Eidgenössische Technische Hochschule Zürich
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In situ fixation of cadmium in New Zealand pastureland using lignite as a fixing additive

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Master Thesis

Lincoln (NZ), April 2012

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Acknowledgements

Firstly I would like to acknowledge the invaluable assistance of my supervisor at Lincoln University in New Zealand, Prof. Brett Robinson. His knowledge and advice made my master thesis a success. I appreciated the time we spent most mornings drinking coffee and discussing our research. He always left space for my own ideas and helped me to develop them. He encouraged me from the start to aim at publishing this work in a peer reviewed journal which gave me a lot of enthusiasm.

I would also like to thank Prof. Rainer Schulin, my supervisor at ETH Zürich, for carefully going through the manuscript and giving me helpful feedback. Furthermore I would like to acknowledge his effort arranging the contact to Prof. Brett Robinson and giving me the opportunity of writing my master's thesis abroad.

I would especially like to mention Lisa Ciadamidaro for her great help in the lab and greenhouse, particularly her time spent helping me harvest, weigh and grind samples.

I am grateful for assistance and advice by:

Lynne Clucas for introducing me to the labs and conducting numerous ICP-OES measurements, René Reiser for sampling and characterising Soil 2 - 6, Dharini Paramashivam for measuring cation exchange capacity of lignite and Tasha Shelby for proofreading the manuscript.

Last but not least I would like to thank my friends and flatmates here in New Zealand for the wonderful, unforgettable time we spent together. I will definitely miss you!

Contents

Abstract

Cadmium (Cd) is a toxic heavy metal that accumulates in New Zealand (NZ) pasture soils through the repeated application of phosphate fertilisers that contain up to 280 mg Cd/kg P. Cadmium in soil is readily taken up by plants and presents a human health risk. Food safety standards limit the concentration of Cd in foodstuffs. Exceeding these standards may result in trade restrictions and economic damage for producers. Risk-mitigation technologies mainly focus on limiting the soil-plant transfer as there is no viable technology to remove Cd from the mineral P fertilisers or pasture soils. *In situ* fixation using a low-cost amendment may transfer Cd to a form that is unavailable for plant uptake. Previous studies showed that adding lignite (brown coal) to heavily contaminated soils effectively rendered Cd less bioavailable to plants. I aimed to determine whether lignite could reduce Cd solubility and phytoavailability in NZ pasture soils with fertiliser-borne Cd levels of 1 - 2 mg/kg. In batch sorption experiments, I tested the capacity of lignite and lignite-soil mixtures to sorb Cd at biologically relevant Cd concentrations. Furthermore, the dependency of Cd (ad)sorption on pH and Cd loading was investigated. In greenhouse experiments, I tested the effect of lignite on the accumulation of Cd and other elements by perennial ryegrass, *Lolium perenne.* The batch experiments revealed that over a pH range of 4 - 7, Cd sorption by lignite was 1 - 2 orders of magnitude greater than by a pasture soil containing 2% carbon. The addition of 5 wt% lignite to a range of soils showed that lignite addition was most effective in reducing soluble Cd in soils with low pH. The addition of just 1 wt% lignite to the aforementioned pasture soil reduced plant Cd uptake by 30%, without adversely affecting biomass or the uptake of essential nutrients. In contrast to Cd, this lignite treatment had no significant effect on the uptake of Cu and Zn by ryegrass. This may be due to preferential binding of Cd to organic S, which appears to be the dominant type of metal-binding groups added to the soil with the application of lignite.

1. Introduction

1.1 Cadmium – a toxic heavy metal

Cadmium (Cd) is a naturally occurring heavy metal that is not essential for life. At high concentrations it is toxic to organisms, mainly due to the ability to react with sulphydryl groups resulting in enzyme inhibition [1]. Cadmium in soil is readily taken up by grass and crops leading to an accumulation in fodder and food products and subsequently in animals and humans [2]. Its phytoaccumulation is primarily a concern for human health; Cd phytotoxicity is lower than for many other non-essential elements [3]. Most Cd enters the human body via food and smoking [2]. Common toxicity symptoms occur after chronic exposure; acute human toxicity is rare. The toxicity is partly due to the long half-life of Cd in mammalian systems (15 years in human kidneys [4]). 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 kidney and prostate), skeletal deformation and low reproductive function [1].

Anthropogenic sources of Cd are important in determining the total Cd concentration in soils. Cadmium enters agricultural soils via soil amendments, particularly phosphate fertiliser and biosolids, as well as from atmospheric deposition [5]. In soil, Cd binds strongly to organic matter, metal oxides and clay minerals. Continuous anthropogenic Cd inputs to soil are usually not balanced by leaching and crop harvest and consequently Cd accumulates in soil. Enrichment of Cd in soils has been reported worldwide [1, 6, 7].

Pastureland in New Zealand covers 13.8 million hectares and carries approximately 46 million sheep, 5 million beef cattle, 4 million dairy cattle and 2 million deer. Pasture farming is the main form of animal production and the main type of farming in New Zealand [8]. Several authors reported enrichment of Cd in New Zealand's pasture soils [9-14]. In a NZ soil survey, Taylor et al. (2007) reported an average Cd concentration in pasture soils of 0.43 mg/kg (N = 825). This is more than double the background concentration of 0.16 mg/kg (N = 372) [14]. The main sources of Cd in these soils are phosphate fertilisers containing Cd as an impurity that originates from the phosphate rock used for their production [8]. Pastoral farming in New Zealand is dependent on such mineral P fertilisers as the potential for re-cycling domestic organic P wastes is small [15] and P is typically a fertility constraint in pastureland [8]. There is no viable method to remove Cd from these fertilisers [16]. An in-depth review of Cd levels, sources and accumulation can be found in Chapter 2.1.

New Zealand has no Cd soil guideline value for agricultural soils. There is a guideline for maximum soil Cd concentration for the disposal of biosolids to land of 1 mg/kg soil [17]. This value has sometimes been adopted for agricultural land [10]. Currently, Soil Guideline Values (SGVs) are being developed as a National Environmental Standard [18].

Grazing animals take up most Cd via consumption of plants; intake through soil ingestion is generally lower [8]. Lee et al. (1996) investigated the accumulation of Cd in grazing sheep, which are known to take in soil at comparably high rates. They found that soil intake accounted for < 2% of total Cd

intake in summer and for up to 27% in winter [19]. Cadmium is accumulated in mammalian tissues, especially the liver and kidney [8]. Cadmium in food produced in New Zealand does not pose a risk to human health and is also not expected to do so in the near future [2]. Nevertheless, there is a risk that Cd concentrations in certain products might exceed food safety standards (see Table 1). Of major concern are offal products and certain vegetables [2]. To date, kidneys from sheep older than 2 years are routinely condemned since testing revealed that a high proportion exceeded the New Zealand Maximum Residue Level (MRL) for Cd of 1 mg/kg in offal for human consumption [13]. Exceeding food standards of overseas partners might restrict international trade [2]. Therefore, protectionist governments might use food safety standards as a non-tariff trade barrier [20].

Table 1: Maximum levels of Cd in food products according to the *Australian New Zealand Food Standards Code (Standard 1.4.1.) [21].*

Product	Maximum level (mg/kg)
Chocolate and cocoa products	0.5
Kidney of cattle, sheep and pig	2.5
Leafy vegetables	0.1
Liver of cattle, sheep and pig	1.25
Meat of cattle, sheep and pig (excluding offal)	0.05
Molluscs (excluding dredge/bluff oysters and queen scallops)	2
Peanuts	0.5
Rice	0.1
Root and tuber vegetables	0.1
Wheat	0.1

1.2 Remediation

Most *in situ* technologies to remediate Cd-contaminated soils were developed to remediate highly metal-contaminated sites, such as mine spoils. The objectives of such technologies are to 1) reduce metal leaching, 2) reduce metal bioavailability to humans and ecological receptors and 3) re-establish vegetation [22]. Metal concentrations in pasture soils are not comparable to those in highly metal-contaminated soils, even after long-term fertilisation. The objectives of a risk-mitigation technology for fertiliser-derived Cd in agricultural soils are therefore different to those targeting contaminated sites. In agricultural soils, Cd leaching is usually not an issue as Cd is strongly bound to the soil matrix. Plant growth is usually unaffected as phytotoxicity occurs at higher Cd concentrations. The main objective is to reduce Cd uptake and accumulation in pasture and thereby reduce bioavailability to grazing animals and eventually to humans.

For agricultural soils, a suitable risk-mitigation technology must be viable over large areas. This requires that the technology has a low cost per area and leaves the soil fertile. Potentially, *in situ* fixation may fulfil these requirements. By applying a fixing additive to soil, Cd is transferred to a form that is unavailable for plant uptake. Numerous low-cost and environmentally safe organic (e.g. leaves, bark sawdust, peat) and inorganic (e.g. lime, hydroxyapatite) soil amendments effectively reduce the phytoavailability of Cd [23].

1.3 *In situ* fixation using lignite

Organic matter can form insoluble organometallic compounds and render Cd less bioavailable to plants. Therefore, organic matter can be used for the *in situ* fixation of Cd [24]. Lignite (brown coal) is discussed as a source of soil organic matter to improve soil fertility in degraded soils that are low in organic matter [25] and as a fixing additive in remediation of metal-contaminated soils [24, 26, 27].

The prevalent mechanism by which metal ions are sorbed to lignite is ion exchange, but specific adsorption also plays a role [28]. Cation exchange capacities (CEC) from 40 to 400 meq/100g are reported for various lignite samples [28-31] whereas the CEC of soil organic matter ranges in the order of 100 to 300 meq/100g [6]. Lignite contains large amounts of humic and fulvic acids [32] that have similar properties to their equivalents in soil [25]. Lignite has many carbonyl (C=O), carboxyl (COOH) and hydroxyl (OH) groups [32]. Carboxyl and hydroxyl groups are the main functional groups participating in ion exchange. Carboxyl groups in humic acids increasingly dissociate between pH 2.5 and 7 and phenolic groups between pH 8 and 13.5. Therefore, the number and type of negatively charged functional groups (COO^- and O^-) available for ion exchange is dependent on the pH value of the surrounding solution [33]. Under oxidising conditions, the density of oxygen bearing functional groups increases [34]. To increase the immediate effectiveness, lignite can be partially oxidised prior to its application to soil [35]. This indicates that the weathering of lignite in soil may result in an initial increase in the amount of functional groups available for ion exchange.

The surface area of dry coal particles is 5 m^2/g and 170 m^2/g obtained with N_2(g)-BET and CO_2(g) respectively. The surface area of hydrated coal is in the order of 1000 m^2/g [36]. Both the large specific surface area and the high concentration of carboxylic and phenolic groups (5 - 7 mmol/g) are likely to account for the capacity of lignite to sorb metals [36]. As Cd is a chalcophile, it is expected to bind to organic S groups [1], R-SH, R-S-R, R-SS-R and heterocyclic S, which are present in lignite in small quantities [37]. Such binding may be important at low, biologically relevant Cd concentrations, typical for low to medium level polluted agricultural soil (e.g. Taylor (2007) [14]). The organic S concentration may partially determine the selectivity of lignite to adsorb Cd over the geochemically similar element Zn as Cd has a stronger affinity to S than Zn [1]. Impregnation of coal with sulphydryl groups is discussed as a pre-treatment to improve metal sorption properties [38].

