30% higher dry shoot biomass than plants grown on Levin soil, most likely due to the different texture of the two soils. Here we consider the Ca(NO₃)₂-extractable trace element fraction to be representative of the plant-available fraction (Black et al., 2011). The Table 9.3 shows the Ca(NO₃)₂-extractable trace element fraction of Pukekohe and Levin rhizospheric soils treated with different lime concentrations. Considering the Levin soil, significant differences were found only for Mn, Ni and Mg concentration, which decreased with increasing lime concentrations. The Ca(NO₃)₂-extractable concentration of elements was more affected by lime treatments in Pukekohe soil. For instance, P, K and Cu, increased by 16, 20 and 30%, respectively, comparing the control with the highest lime concentration. In contrast, Mn, Zn and Ni were significantly reduced by 98, 70 and 90%, respectively. Iron represented the only exception since its extractable concentration was not affected by the lime treatment in either soil.

The contrasting elemental behaviors induced by the lime treatments were also delineated in the pattern recognition techniques, such as PCA (Figure 9.1A). The micronutrients Mn, Zn, Fe and

Cu together with Ni are the main drivers in separating the different lime treatments along the first component (58% of total variance), whereas Na, Mg and P accounted for the different clusters according to the soil type, i.e. Pukekohe and Levin. Within the Pukekohe soil (Figure 9.1A), T1 and T2 could be distinguished from the treatments T3–T7. The concentrations of Mn, Zn and Ni decreased by 50%, 60%, 65%, respectively, between the unamended soil (T1) and 0.3 wt% lime application (T2) (Table 9.3). In the Levin soil, only Mn, Ni and Mg showed significant differences (Table 9.3) and did not allow a separation between the different lime treatments (Figure 9.1B).

The $\text{Ca}(\text{NO}_3)_2$ -extractable elemental compositions in the Pukekohe soil showed a clear clustering of the different lime treatments (Figure 9.1A); treatment 7 and 6 could be well distinguished from treatments 1, 2, 3, 4 and 5.