Batch sorption experiments revealed that lignite, oxyhumolite and leonardite can effectively sorb Cd from aqueous solution [28-30, 33, 36, 39-42]. Oxyhumolite is post-sedimentary oxidised lignite that occurs at the surface of lignite deposits [43]. Similar types of coals from other locations are called leonardite [42]. Table 2 contains information on the sorbent materials, the experimental conditions

and the findings regarding Cd sorption of these studies. The aim of such studies was to investigate the possible application of low-rank coal as sorbent for the removal of Cd from contaminated natural waters or industrial wastewater. Lignite samples were exposed to water with relatively high concentrations of Cd and the ratio between mass of Cd spiked to mass of sorbent was > 1000 mg/kg in all studies [28-30, 33, 36, 39-42]. Therefore, these studies are not representative for agricultural soils with Cd concentrations typically ranging to at most a few mg/kg [5].

Other studies investigated the effect of lignite addition to soil on the solubility and phytoavailability of Cd. Janos et al. (2010) studied the fractionation of Cd after lignite and oxihumolite addition using a standardised sequential extraction test (BCR test) described by Janos et al. (2004) [44]. The results are shown in Figure 1. The fractions "acid extractable" and "bound to Fe/Mn oxides" are considered most mobile or mobilisable and easily bioavailable. The sum of these fractions increased when soil was blended with 1 wt% lignite but was lower than in the untreated soil when 3 wt% or 5 wt% lignite was mixed to the soil. Treatment with 1 wt% or 3 wt% oxihumolite decreased this mobilisable fraction ("acid extractable" and "bound to Fe/Mn oxides") whereas treatment with 5 wt% oxihumolite led to an increase in the respective fraction [45].

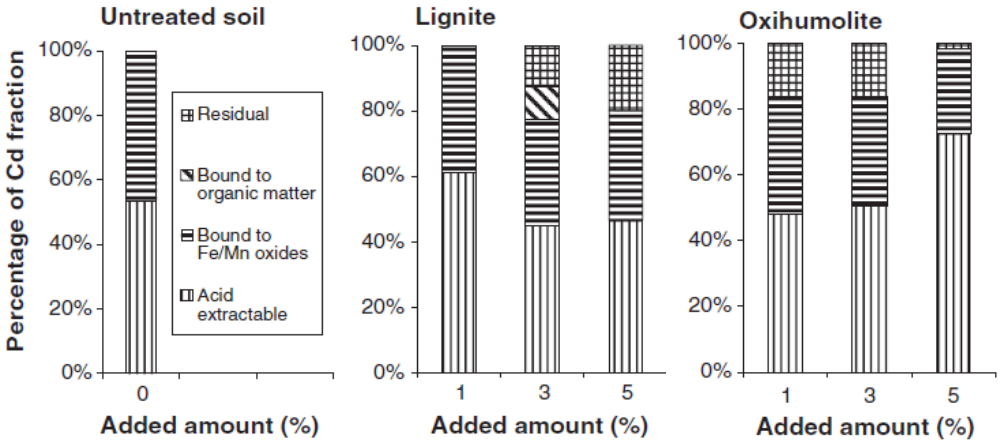


Figure 1: Fraction of Cd in untreated soil and soil amended with lignite or oxihumolite as determined by sequential extraction [45].

In soil, lignite is relatively resistant to decomposition and mineralisation and has long-lasting activity [24]. This is an advantage over other organic amendments such as compost, which are much less persistent in soil [26]. Kwiatkowska et al. (2008) found that seven years after application, soil amended with lignite had a higher C content, slightly higher N content and higher C/N ratio than the control soil. The same observation was made for the soil humic acids. A high C/N ratio indicates high stability. By means of fourier transform infrared spectroscopy (FTIR) and fluorescence spectroscopy, they found evidence of increased aromaticity and carboxylic group content in humic acids extracted from the amended soil compared to the control soil [25].

Studies investigating lignite addition to transform soil Cd in a form less available for plants are listed in Table 3. All studies found a decrease in plant Cd concentration when soil was blended with lignite. The metal concentrations used in these treatments were usually very high and mostly phytotoxic

[24, 26, 27]. The findings of these studies nevertheless indicate that lignite application could potentially also reduce the bioavailability and plant uptake of Cd from pasture soils with non-phytotoxic Cd concentrations of 1 - 2 mg/kg originating from Cd-containing P fertiliser applications.

Hypotheses

I hypothesise that lignite will reduce Cd concentrations in the solution phase of New Zealand pastureland soils and result in reduced Cd uptake by *Lolium perenne.* I hypothesise that this effect will be greater at high soil pH values.

Table 2: References on Cd removal from aqueous solution using lignite or similar low-rank coals as sorbent. K_d at low equilibrium solution concentration was estimated from isotherms by linear approximations according to the formulas in Appendix A1. Note the different pH conditions.

Sorbent	Solution	Sorbent(g) / solution(ml)	Contact time	Initial Cd solution conc. (mg/l)	pH	Cd sorption properties	K_d at low equilibrium concentration	Author	
Greek lignite	water + Cd nitrate salt	1/100	45 min	10 - 1000	4 - 5, no adjustment	• Langmuir[1] Q_{max} = 52.48 mg/g b = 0.033 l/mg • Freundlich[2] K_F = 8.561 $(mg/l)^{-1/n}$ (mg/g) n = 3.4	1732 8561	Pentari et al. (2009)	[28]
Moravia lignite (Czech Republic)	water + Cd nitrate salt	1/200	6 h	1 - 500	initial pH 2 - 12 equilibrium pH 2 - 10 (stabilised by bubbling N_2 to prevent further CO_2 dissolution)	• max. sorption at ca. pH 8 • Langmuir-Freundlich[3] (pH 5): Q_{max} = 435 mg/g K_{LF} = 0.0302 $(mg/l)^{-n}$ n = 0.438	13137	Havelcova et al. (2009)	[39]
Beypazari lignite (Turkey)	water + Cd nitrate salt	1/100	1 h	10 - 100	2 - 6, maintained in range ± 1 pH unit until equilibrium	• max. sorption at pH 4 • Langmuir (pH 4) Q_{max} = 1.70 mg/g b = 0.122 l/mg • 90% of soluble Cd removed after 20 min	207.4	Karabulut et al. (2001)	[40]
Loy Yang lignite (Australia)	0.1 M $NaNO_3$ + Cd nitrate salt	3.75/1000	1 d	56 - 843	2 - 8 readjustment using a automatic titration system	• largest sorption of 135 mg/g at pH 8		Burns et al. (2004)	[36]
Czech lignite (Medard mine) "Ca loaded" (pretreatment with $Ca(OH)_2$)	water + Cd salt	5/(45, 90, 135, 180)	7 d	2248	6 - 7.5, no adjustment	• selectivity determined by Ca displacement $Pb > Fe^{2+} > Cu > Zn \geq Cd \geq Co \geq Ni$		Jochova et al. (2004)	[29]

Three Turkish lignites (Ilgin, Beysehir and Ermenek mine)	water + Cd nitrate salt + buffer	0.2/10	10 h	22 - 2248	2.7 - 5.7, buffered with formate or acetate buffer	• max. adsorption at pH 5.7 (upper end of range investigated) • adsorption capacities of 10.12, 11.46 and 5.77 mg/g for Ilgin, Beysehir and Ermenek respectively		Pehlivan & Arsland (2006)	[33]
Three Turkish lignites (Ilgin, Beysehir and Ermenek mine)	water + Cd nitrate salt + buffer	0.2/10 0.4/10 0.6/10	10 h	22 - 2248	2.7 - 5.7, buffered with formate or acetate buffer	• max. adsorption at pH 5.7 (upper end of range investigated) • adsorption capacities of 10.12, 11.46 and 5.77 mg/g for Ilgin, Beysehir and Ermenek respectively • amount of Cd adsorbed increased with increasing lignite/solution ratio		Pehlivan et al. (2004)	[41]
Czech oxihumolite (North-Bohemian mines)	water + metal salt	0.4/50 (5/500 for kinetic)	72 h	~ 10 - 450	3.6 - 4.5, no adjustment	• Langmuir Q_{max} = 19.90 mg/g b = 0.030 l/mg • Langmuir-Freundlich Q_{max} = 154.11 mg/g K_{LF} = 0.015 $(mg/l)^{-n}$ n = 0.42 • half-time $t_{1/2}$ = 64 min	597 2312	Janos et al. (2007)	[42]
Leonardite provided by SEPHU® (Zaragoza, Spain)	water + metal salt	0.2/200 (1/200 for kinetic)	2 or 6 h	1 - 500	2 - 6 (non-adjusted pH ca. 5.5)	• max. adsorption pH 5 - 6 (upper end of range investigated) • Langmuir Q_{max} = 50.6 mg/g b = 0.070 l/mg • Freundlich (at pH ca. 5.5) K_F = 8.154 $(mg/l)^{-1/n}$ (mg/g) n = 2.11	 3542 8154	Lao et al. (2005)	[30]

[1] $q = \frac{Q_{max} b C_e}{(1+bC_e)}$ [28] [2] $q = K_F C_e^{1/n}$ [28] [3] $q = \frac{Q_{max} K_{LF} C_e^n}{1+K_{LF} C_e^n}$ [39]

q … Cd sorbed (mg/g); C_e … equilibrium Cd solution concentration (mg/l)

Table 3: References on *in situ* fixation of Cd in soil using lignite as fixing additive.

Amendment	Soil properties	Heavy metal soil concentrations	Plant species	Cd uptake	Other effects		
2 wt% lignite	pH(KCl) ca. 4.2 cley sand	**Cd:** 0, 7.5, 15, 22.5 mg/kg (spiked)	triticale (*× Triticosecale*) oilseed rape (*Brassica napus*)	• Cd reduction in triticale grain, straw and roots of 7.4%, 8.9% and 10.1% respectively (mean over all Cd treatments) • Cd reduction slightly lower when soil was limed prior to lignite application	• significant reduction of toxic effects (effects on grain yield, change in elemental composition) • average plant Cd in series with liming was 31 - 38% lower than in the series not limed	Ciecko et al. (2001)	[26]
0.3, 0.6, 1.3 wt% "Rekulter" (85% lignite, 10% low peat, 4% lignite ash, 1% mineral fertiliser [25])	pH(KCl) 5.05 haplic luvisol loamy sand	artificially contaminated **Cd:** 1.6 - 1.9 mg/kg (2M HNO_3 extractable) ca. 100 mg/kg Pb ca. 110 mg/kg Zn	rye (*Secale cereal*)	• significant decrease in plant Cd concentration • largest reduction for the highest treatment accounted for 58% (roots), 73% (stalk) and 80% (ear)	• amendment significantly increased soil pH (pH 6.30 for highest dose)	Sklodowski et al. (2006)	[27]
1, 1.5, 2, 3, 3.5 wt% Polish lignite (Konin mine)	"Zone 1" pH(KCl) 6.7 brown soil cleyed silt "Zone 2" pH(KCl) 6.9 brown soil heavy silty loam Skierniewice lessive soil pH(H_2O) 5.9	**Cd:** 2.3, 1.3 and 0.4 mg/kg in "Zone 1", "Zone 2" and Skierniewice respectively "Zone 1" and "Zone 2" are highly metal-contaminated (mostly Cu, Pb). Skierniewice is weakly contaminated (mostly Zn, Pb).	Grass mixture (*Lolium perenne, Festuca rubra, Lolium multiflorum, Poa pratensis*) rye (*Secale cereal*) serradella (*Ornithopus*) red fescue (*Festuca rubra*)	• significant reduction of crop Cd 56 - 73% in grass mixture 65 - 70% in rye 50 - 58% in serradella 60 - 67% in red fescue	• increasing dose of lignite increased soil pH (pH 7.2, 7.2 and 6.3 respectively for highest dose) • increasing dose increased biomass of all species investigated • improved soil reaction, hydrolytic acidity, sorptive capacity and organic carbon • significant reduction of uptake of Zn, Cu, Pb	Pusz (2007)	[24]

1.4 Objectives

The aim of this study is to investigate whether lignite has potential as a soil amendment for *in situ* fixation of fertiliser-borne Cd in NZ pastureland. Specifically, this investigation seeks to determine:

1) the Cd sorption by lignite at biologically relevant concentrations and pH values,
2) the effect of lignite amendments on Cd sorption and pH of various NZ pasture soils,
3) the effects of lignite treatment on plant growth and uptake of nutrient elements, and
4) the influence of liming on the lignite treatment effects.

I seek to test the concept that lignite could be used at agriculturally relevant application rates to significantly reduce the threat of Cd to New Zealand's economy. However, this is a short-term study. Therefore, even given a positive result, further work will be required to clarify management practices associated with lignite addition to soil. I therefore endeavour to identify key knowledge gaps that could be filled by future research.

2. Background

Part A

2.1 Cadmium in soil

Cd levels in NZ soils

Roberts et al. (1994) measured the total Cd concentration in the topsoil (0 - 7.5 cm) of 86 non-agricultural sites and found an average of 0.20 mg/kg [13]. A similar average concentration of 0.16 mg/kg was calculated by Taylor et al. (2007) for 372 topsoils (mostly 10 cm) described as "unfertilised". Furthermore, they observed that soils that had been used for agriculture show elevated Cd concentrations compared with these "background" values indicating accumulation. Averages in the four major land use classes according to Taylor et al. (2007) are shown in Table 4. Pasture and horticulture have significantly higher Cd concentrations than the national average of 0.35 mg/kg reflecting a higher reported fertiliser input. The average value for cropping was below the national average concentration but this may reflect the greater tilling depth, which dilutes the Cd concentration in the topsoil. Table 5 lists averages for the different pastoral land uses. Soils under dairy farms had the highest average concentration (0.73 mg/kg) reflecting the fertiliser intensity. In opposition, the average for sheep farming sites (0.33 mg/kg) is slightly below the national average of 0.35 mg/kg. The regional distribution pattern reflects these findings. Unlike regions with tradition in dairy farming (Taranaki, Waikato and Bay of Plenty), historic sheep farming areas (Canterbury, Gisborne, Manawatu-Wanganui, Nelson-Marlborough, Otago, Southland and Wellington) show average soil Cd concentrations below the national average [14]. In general, Cd concentrations in New Zealand soils are governed by the fertiliser history and the tillage depth [2] and are comparable to concentrations reported in other industrialised countries (e.g. Traina (1999) [46] or Hooda (2010) [6]).

Table 4: Cd concentration in NZ soils by land use as reported by Taylor et al. (2007) [14].

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**

Table 5: Cd concentration in NZ pasture soils by farm type as reported by Taylor et al. (2007) [14].

Land use	Number of samples	Average Cd (mg/kg)	Range (mg/kg)
Dairy	144	0.73	0.00 - 2.52
Deer	12	0.68	0.40 - 1.20
Beef	48	0.42	0.04 - 1.40
Horses	4	0.53	0.40 - 0.60
Sheep	34	0.33	0.03 - 1.20
All drystock	**111**	**0.40**	**0.00 - 1.40**
All pasture	**825**	**0.43**	**0.00 - 2.52**

Sources of Cd in NZ pastureland

The contribution of geogenic Cd to the overall concentration in NZ pasturelands is low. Therefore, influence of the parent rock on the total Cd-burden is small [13]. Zanders (1998) found a significant decrease in Cd concentration with depth in 17 soil types on NZ farms, indicating the low contribution of the parent rock on the topsoil Cd concentration [47][1]. Major anthropogenic sources are P fertiliser, atmospheric deposition arising from industry and biosolids (sewage sludge) and industrial waste application. While atmospheric deposition and biosolids application are only important in some localised areas, P fertiliser is the most relevant anthropogenic source of Cd in cultivated NZ soils [8].

Atmospheric deposition - Cadmium is relatively volatile[2] and therefore susceptible to atmospheric transport, which is a major component of the global Cd cycle [46]. Gray et al. (2003) determined the rate of atmospheric deposition of Cd at seven rural sites across New Zealand. They observed annual average deposition rates between 0.09 and 0.36 g/ha/y with a mean of 0.2 g/ha/y [49]. Fergusson and Steward (1992) reported rates within 20 km distance around Christchurch City of 1 - 2 g/ha/y but a drop to 0.02 - 0.05 g/ha/y within a distance of 30 - 80 km [50]. Compared to values measured in Europe (e.g. Nicolson et al. (2003) [51]) these rates are relatively low. This may be explained by the lack of high-temperature industrial processes such as metal smelting and fuel combustion, which are the main sources of atmospheric Cd [49, 52]. Apart from local industrial sources, Cd may be transported from overseas, especially from Australia [52-54]. Halstead et al. (2000) found elevated Cd levels in Fiordland (NZ) rainwater relative to crustal material. Furthermore they observed a correlation of Cd with ^{210}Pb ($R^2 = 0.903$). Most atmospheric ^{210}Pb originates from decay of ^{222}Rn (half-life of 3.82 y). ^{222}Rn emitted in NZ is blown offshore before it decays. Therefore the observed correlation shows that Cd is emitted overseas in gaseous form and transported as submicron aerosols in a similar way to ^{210}Pb. This reasoning is consistent with the suggested major source of the measured Cd being Australia's high-temperature industrial processes [52].

[1] The conclusion that elevated Cd concentration in the surface horizon of agricultural soils is entirely anthropogenic may not always be correct. As described by Rasmussen (1996), plant uptake and subsequent deposition of plant residues on the soil surface may result in elevated topsoil Cd concentration [48].

[2] Melting and boiling points of elemental Cd is 321 °C and 767 °C respectively and the heat of vaporisation is 26.8 kcal/mol [46].

Biosolids - Sewage treatment in NZ generates between 700'000 and 1'000'000 tonnes of biosolids annually [55] which contain typically between 1 and 4 mg/kg dw Cd [56]. In NZ, biosolids are used as a soil amendment in production forest and on agricultural land as they can improve fertility [17]. According to NZ guidelines, biosolids with a Cd concentration of up to 10 mg/kg dw may be added to soil that contains less than 1 mg/kg Cd [17]. The importance of biosolids as a soil amendment may grow in response to increasing disposal costs for the biosolids and increased costs of fertilisers [57].

P fertiliser - The pastureland soil fertility constraints of low N, P and S availability have traditionally been addressed by legume-based pasture annually fertilised with single superphosphate (SSP). SSP as well as other types of P fertiliser used in New Zealand today contain up to 280 mg Cd/kg P [58]. Some trace element fertilisers (especially Zn fertiliser) can contain relative high concentrations of Cd but are of less concern because of their lower application rates [8].

Ninety five percent of P fertiliser applied in New Zealand is used to maintain pasturelands (mainly dairy, sheep and deer) [15]. Hedley et al. (2010) calculated for the year 2007 a national maintenance P application of 163'000 t P and predicted increasing P maintenance application for the near future mainly due to expansion of dairying. The annual application rate of P is variable and does not necessarily follow the trend in maintenance P demand. This can be explained by the volatile profitability of sheep and beef [15]. Nevertheless, in the long term, the application should follow the maintenance P application and an increasing trend can be expected. In comparison to other countries, NZ has a low potential source of recyclable organic P via manure from housed animal production and sewage. Hedley et al. (2010) estimated a potential of less than 5% of the national maintenance P application considering manure from the poultry and pig industry, both major sources of animal manure, as well as raw sewage sludge [15]. Therefore the expected increase in P demand will probably mainly be satisfied by mineral P fertiliser.

In NZ, single superphosphate is the dominant type of P fertiliser applied. To a lesser extent, the combined N/P fertiliser diammonium phosphate (25%) and other P fertilisers (10%), mainly reactive phosphate rock, are in use [15]. The source of Cd in P fertilisers is the phosphate rock used for their production. Cadmium concentrations vary widely depending on the source of the P-containing rock used. Cadmium is associated with apatite minerals in which it substitutes for Ca [59]. During the production of soluble P fertilisers, only a limited amount of Cd is lost into by-products. There is no commercially viable process for the removal of Cd from fertiliser. The Cd/P ratio in phosphate rocks is similar to that in processed fertilisers and determines the degree of impurity [16]. Sedimentary rocks and especially guano-derived rocks contain high concentrations of Cd. In contrast, igneous rocks are found to have low Cd concentrations because Cd volatises well below the temperature at which these rocks were formed [8]. The main source of P rock in NZ up to the early 90's was oceanic sedimentary and guano-based rocks from the Christmas Islands and Nauru which, on an international scale, are considered high-Cd rocks [8, 12]. Since 1995, the fertiliser industry in NZ had voluntary Cd limits in place resulting in a reduction of Cd concentration in P fertiliser from initially 340 mg Cd/kg P in 1995 to about 180 mg Cd/kg P today, which is below the upper limit of 280 mg Cd/kg P set in 1997 [58]. This reduction involved the change to other sources of Cd rock. Today the main source of P rock for NZ fertiliser production is low-Cd rock mined in the Western Sahara in Morocco. Low-Cd rock is often difficult to source and the supply can be erratic. Trade of low-Cd sources from different countries (e.g. USA, China) to New Zealand industry is restricted or was denied [2].