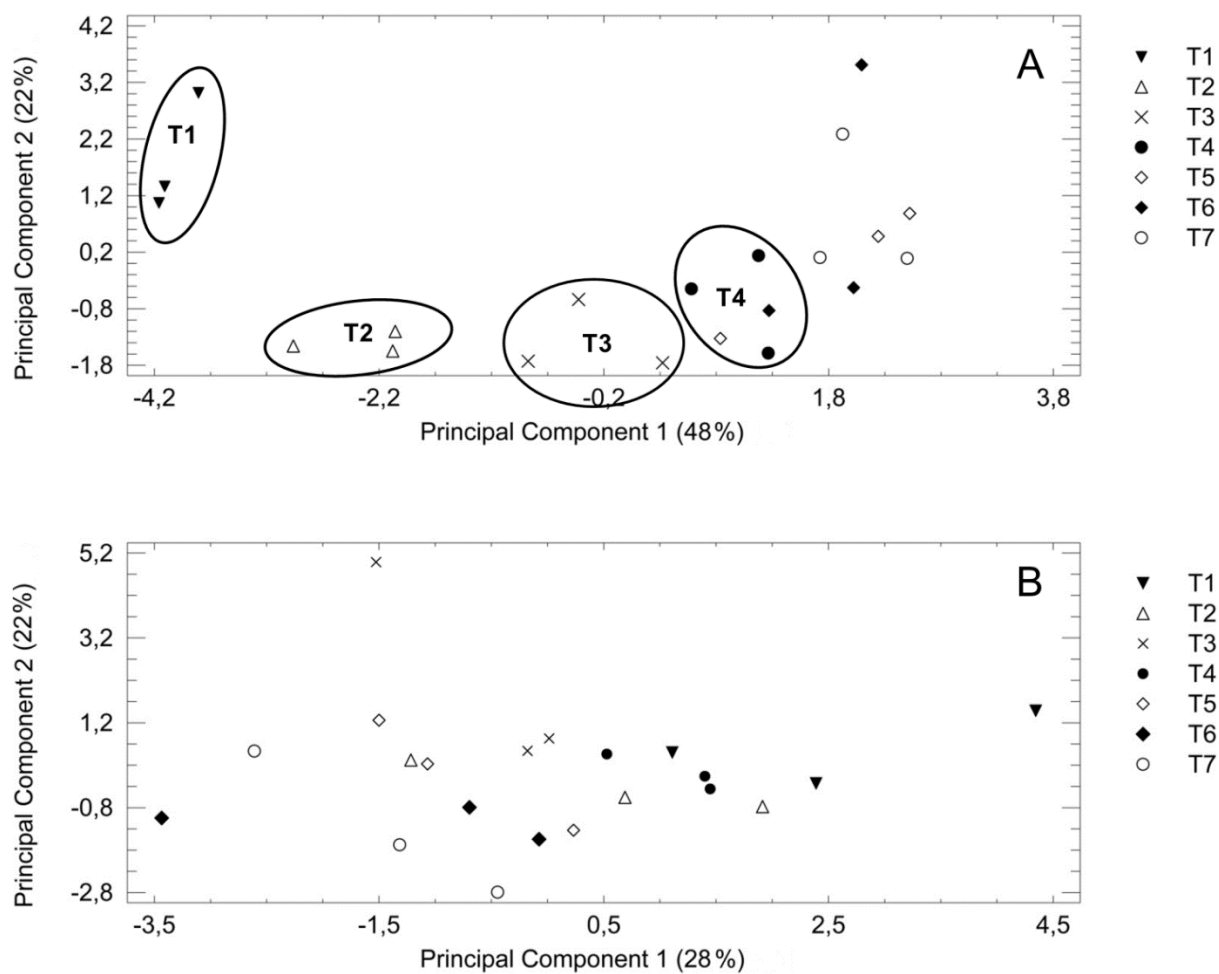


Figure 9.1 Score plots of the first two principal components obtained from the dataset of the mineral composition of the two rhizosphere soils Pukekohe (A) and Levin (B) obtained at the 7 treatments (T1: 0 wt%, T2: 0.3 wt%, T3: 0.6 wt%, T4: 1.3 wt%, T5: 2.5 wt%, T6: 5 wt%, T7: 10 wt%). Clustering of the distinguishable treatments are highlighted by circles.

No clustering of the lime treatments could be seen in the Levin soil, which was consistent with the $\text{Ca}(\text{NO}_3)_2$ -extractable concentrations of Levin rhizospheric soil shown in Table 9.3

Table 9.3 Ca(NO₃)₂-extractable metal fraction (mg/kg) in rhizosphere soils treated with different lime concentrations (T1: 0 wt%, T2: 0.3 wt%, T3: 0.6 wt%, T4: 1.3 wt%, T5: 2.5 wt%, T6: 5 wt%, T7: 10 wt%) expressed as mg/kg DW; mean ± SD (n=3).

Pukekohe	Fe^{ns}	P^{***}	Cu[*]	Mn^{***}	Zn^{***}	Ni^{***}	Mg^{***}	K[*]
T1	0.16 ± 0.03	3.11 ± 0.04 ^b	0.15 ± 0.03 ^{ab}	21.75 ± 1.63 ^a	0.28 ± 0.02 ^a	0.088 ± 0.010 ^a	155.97 ± 1.35 ^a	160.63 ± 5.85 ^b
T2	0.12 ± 0.03	2.77 ± 0.02 ^c	0.13 ± 0.01 ^b	10.19 ± 1.88 ^b	0.11 ± 0.03 ^b	0.034 ± 0.010 ^b	153.57 ± 1.33 ^a	185.35 ± 23.88 ^{ab}
T3	0.16 ± 0.05	2.97 ± 0.14 ^{bc}	0.11 ± 0.01 ^b	2.40 ± 0.85 ^c	0.03 ± 0.01 ^c	0.009 ± 0.003 ^c	143.34 ± 5.31 ^b	210.53 ± 20.76 ^a
T4	0.15 ± 0.05	3.18 ± 0.19 ^b	0.16 ± 0.04 ^{ab}	1.52 ± 0.35 ^c	0.03 ± 0.01 ^c	0.008 ± 0.003 ^c	137.97 ± 1.47 ^b	219.25 ± 31.96 ^a
T5	0.17 ± 0.03	3.56 ± 0.24 ^a	0.16 ± 0.03 ^{ab}	0.61 ± 0.03 ^c	0.02 ± 0.01 ^c	0.005 ± 0.003 ^c	127.16 ± 0.42 ^c	217.09 ± 6.58 ^a
T6	0.22 ± 0.15	3.60 ± 0.14 ^a	0.15 ± 0.02 ^{ab}	0.54 ± 0.05 ^c	0.03 ± 0.02 ^c	0.004 ± 0.006 ^c	121.27 ± 3.69 ^c	207.92 ± 10.77 ^a
T7	0.14 ± 0.05	3.70 ± 0.15 ^a	0.21 ± 0.04 ^a	0.61 ± 0.11 ^c	0.08 ± 0.05 ^{bc}	0.010 ± 0.002 ^c	115.13 ± 5.69 ^d	182.55 ± 12.95 ^{ab}

Levin	Fe^{ns}	P^{ns}	Cu^{ns}	Mn^{**}	Zn^{ns}	Ni[*]	Mg^{***}	K^{ns}
T1	0.17 ± 0.03	5.71 ± 0.35	0.18 ± 0.04	6.42 ± 1.38 ^a	0.03 ± 0.01	0.001 ± 0.005 ^{ab}	123.29 ± 1.32 ^a	97.85 ± 19.96
T2	0.21 ± 0.07	5.37 ± 0.12	0.19 ± 0.04	2.99 ± 0.89 ^b	0.02 ± 0.01	0.002 ± 0.000 ^b	109.55 ± 2.28 ^b	91.42 ± 14.63
T3	0.35 ± 0.15	5.40 ± 0.21	0.25 ± 0.08	2.75 ± 1.77 ^b	0.02 ± 0.01	0.008 ± 0.001 ^{ab}	109.26 ± 1.16 ^b	95.86 ± 6.53
T4	0.23 ± 0.03	5.49 ± 0.03	0.15 ± 0.01	4.34 ± 1.54 ^b	0.01 ± 0.00	0.000 ± 0.004 ^{ab}	105.99 ± 0.79 ^b	98.13 ± 4.23
T5	0.22 ± 0.10	5.51 ± 0.11	0.25 ± 0.07	2.17 ± 0.55 ^b	0.02 ± 0.01	0.004 ± 0.007 ^{ab}	102.23 ± 0.37 ^c	85.65 ± 8.59
T6	0.17 ± 0.03	5.28 ± 0.05	0.21 ± 0.07	1.54 ± 0.73 ^b	0.05 ± 0.05	0.012 ± 0.008 ^a	98.70 ± 0.29 ^d	82.71 ± 8.34
T7	0.16 ± 0.07	5.45 ± 0.16	0.24 ± 0.14	2.42 ± 0.31 ^b	0.01 ± 0.01	0.004 ± 0.002 ^{ab}	93.06 ± 3.60 ^c	71.21 ± 18.42

Ns = not significant, *p<0.05, **p<0.01, ***p<0.001

9.4.2 Pot experiment—Plant elemental composition

The measured elemental concentrations in lupin shoots indicate that the lime treatments strongly affected the uptake of micronutrients in both soils (Figure 9.2A and B), but to a different extent depending on the soil type. The variations of all the elements with increasing lime concentrations resulted significant in the Pukekohe soil, while only Fe, Mn, Zn and Ca lead to significant differences in plants grown in the Levin soil. Lime addition reduced the element uptake by almost 50-60 % in both soils with the only exception of Mn and Mo in the Pukekohe soil grown lupin plants, which were reduced by 75% and increased by 80 %, respectively.

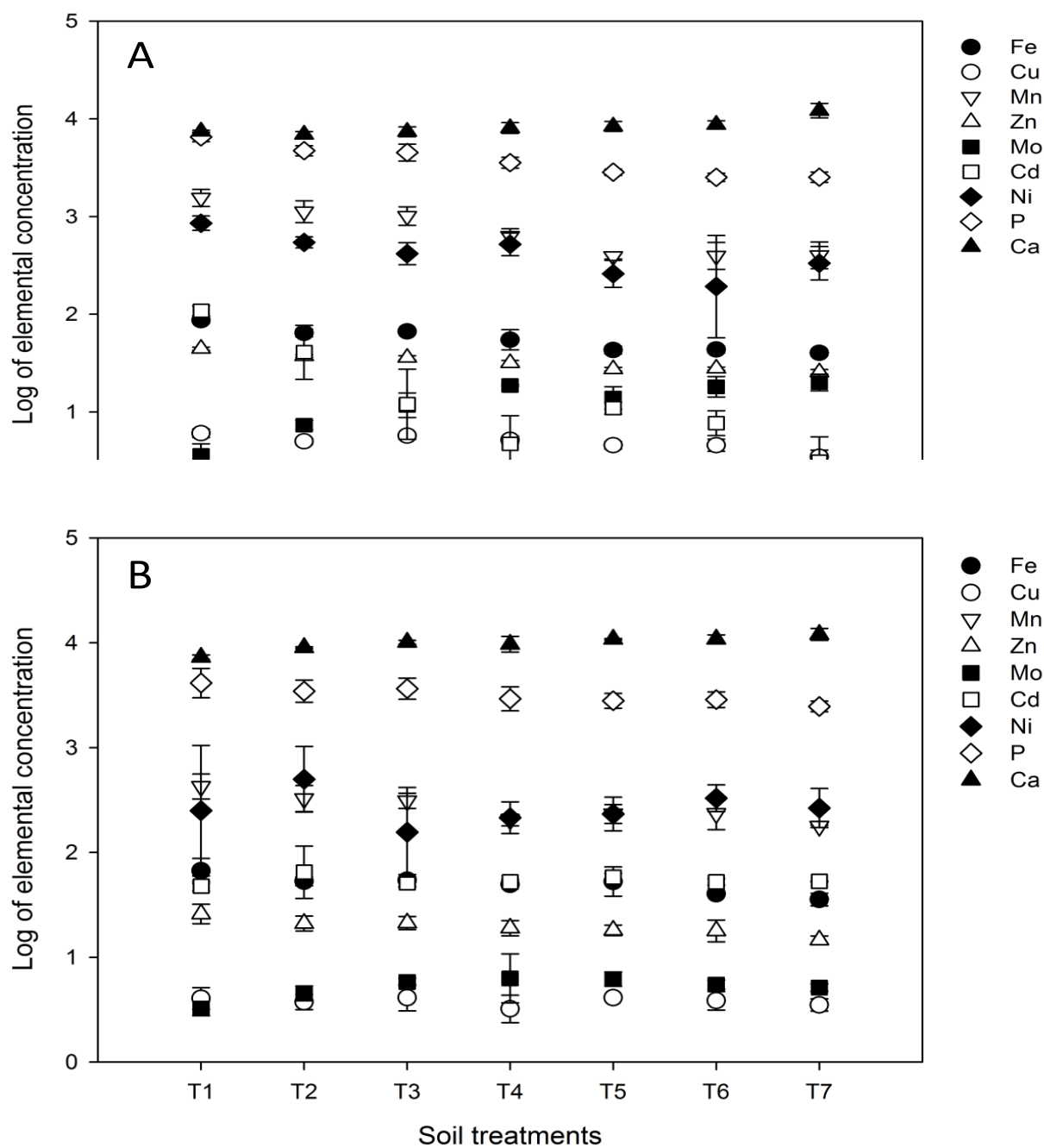


Figure 9.2 Elemental concentration expressed as logarithmic scale of shoots of white lupin plants grown in Pukekohe (A) and Levin soils (B) treated with different lime concentrations (T1: 0 wt%, T2: 0.3 wt%, T3: 0.6 wt%, T4: 1.3 wt%, T5: 2.5 wt%, T6: 5 wt%, T7: 10 wt%).