There is increasing awareness of depletion of the global phosphate rock resources [60-62]. Estimates for the depletion timeline range from 30 to 300 years [61]. Modern agriculture will eventually have to switch to other P sources and/or increasingly recycle P. Phosphorus cannot be produced and there is no substitute as it is an essential plant nutrient. As higher quality (and more easily accessible) rock will be mined first, the quality with regard to P_2O_5 percentage and impurities, such as Cd, is expected to decrease [61]. As an export nation of agricultural products with comparably low potential for domestic P recycling [15], New Zealand will face big challenges to maintain the P status of its agricultural soils while avoiding fertiliser derived contamination.

Accumulation in NZ pastureland

Evidence that Cd progressively accumulates in NZ soils come from analysis of archived soil collections, plot trials with controlled application and field surveys [9]. Numerous authors reported an accumulation of Cd in New Zealand pasture land due to the application of P fertiliser [13, 20, 63-65]. Roberts et al. (1994) found that Cd total concentrations in 312 pastoral topsoils were significantly correlated with the topsoil P concentrations reflecting fertiliser history [13]. Furthermore, a large portion (80%) of historically applied Cd by fertiliser can be recovered in soil as shown by Taylor (1997) comparing soils with archived samples [11]. Loganathan and Hedley (1997) applied 4 different P fertilisers (30 kg P/ha/y) over 10 years on pastoral soil. They showed that approximately 90% of the Cd applied annually was recovered in soil of which 93% remained in the top 120 mm [64]. The high recovery is a result of low Cd uptake by pasture and low leaching and runoff losses [8]. The Zn/Cd ratio can be used to trace the origin of Cd in soil since Zn and Cd are geochemically closely related. A number of authors reported that the Zn/Cd ratio of fertilised soils is closer to that of historically applied single superphosphate than that of unfertilised soils suggesting fertiliser as the origin of the soil Cd [13, 47, 63]. The New Zealand national average accumulation rate of Cd in soil has been cited by the Cadmium Working Group (2011) at 5 µg/kg/y. This rate is lower than the historical rate because of reduction of the Cd concentration in the P fertiliser used [2].

Chemical behaviour of Cd in aerobic soils

Regime controlling Cd solubility - In most soils, 99% of the Cd is associated with the soil solids and just a minor fraction occurs in soil solution. Under oxidising conditions with a pH < 7 adsorption[3]/desorption reactions rather than (co-)precipitation/dissolution reactions usually control the Cd solution concentration [1]. This is indicated by sorption curves as the free ion activity is less affected by soil pH than the 100-fold change per pH unit that is observed when carbonates, oxides or hydroxides control the solubility of a divalent metal [67]. Carbonate, hydroxide, phosphate and sulphide are solid Cd species that may be formed in soils [68]. Kabata-Pendias et al. (2007) state that

[3] Adsorption can be defined as the accumulation of solute molecules (or in general material) on an interface between a solid phase and the surrounding solution. It does not include surface precipitation and polymerisation. It can be followed by diffusion into the solid phase and possibly, in case of a mineral phase, substitution in the mineral lattice [66].

above pH 7 precipitation of $CdCO_3$ potentially governs the Cd solution concentration [1]. However, Christensen & Haung (1999) mention that Cd carbonate may just exist at pH > 8.5 in high alkalinity environments (> 1 meq/l) [68]. Such conditions exist only in sodic environments [68] with no relevance for NZ agriculture. Nevertheless, Krishnamurti et al. (1996) observed that in the rhizosphere, Cd can precipitate as carbonate facilitated by the release of CO_2 via root respiration [69]. Cadmium hydroxide and Cd phosphate are unlikely to control Cd distribution since the anion activities in soil are typically too low [68]. Under reducing conditions the amount of Cd in solution is controlled by sulphide precipitate if sufficient S(-II)(aq) is present [1, 70]. This is of special importance in temporarily flooded agricultural soils (e.g. rice fields) as in the flooded period reducing condition may establish and the availability of Cd may be reduced [6]. The solubility products of selected Cd compounds and calculated minimum anion activity controlling[4] the Cd concentration at 10^{-7} M are listed in Table 6 [1]. Although Cd soil solution concentration may not be controlled by solid Cd phases, Cd in pure or mixed solids is likely to be present as an inert or very slow reacting phase [67] e.g. incorporated in precipitates of Fe-, Mn- or Al-oxides, in the crystal lattice of secondary clay minerals [72], as $CaCO_3/CdCO_3$ solid solution or as substitute for Ca in many Ca-bearing minerals [68]. In New Zealand soils, adsorption/desorption reactions are likely to control Cd solution concentration since most New Zealand soils are slightly acidic (pH 5 - 6) [73] and pastureland is maintained under aerobic conditions.

Table 6: Solubility products of Cd minerals and calculated minimum anion activity controlling the Cd concentration at 10^{-7} M [68].

Cd compounds	Solubility product pK_{SO}	Anion activity at Cd concentration of 10^{-7} M
CdS	27.9	$S^{2-} = 10^{-20.9}$
$CdCO_3$	12.1	$CO_3^{2-} = 10^{-5.1}$
$Cd(OH)_2$	13.7	$OH^- = 10^{-3.35}$
$Cd_3(PO_4)_2$	32.6	$PO_4^{3-} = 10^{-5.8}$

Solution speciation - The solution speciation influences the total solubility and phytoavailability of Cd in soil. The soluble Cd species differ in their (ad)sorption behaviour to soil solids and biological surfaces and might or might not be taken up by plants. There was a general consensus that Cd in soil solution exists mainly as free cation (Cd^{2+}) followed by chloro and sulphate complexes [1, 74, 75]. A frequently cited model prediction for Cd speciation in oxic soils can be found in Sposito (1983). The prediction includes the following species: $CdSO_4^0$ and $CdCl^+$ in acidic soil solution, and Cd^{2+}, $CdCl^+$, $CdSO_4^0$ and $CdHCO_3^+$ in alkaline soil solution. Nevertheless, several studies show that soluble organic complexes might be of great importance in soils [76-78]. Krishnamurti & Naidu (2003) studied the soil solution speciation of 7 Cd-treated soils with contrasting pH (4.9 - 8.4), organic matter content (0.1 - 1.8%) and mineralogy. They found that organic Cd complexes were the major species of Cd in soil solution. Estimated fractions ranged from 82.1 - 99.9% and 0.1 - 16% for Cd-organic complexes and free Cd^{2+} respectively [78]. Sauve et al. (2000) investigated the Cd solution speciation for 64 contaminated soils (0.1 - 38 mg/kg Cd) with a broad range of pH values (3.5 - 8.1) and organic carbon contents (8.0 - 108 g/kg). Figure 2 shows the fractions of solution Cd present as free ion, inorganic

[4] Exceeding the solubility product does not prove that the solution Cd concentration is controlled by this solid species since slow kinetics may control the precipitation, e.g. as observed for $CdCO_3$ [71].

complexes and organic complexes as a function of soil pH. Organically bound Cd was a major component of soluble Cd in most of the studied soil solutions [77].

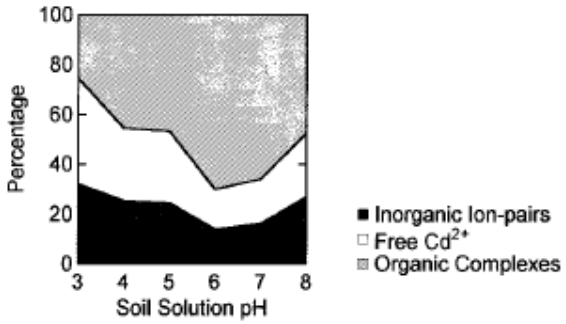


Figure 2: Solution speciation of Cd in 64 contaminated soils as observed by Sauve et al. (2000). Data is averaged over single pH unit intervals [77].

Cd (ad)sorption - The free Cd ion is considered the most reactive Cd solution species regarding adsorption on the solid phase, but some complexes adsorb to solid surfaces too [67]. It adsorbs primarily to organic matter, (hydr)oxides and clay minerals [67] but also to other minerals present, e.g. $CaCO_3$ [79] and hydroxyapatite [80]. Two modes of chemical adsorption are distinguished. The free ion can sorb, along with the surrounding hydration water via ion-dipole interactions and electrostatic forces. This mode of adsorption is referred to as outer sphere, ion exchange or non-specific adsorption and is generally considered reversible. The potential of a soil (or other sorbent) to adsorb cations by ion exchange is described by the cation exchange capacity. The second mode of adsorption is termed inner sphere, chemisorption or specific adsorption. Here, the free ion loses the hydration water and forms chemical bonds (coordinative or other types) with solid surface functional groups. Further details on the two mechanisms can be found in Stumm (1992) [81]. Cadmium can bind to soil constituents both via non-specific (outer sphere) and specific (inner sphere) complexation depending on the surface site to which the bond is established. On permanently charged sites of clay minerals (resulting from isomorphic substitution) Cd is known to bind non-specifically whereas on edges of clay minerals it is known to specifically adsorb to edge-OH^- and O^{2-} groups. Therefore, the strength and extent of Cd binding to different clay minerals depend on the degree of isomorphic substitution, lattice impurities and exposed structural hydroxyl groups of the particular mineral [68]. Aluminium, Fe and Mn (hydr)oxides and amorphous aluminosilicates provide predominantly specific adsorption sites (OH groups) [68]. Soil organic matter and amorphous oxide-organic complexes are often found as the major sorbent for Cd [68]. Cadmium is bound to the soil organic matter via ion exchange and predominantly chemisorption mainly to carboxylic and phenolic functional groups. Besides sorption to this O-bearing groups, Cd tends to bind to N and in particular S-bearing groups such as sulphydryl groups [82]. Organic matter and oxides often form organo-mineral associates that show different Cd sorption properties than their separated constituents [68]. Distortion of the structure of Al precipitates by organics enhances the exposure of mineral surface groups that can bind Cd [83]. Organic components play an important role in promoting the formation of amorphous Fe oxides. The presence of organic material during the precipitation of Fe oxides increases their negative charge, lowers their point of zero charge and

therefore increases the capability to adsorb Cd. Such amorphous oxide-organic complexes may be resilient against degradation by microorganisms if the organic matter is physically protected. Therefore these complexes might exist over pedogenic time scales [68].

Factors influencing Cd solubility - Numerous factors influence the solubility of Cd in aerobic soils. The most important are the mineral and organic composition of the soil, the pH value, the concentrations of dissolved inorganic and organic ligands, and the presence of competing ions [84].