The elemental composition of white lupin shoots grown in Pukekohe and Levin soils were further analyzed by PCA (Figure 9.3A and B). As shown in Figure 9.3A, the different

treatments are separated along the first principal component which explains the 50% of total the variance. The samples of shoots grown in Pukekohe soil can be clearly clustered in seven groups which correspond at the different treatments. In particular clusters of T1, T4 and T7 are well separated from the other samples. This separation reflects the significant differences of the concentration of the elements in white lupin shoots. Regarding shoots grown in Levin soil, the PCA (Figure 9.3B), grouped the samples of the different treatments in separated clusters. However, the different clusters are not as well separated when compared to plants in the Pukekohe soil. While there was a clear separation between the control and the highest lime treatment, samples from the other treatments are not well distinguished, indicating that the increasing lime levels are not significantly affecting all the components or the plants are compensating for lime addition by mobilizing elements in the rhizosphere.

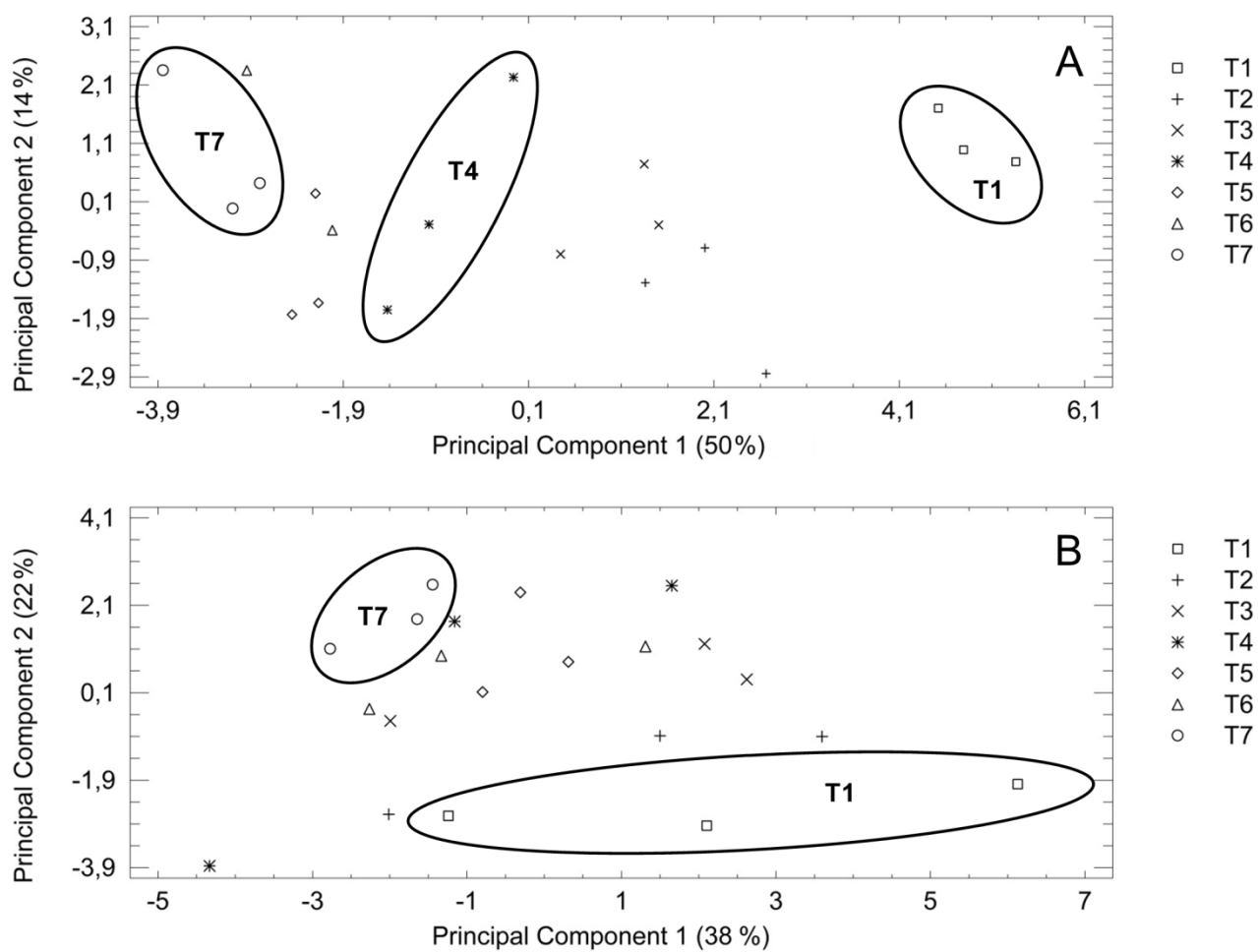


Figure 9.3 Score plots of the first two principal components obtained from the dataset of the elemental composition of white lupin shoots of plants grown in Pukekohe (A) and Levin (B) soils at different lime treatments (T1: 0 wt%, T2: 0.3 wt%, T3: 0.6 wt%, T4: 1.3 wt%, T5: 2.5 wt%, T6: 5 wt%, T7: 10 wt%). Clustering of the distinguishable treatments are highlighted by circles.

9.4.3 HR-DGT and LA ICP-MS analysis

Due to the chemical physical characteristics and to the significant differences of the $\text{Ca}(\text{NO}_3)_2$ -extractable fraction of rhizosphere soil and plant element concentration (Table 9.2, Table 9.3, Figure 9.1, Figure 9.3) caused by lime addition, the Pukekohe soil (T1, T4 and T7) was chosen for the rhizotrons experiment to investigate element bioavailability in response to different lime concentration on some selected root zones of white lupin. However, the high-resolution LA-ICP-MS analysis of the DGT gels (forthwith referred to as “HR-DGT analysis”) from the three treatments showed element mobilization in only the rhizosphere of the plant grown in the un-amended (T7) treatment (Figure 9.4), where a 21.67 x 23.50 mm area was analyzed at the location of a lupin cluster root.

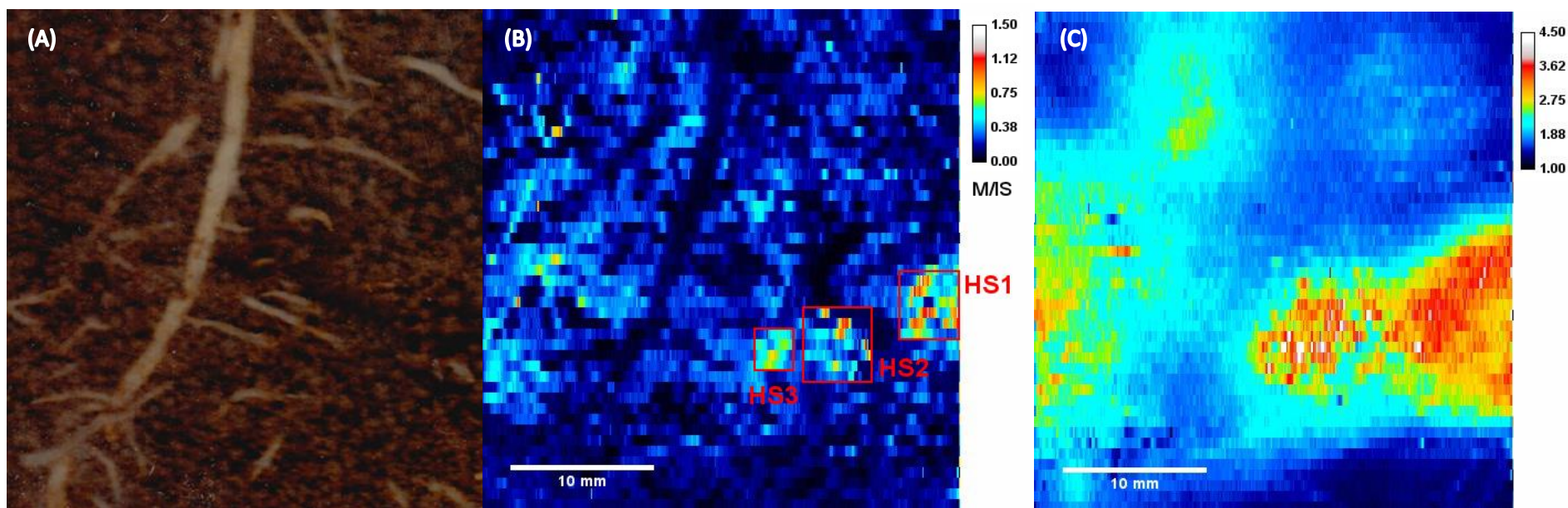


Figure 9.4 Selected white lupin cluster root for DGT deployment in T1 treatment (A) and a visual representation of Fe (B) and Mn (C) mobilization around obtained by HR-DGT; each pixel represents a discrete measurement point acquired using this method, where relative Fe flux to the DGT is represented by M/IS data; Mn flux is shown as $\text{pg}/\text{cm}^2/\text{s}$

In particular, three distinct areas of elevated Fe supply indicated as HS1, HS2 and HS3 in Figure 9.4 of element mobilization could be observed. These ‘hotspots’ were defined by measurement points showing Fe mobilization that was greater than two standard deviations of the measurements across the entire area of ablation (Figure 9.4). They are defined by 137, 59 and 62 unique measurements respectively (Table 9.4) and correspond to the location of the observed cluster root (Figure 9.4).

Table 9.4 Distribution of Fe, Cu, Zn, Pb and Mn taken up by the DGT gel in T1 treatment of Pukekohe soil (M/IS, M: metal of interest, IS: internal standard); mean \pm SD.