Soil composition - The composition of the soil solids is crucial regarding Cd solubility as the constituents are characterised by different potentials to adsorb Cd. New Zealand soils are geologically young and therefore less weathered than soils from Europe and North America. Variably charged oxide minerals form an important constituent of NZ soils whereas the soils overseas are dominated by permanently charged clay minerals. Furthermore, the organic matter content is relatively high compared to similar soil in most other countries [85]. Several authors emphasised the importance of organic matter regarding Cd mobility in NZ soils [86-89]. For example, Kim et al. (1992) found that removing the organic matter from a NZ soil by hydrogen peroxide resulted in a reduction of the percentage of Cd adsorbed from 87.3% to 37.3%. Removal of the Fe and Mn oxides reduced the percentage of Cd adsorbed significantly from 87.3% to 80% [86]. Gray et al. (2000) studied the Cd fraction in 12 NZ topsoils by using the sequential fractionation procedure described by Shuman (1985) [87, 90]. They observed that on average, the greatest proportions of Cd are associated with organic matter (34%) and the residual fraction (38%). Some 13% was associated with amorphous oxides and 12% was associated with crystalline oxides. Just a minor fraction was in an exchangeable form (3%) [87]. Krishnamurti et al. (1995) developed a sequential extraction procedure for Cd which can be used to determine a metal-organic complex-bound fraction apart from an organic-bound fraction. Applying this procedure to study the speciation of particulate-bound Cd in 12 temperate soils from Saskatchewan (Canada) they found that on average, the metal-organic complex-bound fraction accounted for 40.5% and the organic-bound fraction for 13.3% of total Cd in these soils [91]. Using the extraction procedure by Krishnamurti et al. (1995) to study the speciation in tropical soils from the main agricultural areas in Kenya, Onyatta & Huang (1999) observed that on average, the metal-organic complex-bound and the organic-bound Cd accounted for 37.1% and 10.0% of topsoil Cd respectively [92]. These two studies highlight the importance of mixed metal oxide-organic complexes as a sorbent of Cd in soils.

Soil pH - The pH value is the most dominating solute factor influencing adsorption of Cd in soil [68]. Under aerobic conditions, the solubility of Cd increases with decreasing pH value. Variably negatively charged adsorption sites are progressively protonated with increasing H^+ solution concentration and are therefore no longer available for adsorption. Additionally, competition at permanently negatively charged adsorption sites by H^+ and acidic cations (mainly Al^{3+}) is intensified [74]. Figure 3 shows Cd concentration in solution in equilibrium with different soil samples as a function of the pH as observed by Hermes & Brümmer (1980). The pH value was adjusted after equilibrating the samples with 15 mg/kg Cd [93]. Below pH 6.5 a strong increase of the Cd solubility is observed. Above pH 7 Cd can be mobilised due to formation of soluble organic complexes [74] as seen for the humic podsol in Figure 3 (more about this effect later). The pH value in the rhizosphere might be lower than that of the bulk soil due to root exudation of protons and organic acids [74].

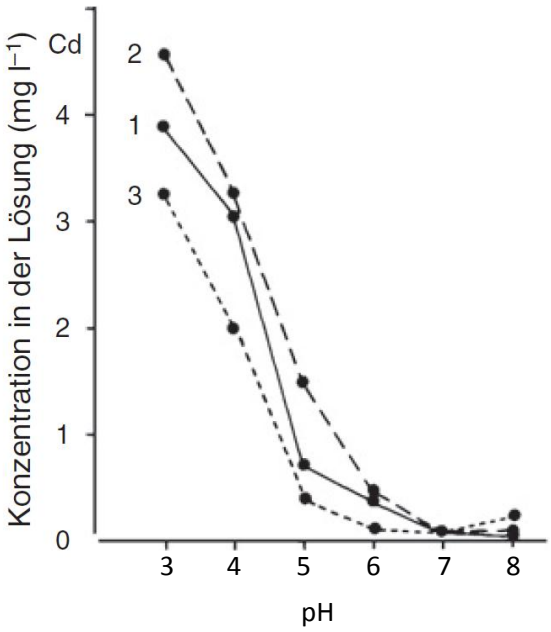


Figure 3: Cadmium equilibrium concentration as a function of adjusted pH for three different soil samples. Samples were equilibrated with 15 mg/kg Cd before pH adjustment. 1 = leptic podsol, 2 = loamy luvisol, 3 = humic podsol. Figure adapted from Blume et al. (2010) [74]. Data by Herms & Brümmer (1980) [93].

Competing cations - The composition of major cations in soil solution (at the mM level) can affect Cd adsorption beyond what can be attributed to ionic strength effects. In particular, Ca competes strongly with Cd for binding sites in temperate soils [68]. Competition is expected to occur at ion exchange sites since Ca is not expected to form inner sphere complexes with soil constituents [74, 84]. The level of effect is similar to that of pH. However, the variation in solution Ca concentration between soils is generally not as dramatic as for the proton concentration and the effect of Ca is expected to be within a factor of three to four. Magnesium, K, and Na are usually present in lower concentrations and therefore less competitive [68]. 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 << Hg [74]. Zinc is normally present in higher concentrations than other trace metals and is chemically similar to Cd, making it the most important competing trace metal [68]. Figure 4 shows Cd distribution as a function of solution Zn concentration in a sandy soil as determined by Christensen (1987). The Cd concentration in soil solution increases with increasing Zn concentration indicating adsorption competition. A competitive Langmuir isotherm gave a good fit under the assumption that the same sorption sites are available for Cd than for Zn [94]. Sorption competition of Cd with other metals than Zn was demonstrated by several authors (e.g. Liao et al. (2009) for Ni [95], Serrano et al. (2005) for Pb [96] and Vergara & Schalscha (1992) for Cu [97]) but is usually of less importance unless the concentrations of these trace metals are elevated.

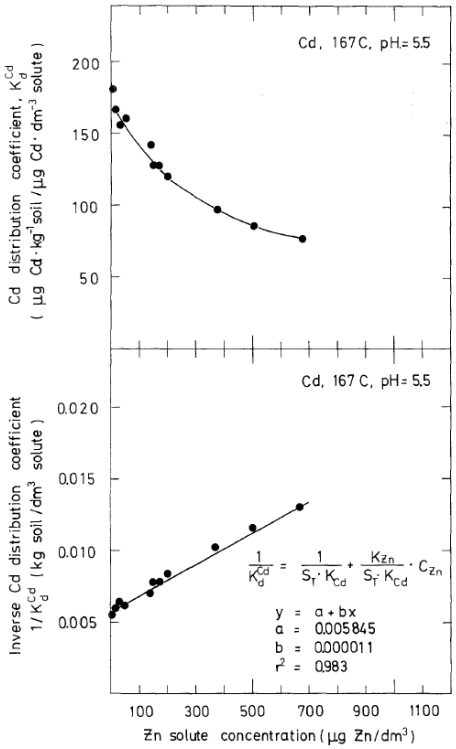


Figure 4: Cd solid-solution distribution coefficient K_d in soil as a function of Zn solute equilibrium concentration as measured by Christensen (1987) [94].

Dissolved ligands - The presence of inorganic and organic ligands in soil solution might limit the metal adsorption at low metal concentrations [67, 68]. Little effect is expected at high metal concentrations when the soluble ligands are saturated with the metal [67].

Cadmium forms a range of soluble chloro complexes and chloride concentrations in some soils may be high enough to result in significant complexation and a decrease in adsorption of Cd in soil. The effect of sulphate is less clear and depends on the adsorbing surfaces present [68].

Dissolved organic matter (DOM) increases the solubility of Cd in soils [98-102]. Natural low molecular weight organic acids originate from root exudates, canopy drip, oxidative decay of plant and animal residues and microbial activity [68]. Naidu & Harter (1998) observed that dissolved low molecular weight acids (e.g. acetate, citrate, fumarate or malonate) increase Cd solubility in some soils due to formation of soluble complexes but decrease Cd solubility in other soils. The later effect might be caused by soil surface charge reversal by organic anion binding to positively charged surface sites [103]. Higher concentrations of low molecular weight acids are expected localised in zones of high biological activity, e.g. near roots [68]. Li et al. (2010) observed higher DOM concentration in the rhizosphere than in the bulk soil enhancing locally the solubility of Cd [100]. Besides low molecular weight compounds, larger and more complex organic acids contribute to the increase in Cd solubility by DOM. Kaschl et al. (2002) observed that Cd preferentially binds to a fraction of DOM that consists of larger, humified and less soluble organic molecules such as humic and fulfic acids since they possess the strongest Cd binding groups [98]. Above pH 7, Cd can be mobilised due to formation of stable organic complexes as soil organic matter is increasingly soluble at high pH [74]. This effect is visible in Figure 3. At the same DOM concentration, the organic ligands

are most competitive to the solid sorbents in the pH range 5 - 7 which is the typical range of agricultural soils [104].

Aging - It is debated whether increased periods of aging of soils causes reduction in Cd desorption. Aging effects following the rapid sorption processes might be caused by a slow shift from outer sphere to inner sphere sorption, occlusion with organic or inorganic materials [105] and/or diffusion into the soil solid phase matrix [106]. Decreasing Cd solubility with increasing aging period was described by several authors [89, 107-110]. Gray et al. (1998) observed decreasing desorption of Cd with increasing contact time for six New Zealand soils [89]. Other references investigating aging effects in soil found no conclusive evidence for decreasing solubility with increasing aging period [111, 112]. The aging effect might be a function of soil type as the constituents responsible for the slow reactions that fix Cd or agents that may inhibit fixation might or might not be present in a soil [113]. Statistically significant aging effects might as well depend on the experimental conditions, e.g. the aging time or Cd loading used.

2.2 Cadmium uptake by plants

Plants take up Cd from soil and air. Smolders (2001) reviewed literature about the relative contribution of root uptake and direct atmospheric deposition of Cd in crops. He found that direct deposition of airborne Cd on plants has only a marginal influence on the crop Cd concentration in areas with low atmospheric deposition, i.e. < 2 g/ha/y [114]. The Cd in NZ pasture can be considered primarily derived from soil as the atmospheric deposition in NZ is much lower than 2 g/ha/y [49] (see Chapter 2.1).

Only a fraction of the total Cd concentration in soil is accessible to plants. This so-called bioavailable fraction can be taken up and causes the plant's response (e.g. accumulation in leaves or fruits) to Cd exposure. Soluble species can potentially be taken up whereas Cd associated with the soil solid must dissolve prior to uptake. The free Cd ion is the most bioavailable, but some complexes are known to contribute to the overall plant uptake [6, 84]. Numerous authors found that an increase in Cl^- soil and/or soil solution concentration resulted in an increase in Cd plant uptake indicating that Cd chloro complexes are phytoavailable [115-117]. Some evidence was also found that increasing SO_4^{2-} solution concentration increases plant Cd uptake [118-120]. This might indicate the phytoavailability of Cd sulphate complexes [118-120] and/or be a result of improved S nutrient status of the plant as the synthesis of Cd transporters might be limited by S. Phytometallophores are suspected to contribute to the bioavailable fraction but evidence is lacking. Several studies reported that phytosiderophores not only facilitate Fe but also Zn uptake in some plants [121-123]. The stability constant of Cd-phytosiderophore complexes are likely to be close to the equivalent ones for Zn [124] and therefore facilitated uptake of Cd by phytosiderophores is a reasonable hypotheses. Shenker et al. (2001) investigated the influence of phytosiderophores on Cd uptake by wheat and barley plants. They found no influence of phytosiderophores on plant Cd uptake [125].