Area of interest	No. discrete measurements	Total area	Iron		Copper		Zinc		Lead	
			Average M/IS across area of interest	Maximum	Average Flux across area of interest	Maximum flux	Average Flux across area of interest	Maximum flux	Average Flux across area of interest	Maximum flux
Units		mm ²	M/IS	M/IS	pg/cm ² /s	pg/cm ² /s	pg/cm ² /s	pg/cm ² /s	pg/cm ² /s	pg/cm ² /s
Entire ablation area	13442	509	0.18 \pm 0.13	2.05	4.42 \pm 2.09	12.88	0.62 \pm 0.56	3.61	1.38 \pm 1.52	102.31
HS1	137	5.25	0.71 \pm 0.23	2.05	5.51 \pm 1.05	12.88	1.15 \pm 0.42	3.61	3.31 \pm 8.69	102.31
HS2	59	2.26	0.64 \pm 0.20	1.13	4.16 \pm 1.81	8.80	0.95 \pm 0.29	1.93	4.32 \pm 2.85	12.35
HS3	62	2.37	0.57 \pm 0.09	0.82	7.45 \pm 0.91	9.47	1.14 \pm 0.23	1.66	6.48 \pm 2.30	11.64
Manganese										
Area of interest	No. discrete measurements		Total area		Average Flux across area of interest			Maximum flux		
Units			mm ²		pg/cm ² /s			pg/cm ² /s		
Entire ablation area	13442		509		2.04 \pm 0.51			6.32		
HS1	685		26		3.40 \pm 0.36			6.32		

The Table 9.4 shows the distribution of Fe, Cu, Zn and Pb in the entire ablation area and in the three hotspots. The total area of these three hotspots is 1.95 % of the entire area of analysis. The relative average fluxes of Fe from the three hotspots was 3.9 (HS1), 3.5 (HS2) and 3.2 (HS3) times higher than the average Fe flux across the entire area of analysis. The areas of high Fe flux to the DGT can also be seen to broadly correspond to localized areas of high Cu, Zn and Pb fluxes. Cu and Zn were also detected in $\text{Ca}(\text{NO}_3)_2$ -extractable fraction of rhizosphere soil whereas Pb was below the limit of detection (LOD). Considered together, the average fluxes of Cu ($5.71 \text{ pg/cm}^2/\text{s}$), Zn ($1.08 \text{ pg/cm}^2/\text{s}$) and Pb ($4.70 \text{ pg/cm}^2/\text{s}$) measured by the HR-DGT within these three areas are 1.29, 1.74 and 3.40 times higher than the respective average fluxes of these metals across the entire area of measurement. In Table 9.4 are also present the data of a selected hotspot of Mn defined as before by the measurement points showing Mn fluxes greater than those in the bulk soil. The total area of this hotspot is 26 mm^2 in size and consists of 685 unique measurements (5.17% of the total area of analysis). The average flux across these points is $3.40 \text{ pg/cm}^2/\text{s}$ while the average flux across the entire area of analysis is $2.04 \text{ pg/cm}^2/\text{s}$ (1.66 times higher than the respective average flux across the entire area of measurement). For all five metals measured using this technique, the highest observed flux across the entire ablation area was found in HS1.

The masses of all of the cationic elements bound by DGT gels deployed on the other treatments were below the detection limits (not shown).

9.5 Discussion

9.5.1 Pot experiment— $\text{Ca}(\text{NO}_3)_2$ -extractions

The maximum addition of lime (10 % w/w) increased the pH by *ca.* 1.52 and 0.56 pH units in the Pukekohe and Levin soil respectively (Table 9.2), but this increase did not have any significant effect on the lupin shoot biomass (Table 9.2). This can be explained by comparing the plant-available fractions of the major macro-and micronutrient before and after lupin

harvest (Table 9.1 and Table 9.3, respectively). Considering treatment T1, *i.e.* both soils without lime addition, the concentrations detected in the $\text{Ca}(\text{NO}_3)_2$ -extractable rhizosphere soil solution at harvest were significantly decreased. For instance, in the Pukekohe soil, Fe was reduced by approximately 70%, Mn by 50%, Zn by 10% and Cu by 20 %. Despite this decrease, the plant-available concentration of these nutrients was still in the optimal range for plant growth (Kabata-Pendias, 2010). Iron for instance is one of the nutrients with the lowest solubility in soil usually resulting in soil solution concentrations of about 10^{-7} – 10^{-10} M over a pH range from 5.0 to 8.5 (Kraemer et al., 2006), a concentration too small for optimal plant growth. In the present study, despite plant uptake, the $\text{Ca}(\text{NO}_3)_2$ -extractable rhizosphere soil solution concentration of white lupin was in the range of 10^{-6} M, meeting both microbe (10^{-5} – 10^{-7} M) and plant (10^{-4} – 10^{-9} M) requirements (Lemanceau et al., 2009). White lupin are highly efficient plants in mobilizing nutrients thanks the excretions of organic acids, especially citric and malic acid (Neumann et al., 2000) from closely-spaced lateral rootlets arranged in clusters, the so-called “proteoid” roots. Previous studies showed that white lupin accumulates up to 50 ± 90 mmol of citric acid per g soil in the rhizosphere of cluster roots (Dinkelaker et al., 1989; Gerke et al., 1994), which is sufficient to desorb for instance P from sparingly soluble Ca-, Al- and/or Fe-P and from Fe/Al humic acid complexes by ligand exchange reactions and dissolution of P sorption sites (Gardner et al., 1983; Gerke et al., 1994). Peaks of labile P have also been detected in the depletion zones around *Brassica napus* roots and have been attributed either to organic acids or protons (Santner et al., 2012). In fact, in addition to the organic acid exudation, white lupin releases also protons acidifying its rhizosphere. This has been detected even in a well-buffered calcareous soils in pH ranges similar to the ones of the present study (around 7.50 at the maximum lime addition) dissolving acid-soluble Ca-P (Dinkelaker et al., 1989). Our results indicate that even with increasing lime addition, the plant-available P fraction increased significantly between the control and the 10 wt% lime application (Table

9.3), which agrees with previous studies that have demonstrated efficiency of white lupin in taking up P and utilizing soil phosphorus sources. Lupin root activity did not affect the availability of the other essential micronutrients as Mn, Zn and Ni which decreased with increasing lime content (Table 9.3)

. In well-aerated calcareous soils, the solubility of Mn decreases due to the adsorption of Mn on CaCO_3 , its oxidation on MnO_2 surfaces and, probably, to precipitation of Mn calcite (Jauregui and Reisenauer, 1982).

9.5.2 Pot experiment–Plant elemental composition

Regarding elemental concentration in lupin shoots, lime treatments strongly affected the uptake of micronutrients from both soils (Figure 9.2). In particular, Fe, and Zn concentration decreased significantly in both soils at increasing lime concentration, while Cu, Ni, Mn and Cd decreased only in the Pukekohe soil. These micronutrients were also the main elements contributing to the distinct clustering (Figure 9.3A) along the first component which accounted for 50.2% of the total variance. A decrease of Mn concentration as well as Zn and Ni could be a direct consequence of a decrease in the availability of these elements in the rhizosphere (Figure 9.3) even though the plants did not show any deficiency symptoms and biomass was not significantly reduced. Zinc ranged from 45 mg/kg in T1 to 25 mg/kg in T7 in white lupin shoots, (Figure 9.2), concentrations far above those reported for Zn deficient plants (10–20 mg/kg DW, (Boehle and Lindsay, 1969)). Even though the Mn concentration decreased with increasing lime addition, the concentrations in lupin shoots were high in all the treatments (ranging from 1400 mg/kg DW in T1 to 400 mg/kg DW in T7). This suggests that 0.05 M $\text{Ca}(\text{NO}_3)_2$ -extractable fraction of Mn did not accurately represent the Mn available to the white lupin plant in these treatments. White lupin is known to accumulate Mn in leaves (Zornoza et al., 2010). Reuter and Robinson (1997) and Martínez-Alcalá et al. (2009) have shown Mn concentrations as high as 1300 mg/kg DW and 4960 mg/kg DW in leaves and shoots

respectively. This high rate of Mn uptake is believed to be due to an increased secretion of organic acids into the plant's rhizosphere, which promotes the metal's solubilization and thus facilitates its uptake by the plant (Dinkelaker et al., 1995; Oliver et al., 1996). Manganese accumulation in lupin shoots is highest at low and zero lime levels indicating that at the higher liming rates the solubilizing effect of the organic acids might be neutralized by the high calcium carbonate of the soil, thus lowering the uptake.

Although Cd was below the detection limit in the $\text{Ca}(\text{NO}_3)_2$ extraction, the Cd concentration in the lupin shoots were significantly affected by lime treatment, with a decrease of 97% from T1 to T7 in the plants grown on the lime-treated Pukekohe soils. This is consistent with other studies that reported the effectiveness of liming to minimize the Cd uptake by plants (Oliver et al., 1996).

Organic acids play also a fundamental role in the reduction- based Fe uptake of white lupin as a *strategy I* plant, (Römheld and Marschner, 1983). However, while there was no change in the concentration of the available Fe in the rhizosphere of the soils with the different treatments (Table 9.3), Fe concentration in shoots decreased significantly ($P < 0.001$). However, the concentration of Fe in green plant tissues normally occurs at 50–100 mg/kg DW (Mengel and Kirkby, 2001). Only lime treatments $>2.5\%$ (w/w) lead in both soils to deficient conditions (<45 mg/kg). The discrepancy between the phytoavailable Fe concentration in the rhizosphere soil solution and the Fe concentration detected in lupin shoot analysis might be due to a methodological drawback. Even though calcium nitrate is commonly used to determine the phytoavailable fraction of elements, it might not be suitable for nutrients such as Fe. Many authors (de Santiago and Delgado, 2006; Gough et al., 1979; Menzies et al., 2007; Walsh and Beaton, 1973) asserted that caution should be used in formulating methods for the determination of the plant-available levels, yet an official and generally accepted method is still missing.

9.5.3 HR-DGT and LA ICP-MS analysis

The diffusive gradients in a thin film (DGT) technique is a valuable alternative to assess the phytoavailable fraction since it represents a well-established in situ, time-integrated, passive sampling method that is designed to accumulate labile cationic and anionic species (Zhang and Davison, 1995). Mimicking a plant root, DGT takes up elements from the soil solution and induces resupply from the solid phase (Lehto et al., 2006) and thus provides valuable data on spatial differences in metal bioavailability when used to provide 2D measurements. In the present study DGT gels were deployed on root tips and cluster roots of white lupins grown in rhizotrons. The HR-DGT showed metal mobilization only at the location of a cluster root of the plant grown in the un-amended (T1) treatment (Figure 9.4). In the lime treatments, all analytes were below the detection limits of LA-ICP-MS analysis. A similar trend was observed in the data obtained with the $\text{Ca}(\text{NO}_3)_2$ extraction of rhizosphere soil (Table 9.3) considering Mn, Cu and Zn. Iron on the other hand, showed a different trend. Its concentration did not seem to be affected by lime addition observing the calcium nitrate extract, but could not be detected by HR-DGT analysis of the white lupin rhizospheres in T4 and T7. As previously mentioned, calcium nitrate extraction might not be the most appropriate method to determine Fe availability. This method relies on cation exchange, whereas normally Fe tends to form insoluble species that this extraction method is unlikely to measure; hence no significant changes could be observed in extractable Fe despite the big decrease in plant uptake.