In most plants, the accumulation of Cd in shoots is limited by the restricted movement of Cd through the outer root via the symplastic and apoplastic pathway to the stele. Passing the epidermis, cortex and endodermis, Cd is eventually transported from the root to above-ground plant organs through

the xylem vessels [126]. In the following paragraphs the symplastic and apoplastic pathways are described and their relative contribution discussed.

Symplastic pathway

The symplastic pathway requires that the solute crosses the cell membrane, which serves as a selective barrier [126]. The free Cd ion is considered the most likely species to be transported through biological membranes. As a metal cation, its hydrophilic character hinders its simple diffusion through the hydrophobic portion of biological membranes. However, its transfer across the plasma membrane is facilitated by specific membrane-spanning proteins (transporters and/or ion channels) [126]. Under normal circumstances, no active transport (i.e. that uses energy in form of ATP) is required to transport Cd^{2+} through the membrane in a thermodynamic sense. The negative membrane potential alone provides enough energy therefore [124] as the concentration of free Cd in the cytoplasma is expected to be depressed by chelation [127]. Numerous transporters and ion channels transporting Cd^{2+} have been described, e.g. ZIP transporters, orthologues of wheat TaLCT1 transporter, depolarisation-activated Ca channels (DACC), hyperpolarisation-activated Ca channels (HACC) and voltage-insensitive cation channels (VICC) [126]. Little is known about the possibility of *in toto* cell uptake of Cd complexes [124]. Cadmium-chelate complexes may enter root cells via YSL1-like proteins which are involved in Fe-phytochelatin uptake [128]. Welch et al. (1999) hypothesised that $CdCl^{+}$ might enter via a monovalent ion channel (e.g. K^{+} channel) and that neutral Cd complexes ($CdCl_2^{0}$ and $CdSO_4^{0}$) might cross the membrane by passive diffusion [124]. Once in the symplastic continuum, the movement of Cd is restricted by the production of phytochelatines and the sequestering of Cd-chelate complexes in vacuoles. The Cd species that are transported within the root symplast are unknown [126] but the high sulphydryl reactivity of Cd^{2+} indicates that Cd may exist as complexes with thiols in gluthation and phytochelatins, which are considered to be produced as part of the plant's detoxification mechanisms [127].

Apoplastic pathway

The transport of Cd species across the endodermis via the apoplastic pathway is hindered by the Casparian strip. However, in locations where the Casparian strip is not present (e.g. root apex) or disrupted (e.g. where lateral roots form), apoplastic movement of chemical species into the xylem may be possible [126]. This was suggested to contribute to the transport from root to shoot for Na [129], Ca [130] and Zn [131] and might also be the case for Cd [126, 132]. Evidence for the presence of apoplastically-transported Cd comes from the positive correlation between Cd accumulation in wheat cultivars and their number of root apices [133], the fact that the root tip is the most active part of the root regarding Cd influx [134] and the observation that willow clones developing the Casparian strip further away from the root apex show higher Cd uptake [135]. In contrast to the symplastic route, the apoplastic route is not particularly selective because the processes governing apoplastic transport are purely physical (e.g. transpiration mass flow and diffusion). The cell walls forming the apoplast act as ion exchangers that adsorb and therefore retard cations. Most adsorption sites are provided by dissociated weak acids (e.g. uronic acids) and are negatively

charged [136]. Therefore the retention of monovalent and neutral Cd complexes in the apoplast might be lower than that of the Cd^{2+} ion [137]. Negatively charged complexes might be retarded compared to neutral complexes as they are repelled by the negative charges of the cell wall decreasing the effective pore diameter available for diffusion. Large Cd-chelate complexes might be retained due to steric hindrance [138].

Relative contribution of apoplastic and symplastic pathway

The relative contribution of the symplastic and the apoplastic pathway to plant Cd uptake is unknown. As proposed for Na [129] and Zn [131], the contribution of the apoplastic pathway may increase with increasing Cd concentration in the rhizosphere solution [126]. Generally, the adsorption of Cd by roots shows a saturable and a linear component at low and high Cd solution concentration respectively. The saturable nature at low concentration indicates that the uptake is controlled by a transport protein in the plasma membrane exhibiting Michaelis-Menten enzyme kinetics [124, 132]. The linear component at higher concentration might be attributed to non-specific Cd^{2+} influx via ion channels of a divalent metal such as Ca^{2+} or Mg^{2+} [124] or to apoplastic absorption [132]. The linear component might rather be relevant for uptake from contaminated sites than from agricultural soils as it operates at relatively high Cd^{2+} concentrations [124].

Contribution of labile complexes to uptake under diffusion-limited conditions

Labile Cd complexes may contribute to the Cd uptake without being absorbed *in toto* under conditions where the plant uptake is diffusion-limited. These conditions occur when the supply via mass flow driven by transpiration is less than the rate of Cd uptake. Labile complexes that dissociate during diffusion contribute to the overall flux of Cd^{2+} towards the root and can thereby increase plant uptake [139]. Degryse et al. (2009) estimated that diffusional resupply from soil solution may be the rate-limiting step in plant uptake for elements with a concentration factor $CF = C_{solution}/C_{plant} >$ 100 l/kg dw [139]. Using values for a typical temperate agricultural soil ($C_{Cd,\ solution}$ = 0.5 µg/l; $C_{Cd,\ plant}$ = 0.1 mg/kg dw [68]) a concentration factor of 200 results, indicating that diffusion may be limiting. Several authors reported that under diffusion-limited conditions, plant uptake follows the sum of the free Cd ion plus labile Cd complexes rather than Cd^{2+} alone [140-142]. Oporto et al. (2009) found that $CdCl_n^{2-n}$ complexes contribute to plant Cd uptake at low but not at high Cd supply indicating diffusion limitation at low but not at high Cd concentrations. Labile complexes may therefore contribute to overall uptake on typical agricultural soils but not on contaminated sites [140].

Factors influencing plant uptake

Soil factors - The plant uptake of Cd is more influenced by factors that affect the bioavailability of Cd than by the total soil Cd [114]. The Cd concentration in soil solution or in neutral salt extracts are better predictors of plant Cd than the total soil Cd [114], e.g. Gray et al. (1999) and Adrews et al. (1996) predicted plant-available Cd in New Zealand soils using diluted NH_4OAc, $Ca(NO_3)_2$ and $CaCl_2$

solutions as extractants [143, 144]. This indicates that plant availability is related to solubility in soil [114]. Therefore, soil factors affecting the solubility are suspected to influence plant uptake. Clays, oxides and soil organic matter provide adsorption sites for Cd and decrease its mobility and plant uptake [106]. Chloride salinity increases solubility and increases plant uptake [116, 145]. Several authors reported that increasing pH decreases plant uptake [8, 146]. The effect is mainly ascribed to the large effect of pH on Cd binding in soil [146]. Root exudates might increase Cd phytoavailability by acidification of the rhizosphere [147]. However, solubility and plant uptake are often not correlated. Some authors reported increasing plant Cd uptake with increasing pH despite decreasing solubility [114, 146]. At low pH, easing proton competition with Cd^{2+} for uptake might cause this effect [146]. At higher pH, Zn deficiency in plant might be the reason for the increased uptake (see later) [114].

Plant factors - Plant species and cultivars differ in their ability to take up and accumulate Cd [8, 124]. Gray et al. (1999) found in a pot trial using 10 New Zealand soils (mainly pasture soils) lower Cd concentrations in the common pasture species perennial ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*) than in lettuce, carrot (root/top) and lucerne. The average soil-plant transfer factors (concentration in plant/concentration in soil) were 0.49 and 0.47 for ryegrass and clover respectively [143]. The relatively low accumulation in above-ground biomass shown by *Lolium perenne* might be a result of its low root-to-shoot transport rate [148]. The species composition is an important factor determining Cd concentration in pasture [8]. Roberts et al. (1994) found in a comprehensive survey (including 312 pastoral and 86 non-agricultural sites), similar concentrations in grass than in 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 dw for the grass, legume and weed species respectively [13]. Selecting and breeding low-Cd varieties is widely discussed as a means to cope with increasing pasture Cd concentrations [132, 149]. Gray et al. (2005) studied the accumulation of a range of metals by 11 different perennial ryegrass varieties grown on a contaminated soil collected in Christchurch, NZ. He found as much as a two-fold difference in grass Cd concentration between the different varieties and concluded that there may be potential to select ryegrass varieties to manage trace metal uptake by pasture [150]. For some crops other than pasture, grafting on a different rootstock might be an option to reduce crop Cd concentrations, e.g. as has been demonstrated for eggplants [151, 152].

There are seasonal patterns in plant Cd uptake [153]. Loganathan et al. (1997) observed a strong seasonal pattern in herbage Cd in a field trial over 10 years. Cadmium concentrations were highest in autumn and lowest in spring. They suggested that the pattern might be explained by different growth rates as the fast growth in spring may lead to a dilution of the Cd concentration [153]. This effect may occur in low fertility situations as the slow plant growth leads to low water-use efficiency by the plant, resulting in higher concentrations of elements that are passively taken up in the transpiration flow [8]. Older leaves tend to show higher concentrations of trace elements because more water was evaporated (per unit leaf area) leaving solutes behind [154]. However, seasonal variation in plant uptake might also be a result of differences in temperature or soil moisture content [153]. Hooda & Alloway (1993) studied the accumulation of Cd by *Lolium perenne* at two ambient temperatures (15˚C and 25˚C) in a pot experiment using soil blended with biosolids. They found that ryegrass grown at the higher ambient temperature (25˚C) accumulated significantly more Cd than that grown in the cooler environment (15˚C) [155].

The plant nutrient status influences Cd uptake [114, 146, 149]. Nutrient deficiencies might cause slow plant growth leading to the aforementioned concentration effect. Nutrients may also have more specific influence on Cd uptake. Increasing Zn in soil may elevate or lower plant uptake of Cd [149]. Under conditions where Zn is low or deficient, application of Zn decreases plant uptake of Cd [114, 149]. This effect might be caused by competition of Cd and Zn for transporters in the plasma membrane [156]. Under non-Zn-deficiency conditions the opposite effect can be observed. An increase in Zn causes enhanced Cd uptake due to competition for binding sites in the soil system resulting in elevated availability of dissolved Cd [149]. Several authors reported that plants deficient in Fe take up more Cd than non-Fe-deficient plants [157-159]. The effect may be caused by enhanced root excretion of protons, organic acids and other organic compounds increasing Cd availability by changing pH and/or Eh conditions in the rhizosphere [159] or by inducing Fe^{2+} transporters that can facilitate Cd uptake [160, 161]. Grasses (graminaceous monocotyledonous plants) are so-called strategy-II plants [162]. As part of their Fe acquisition strategy induced by Fe deficiency, grass roots exude Fe binding chelates (siderophores) that form strong complexes with Fe [162] and other divalent metals (e.g. Zn) [124]. Fe-siderophore complexes are taken up by specific transporters [162, 163]. As mentioned earlier, Zn and potentially Cd uptake might be facilitated by phytosiderophores [124]. Shao et al. (2007) observed that Fe nutrition affects Cd accumulation in rice with higher accumulation at low Fe nutrition [164]. However, this observation might not be directly related to phytosiderophores as Shenker et al. (2001) found no influence of phytosiderophores on Cd uptake by wheat and barley [125]. Clovers and typical pastoral weeds are, like most non-graminaceous monocotyledonae and dicotyledonae, strategy-I plants. Their root response to Fe deficiency includes active rhizosphere acidification by exudation of protons and active alteration of the rhizosphere Eh conditions by exudation of reductants. This results in thermodynamic and kinetic destabilisation of Fe(III) bearing minerals and in soluble Fe(II) that is eventually taken up by membrane transporters [162, 165]. The decrease in pH and dissolution of Fe oxides might result in increasing Cd phytoavailability. Rodecap et al. (1994) and Boa et al. (2009) observed that Fe-deficiency induces Cd uptake by *Arabidopsis thaliana* and *Solanum nigrum* respectively [157, 159]. Inhibitory effects on Cd plant uptake under certain soil conditions are discussed for a range of other micronutrients, e.g. Cu, Mn, Ni, Se and Ca [7]. Cd uptake and/or translocation in the plant are also reported to be influenced by the macronutrients N, P and K but the results are not clear to date. After N fertilisation, increased and decreased Cd accumulation in crops can be observed. An increase might be attributed to Cd mobilisation (ionic strength effects, ion exchange reactions and/or soil acidification) or physiological processes [149, 166, 167] whereas a decrease is possible due to dilution in increased biomass [168]. The effect differs between different types of N fertiliser [149]. Increased and decreased crop Cd levels are also observed after P application. Apparently the effect of P application on Cd uptake may differ between soils and between plant species [7].

Complex soil-plant-microorganism interactions - The chemical and physical conditions of the rhizosphere, the soil that is directly influenced by the roots, are distinct from that in the bulk soil. They are altered by numerous plant physiological processes which might change as a response to the conditions the plant roots encounter [169]. The rhizosphere is characterised by higher density and metabolic activity of microorganisms than the bulk soil. Root exudates provide nutrition for these rhizosphere microorganisms, which in turn interact with the plant roots and stimulate plant growth [170].

The response of plant roots and microorganisms to the chemical and physical conditions in the rhizosphere involves processes that can influence Cd phytoavailability [171]. The response of roots to Cd exposure in the rhizosphere was recently reviewed by Lux et al. (2011) [126]. Plants exposed to high Cd concentration[5] in the rhizosphere show root anatomy alterations and inhibited root elongation. The roots of most plants show reduced growth into patches with elevated Cd concentrations. Whether or not such growth patterns are adaptive is debated. For some plants, acceleration of maturation and chemical alteration of the endodermal barrier and an increase in root diameter attributed to enlargement of cortical cells is observed [126]. Root exudates can change the physicochemical conditions in the rhizosphere. They markedly alter in quality (species) and quantity under different stress conditions (e.g. metal toxicities, nutrient deficiencies) [171, 172]. Roots excrete protons, inorganic ligands (e.g. Cl^-, SO_4^{2-}, NH_4^+, CO_3^{2-}, PO_4^{3-}) and organic ligands (e.g. carbohydrates, humic acids, polypeptides, proteins, amino acids, nucleic acids) [171]. Hinsinger et al. (2003) reviewed the origin of root mediated pH changes in the rhizosphere. He reported enhanced proton and organic anion release by roots as a result of various types of environmental stresses, e.g. Fe deficiency, P deficiency, toxicity of Al and maybe other metals. In contrast to Al-sensitive genotypes showing elevated proton excretion, Al-resistant genotypes are reported to be able to increase pH which might be a way to alleviate Al toxicity [172]. Tue et al. (1989) found that Cd in solution decreased H^+-ATPase activity in purified tonoplast vesicles indicating that Cd has an inhibitory effect on H^+ excretion [173] which in turn might be part of the plants strategy to cope with Cd stress. Some plants are known to excrete organic compounds that can chelate Cd^{2+} and prevent its entrance into to root. This might be part of the response on Cd exposure [171].

Microorganisms in the rhizosphere are induced by root secretion and influence plant growth via numerous processes, e.g. nutrient sourcing, production of phytohormones, specific enzymatic activities, production of antibiotics and production of siderophores/chelating agents. Typically, free-living as well as symbiotic rhizobacteria and mycorrhizal fungi are present in the rhizosphere. This microflora crucially influences the uptake of trace elements, including Cd, by plants [170, 171]. Some important physicochemical reactions influencing the fate of Cd in the soil-plant system involving microorganisms are: (i) Changing Cd solubility via changing rhizosphere pH or metal valence; (ii) formation of insoluble metal sulphides by releasing H_2S; (iii) producing numerous organic substances; (iv) binding/sequestration of the toxic metal via the cell walls or the mucous layer of the cell surface of microorganisms, or via proteins and extracellular polymers [171]. Some microorganisms produce phytohormones influencing the plant root physiology [174] which might in turn elevate or decrease plant Cd uptake. Pathogenic microorganisms can damage the epidermis, opening gaps for apoplastic transport [175]. Arbuscular mycorrhizal fungi are one of the major components of the rhizosphere [176] and form symbiotic relationships with 80 - 90% of land plants in natural and managed ecosystems [170]. Their fungal hyphae exploit a large volume of soil making nutrients phytoavailable that are unavailable for uptake by the plant roots alone [170]. The types of mycorrhizal fungi and/or other rhizosphere microorganisms markedly influence the Cd uptake by plants as shown by numerous authors, e.g. recently by Malekzadeh et al. (2011) [177] and Garg & Aggarwal (2012) [176].

[5] Some of the studies cited here might not be relevant for agricultural soils as they investigated biological response to rhizosphere Cd levels typically not encountered in soils used for food production. Nevertheless, they exemplify how the biological response to rhizosphere conditions might influence Cd uptake by plants.

Part B

2.3 Lignite – a young coal

Lignite is a microheterogenic sedimentary rock composed of organic and inorganic materials [178]. Lignite rock is abundant worldwide and is primarily mined for energy production. The proved and recoverable world lignite resources are cited by the World Energy Council (2010) to be ca. 195 billion tonnes, with 333 million tonnes being located in New Zealand [179]. The inorganic fraction of lignite rock consists primarily of clay minerals, quartz, carbonates, sulphides and sulphates and can range from a few percent to more than 50%. The organic fraction originated mainly from plant residues that have undergone various degrees of decomposition and physical and chemical alterations. Under waterlogged and anoxic conditions, plant debris is turned into large peat deposits via bacterial action (biochemical phase). The peat is buried by ongoing sedimentation and subsequently coalified under influence of pressure and temperature arising from overlying sediments (geochemical phase). The coalification process takes several hundred million years and results first in lignite and, with increasing degree of coalification, in bituminous coal and anthracite [178]. Lignite is coal of low rank (degree of coalification) and, because the rank usually correlates with the heat content, of low grade regarding heat generation. Coalification is a deoxygenation-aromatisation process. The degree of coalification is negatively correlated with the oxygen and hydrogen content but positively correlated with the carbon content and the fraction of aromatic carbon [180]. A typical elemental composition of lignite is 70% C, 8 - 5% H and 25% O. Approximately half of the C atoms are part of aromatic structures. Generally, only a few percent of S and N is present and contents do not significantly change with degree of coalification [178]. The common concept of the structure of lignite is that it consists of aromatic rings, ether and ester linkages, bridges such as alkylene and functional groups such as alkyl, carbonyl, carboxyl and hydroxyl groups [25]. Figure 5 shows a possible model of the structure of lignite.

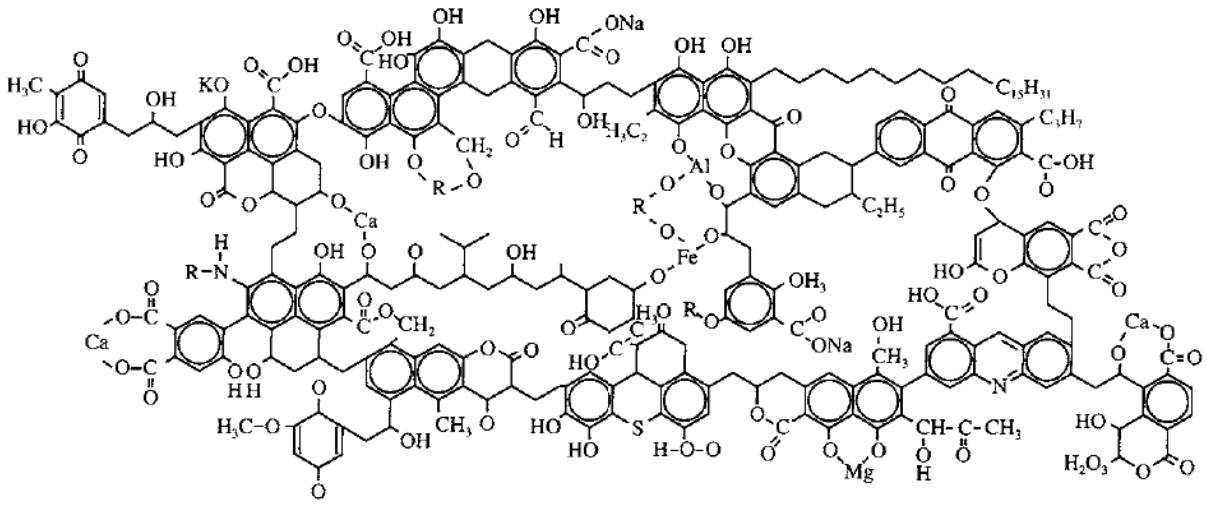


Figure 5: Possible model of a lignite structure [178].

3. Materials and methods

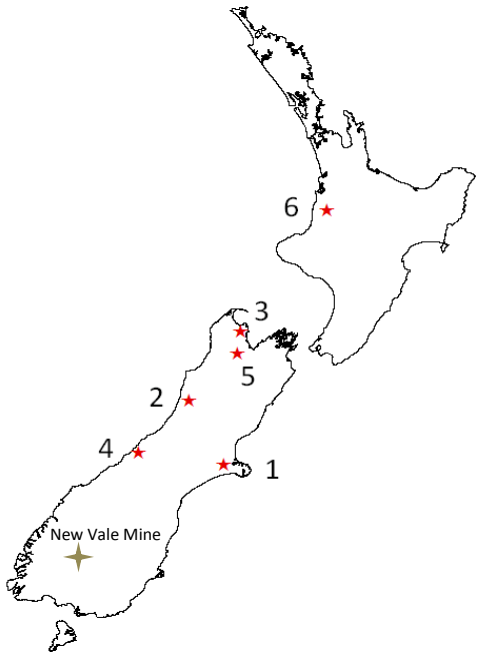
3.1 Materials

Lignite

Powdered lignite was provided by Solid Energy New Zealand Ltd. Samples were mined in the New Vale open cast mine in Southland, NZ. The powder was produced using a crusher with an air swept classifier. The crushed material was blown over a partition by a fan. The particles of the desired size pass over the partition, whereas bigger particles return to the crusher by falling through the partition [181]. Table 7 shows the physicochemical properties of the lignite.