The plant appears to have a highly localized means of mobilizing Fe (despite it is not appearing to be very extractable) as shown by the HR-DGT data, but only without lime. The extent of the exudation-induced rhizosphere effect depends in fact strongly on the soil buffering capacity. For instance, it has been shown that the extent of the acidification by chickpea decreases from several (15% CaCO_3) to almost zero mm (60% CaCO_3) with increasing concentrations of CaCO_3 in the soil (Neumann and Römheld, 2012). Yet, the extent of this effect is most likely

related to the type of carbonate, i.e. active or total. Usually high lime concentrations are needed to neutralize the root activity, whereas in the present study low concentrations as 1.25% were sufficient to completely suppress the available fraction of Fe below the level where it could be observed by the DGT. However, we can hypothesize that the fine powdery laboratory grade lime used in this experiment can be considered almost 100% active and was able to react immediately with the soil, in contrast with common agricultural lime, which takes more time to react with the soil because constituted by particles with a larger size.

The DGT gel was deployed early in the plant's light-dark cycle to ensure that effects of one cycle of exudation by the roots of the white lupin on the rhizosphere soil were recorded. Previous studies showed that the release of citrate in white lupin follows a diurnal rhythm with a peak of exudation after 5 h of the onset of light (Tomasi et al., 2009). The observed co-mobilization of Cu, Zn and Pb with Fe at the location of the cluster root indicates that similar mechanisms are acting on these metals. Some authors reported that white lupin is able to increase the availability of Cu and Zn (Braum and Helmke, 1995; Dessureault-Rompré et al., 2006; Duffner et al., 2012; Martínez-Alcalá et al., 2010) through the action of root exudates in the rhizosphere. Braum and Helmke (1995) also showed that soybean intercropped with *L. albus* had greater uptake rates of Cu, Fe, and Zn when compared to soybean grown alone. Martínez-Alcalá et al. (2009) found an overall decrease in the EDTA-extractable fraction of Pb, Zn and Fe in the rhizosphere soil of *L. albus* L. They attributed this decrease to the precipitation of Fe into iron oxyhydroxides which also immobilized the Pb and Zn; however, it should be noted that the soils used for their study had a considerably higher pH (7.86) than those considered here, which would be expected to promote the precipitation of Fe into insoluble minerals and the co-precipitation of other trace elements. Furthermore, high-resolution analyses of plant-induced rhizosphere changes are more likely to provide a better

representation of small-scale trace element mobilization at the plant-root interface than methods where bulk samples of rhizosphere soils are considered (Hinsinger et al., 2005).

A clear hotspot at the location of the selected cluster roots can be observed also for Mn (Figure 9.4c). In fact the average flux of Mn across the area defined as the hotspot is ca. 75% higher compared to the entire ablation area confirming a higher mobilization of the element in this highly localized part of the white lupin rhizosphere. This observation indicates that highly localized exudation processes occurring in the rhizosphere of white lupin may be important factor in this plant's ability to mobilize this element (Dinkelaker et al., 1995; Martínez-Alcalá et al., 2009; Page et al., 2006).

While the ability of white lupin roots to mobilize trace elements nutrients can be beneficial for the plant, the root exudates may also mobilize toxic metals, such as Pb. Yet, Pb could only be detected by HR-DGT and was below the LOD both in lupin shoots and in the $\text{Ca}(\text{NO}_3)_2$ -extractable rhizosphere soil solution most likely due to a dilution during the extraction. Previous studies have found that while the roots of white lupin can take up Pb, it is highly immobile within the plant (Kabata-Pendias, 2010; Martínez-Alcalá et al., 2009) and therefore plant uptake of this metal is unlikely to present a significant risk to human and animal health. However, the mobilization of other metals, that are relatively easily translocated from roots to shoots, such as Cd, Co, Mo and Se, could theoretically pose a threat when present in sufficient concentrations in soils; however, this is unlikely to be an issue in the soils considered here.

9.6 Conclusion

We found that lime treatment affected both the solubility of $\text{Ca}(\text{NO}_3)_2$ -extractable elements and their plant uptake even though HR-DGT was not able to detect any mobilization when CaCO_3 was added to the soil at a rate ≥ 1.3 wt%. Yet, plants grown in the pot trials using lime treated soils showed that there was sufficient trace element uptake to avoid nutrient deficiency. While we could not detect nutrient mobilization at the lupin root structures HR-DGT in these

cases, we cannot rule out the possibility that root exudates are still present but their ability to mobilize nutrients to a level where they can be detected by HR-DGT is buffered by the lime. Furthermore, lupin shoot elemental concentrations reflect the nutrient uptake through the whole root system whereas HR- DGT was applied only on selected cluster roots. Different areas of the rhizosphere or at the best the whole root system should be investigated by HR-DGT. Longer DGT deployment on root zones might provide further information to overcome the limitations of the method detection limit, especially under circumstances where the availability of nutrients by DGT is reduced by high levels of lime.