Soils

Six pasture soils from New Zealand were used. Soil 1 was collected on the Lincoln University Commercial Dairy Farm. Soils 2 to 6 were selected from a soil survey of a total of 69 soils from both islands. They were selected on the rationale of covering a broad range of soil pH values, organic carbon contents and textures. Figure 6 shows the soil sampling sites on a map of New Zealand. The legend gives the soil types according to the New Zealand Soil Classification [182] as found in the Fundamental Soil Layer of New Zealand [183]. All soils had been modified by agriculture[6]. Table 7 shows the physicochemical soil properties.



1 – Typic immature pallic soil
43°38'11.35" S 172°26'17.00" E

2 – Typic orthic brown soil
42°20'18.51" S 171°33'54.34" E

3 – Weathered rendzic melanic soil
40°56'36.24" S 172°53'33.53" E

4 – Typic sandy recent soil
43°22'4.00" S 170°11'12.20" E

5 – Acidic orthic brown soil
41°23'18.27" S 172°48'47.73" E

6 – Pallic orthic brown soil
38°29'5.48" S 174°59'49.38" E

Figure 6: Map of New Zealand with soil sampling sites. The legend shows the soil types (New Zealand Soil Classification [182]) as found in the Fundamental Soil Layer of New Zealand [183].

[6] Common practice for pastureland in NZ includes amendment of liming agents and fertilisers and occasionally tilling and sowing.

Biosolids

Biosolids were obtained from Kaikoura Regional treatment works, New Zealand. Knowles et al. (2011) described the preparation. About 160 kg were homogenized in a concrete mixer and subsequently sieved to a grain size of < 20 mm. Physicochemical characteristics of the biosolids used as determined by Knowles et al. (2011) are given in Table 7 [184].

Table 7: Physicochemical properties of the biosolids, lignite and Soils 1 - 6. Values in brackets represent standard error (SE) of the mean. (N = 3 when SE is given; N = 1 when no SE is given.)

	Biosolids*	Lignite	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6
moisture (%)	53	38						
clay/silt/sand (%)		< 200 μm†	4/20/76#	3/42/55	40/46/14	17/44/39	20/30/50	19/25/56
pH (H_20)	4.1	4.5	5.1	5.5	5.3	4.8	6.8	5.5
CEC (meq/100g)		44.8	12.3‡					
BS (%)		95.2	50.3‡					
C (%)	28.0 (0.2)	57.2 (0.2)	3.3 (0.03)	6.1	4.9	8.7	2.0	13.3
N (%)	2.7 (0.03)	0.8 (0.01)	0.3 (0.00)	0.6	0.3	0.6	0.2	1.0
P (mg/kg)	4683 (2)	57.6 (0.2)	732 (11)	1470	876	786	605	2108
S (mg/kg)	6972 (43)	6539 (35)	383 (6)	784	447	578	217	1381
Ca (mg/kg)	9818 (176)	17502 (119)	3229 (58)	4350	3310	8272	11090	4210
Mg (mg/kg)	2204 (17)	2815 (11)	3426 (71)	1235	1921	1779	1934	1231
K (mg/kg)	4330 (67)	219 (2)	2541 (279)	3781	3768	4422	3585	1256
Cd (mg/kg)	2.8 (0.0)	0.06 (0.007)	0.13 (0.00)	0.86	1.34	0.75	1.07	1.53
Zn (mg/kg)	878 (13)	9 (1)	70 (2)	43	76	49	67	61
Cu (mg/kg)	561 (33)	2 (0)	5 (0)	6	23	6	23	38
Mo (mg/kg)		0.1 (0.00)	0.1 (0.01)	0.3	0.6	0.2	0.2	0.9
B (mg/kg)		36.3 (0.1)	7.3 (1.0)	4.1	4.6	3.1	5.6	4.5
Fe (mg/kg)		12918 (145)	17727 (353)	21039	38664	20501	34912	33082
Mn (mg/kg)		280 (3)	357 (20)	154	2346	320	577	814

*[184] †[181] ‡[185] #[186]

3.2 Experiment settings

Batch sorption experiments

The influence of pH and spiked Cd solution concentration on Cd sorption by lignite and soil was studied in Batch Experiment 1. How Cd sorption is influenced by soil type and lignite addition to soil was investigated in Batch Experiment 2. The soils used for the experiments were dried and passed through a 2 mm nylon sieve. The lignite powder was used without drying to avoid hydrophobicity. Solid/solution ratios were determined taking account of the moisture content of the lignite. Both sorption experiments were conducted using 40 ml centrifuge tubes with 4 replicates per treatment. Three replicates per treatment were used for element analysis and one for pH determination. The tubes were continuously agitated for 2 hours on an end-over-end shaker in order to reach sorption equilibrium (see Appendix C1). The pH of the slurry was measured after shaking. The tubes were centrifuged for 10 minutes at 3300 rpm. The supernatant was decanted and filtered with a Whatman 52 filter paper. Solution element concentrations were measured by ICP-OES. Total and organic carbon in solution was determined in Batch Experiment 1 using a total carbon analyser.

Treatments Batch Experiment 1 - Five grams of lignite or Soil 1 was added to 30 ml 0.05 M $Ca(NO_3)_2$ (BDH AnalaR $Ca(NO_3)_2x4H_2O$) solution spiked with varying amounts of Cd (BDH AnalaR $3Cd(SO_4)x8H_2O$) and different pH values. The initial solution Cd concentrations were 0, 0.12, 0.39, 1.26 and 3.75 mg/l. They were determined separately in treatments without addition of sorbent, henceforth referred to as “SO” (Solution Only). Different pH values ranging from 2.8 to 8.3 were adjusted after addition of the sorbent by using HNO_3 (BDH ARISTAR nitric acid 70%) or KOH (BDH AnalaR KOH) to decrease or increase pH respectively. The different treatments are listed in Appendix C2.

Treatments Batch Experiment 2 - Six soils (Soil 1 - 6) and mixtures of 4.75 g of the corresponding soils with 0.25 g lignite (5 wt%) were studied. Additionally, a mixture of 4.5 g Soil 1 with 0.5 g lignite (10 wt%) was studied. Five grams of sorbent was added to 30 ml 0.05 M $Ca(NO_3)_2$ solution without spiking or spiked with Cd. The initial solution concentrations were 0 and 0.39 mg/l Cd. They were determined as part of Batch Experiment 1.

Pot experiment

A pot experiment was conducted in a greenhouse at Lincoln University (NZ*). Lolium perenne* (perennial ryegrass)[7] was grown in pots of a volume of 2.5 l holding ca. 3 kg of Soil 1. Table 8 shows the soil treatments. All treatments were prepared using a concrete mixer. The filled pots were placed in a randomised block design and allowed to stand for 2 weeks in order to equilibrate. Soil samples for chemical analysis were taken prior to sowing. *Lolium perenne* was sown directly on the wet soil surface without any further soil working. A dense surface cover established in all pots. Plants were irrigated daily and no fertilizer was applied. The above-ground biomass was harvested 29 days after sowing.

Table 8: Treatments for the pot experiment. The numbers represent the wt%[8] of lignite added[9] to each soil. There were five replicates of each treatment. The spiked soil received 1.1 mg/kg[10] Cd as $CdSO_4$ solution. Biosolids were added at a rate of 10% by volume giving 3.7 wt%[11] and adding 0.07 mg/kg[12] Cd. Lime (Ravensdown AgLime) was added at a rate of 65g per pot.

	unspiked	spiked	biosolids
unlimed	0, 1.0, 3.4, 7.1	0, 1.0, 3.4	0, 1.0, 3.4, 7.1
limed	0, 1.0, 3.4, 7.1	0, 1.0, 3.4	0, 1.0, 3.4, 7.1

3.3 Analysis of lignite, soil and plant material

Soil and lignite material was dried at 105°C until a constant weight was obtained. Soil material was subsequently passed through a nylon sieve with a pore size of 2 mm. The moisture content of the lignite was calculated from weight loss during drying. Plant material was dried at 70°C and ground using a centrifugal mill. Dry plant material was weighed. Dried soil and plant material was stored in sealed containers.

Total element concentrations

The C and N content of the lignite, soil and plant material was determined using an Elementar vario MAX CN element analyser. Pseudo-total element concentrations were measured in acid digests using ICP-OES. Half a gram lignite or soil respectively was digested in 5 ml HNO_3/ 1 ml H_2O_2 (Merck

[7] *Lolium perenne* represents the major fraction of New Zealand pasture biomass as typical botanical composition of pasture in New Zealand is approximately 70% ryegrass, 20% white clover, and 10% weeds [20].
[8] Percentage of lignite additions on dry weight basis were calculated from average C contents in treatments "unspiked X wt% lig", "unspiked" and the C content in lignite according to the formula in Appendix A4.
[9] Moist lignite was added at rates of 0, 25, 100 and 250 g per pot.
[10] Difference of measured total Cd concentrations in spiked (N = 15) and unspiked (N = 15) treatments.
[11] Percentage of biosolids addition on dry weight basis was calculated from C contents in treatments "biosolids" and "unspiked" and the C content in biosolids according to the formula in Appendix A4.
[12] Difference of measured total Cd concentrations in biosolids (N = 20) and unspiked (N = 15) treatments.

hydrogen peroxide 30%). The digest was diluted with Milli Q (Barnstead, EASYpure RF, 18.3 MΩ-cm) to a volume of 25 ml and filtered with a Whatman 52 filter paper (pore size 7 µm). Plant material (0.3 g) was digested in 5 ml HNO_3 and subsequently diluted to a volume of 20 ml. Wageningen reference soil (ISE 989) and plant (IPE 100) material were analysed for quality assurance [187].

Soluble element concentrations

Soluble element concentrations in soil samples were measured in $Ca(NO_3)_2$ extracts using ICP-OES. Five grams of soil were weighed into centrifuge tubes (V = 40ml) and 30 ml 0.05 M $Ca(NO_3)_2$ was added. Tubes were agitated for 2 hours on an end-over-end shaker, subsequently centrifuged for 10 min at 3300 rpm and finally filtered using a Whatman 52 filter paper. Extracts were stored at 4°C.

Soil pH

The pH values of the soil samples were determined in H_2O at a solid/water ratio of 1:2.5. Five grams of soil was added to 25 ml Milli Q in tubes of a volume of 40 ml. The tubes were vigorously shaken by hand to homogenise the slurry and left to stand for a minimum of four hours. The pH was then measured without stirring using a pH electrode.

Cation exchange capacity

The cation exchange capacity (CEC) and base saturation (BS) for the lignite powder and Soil 1 was determined using the silver thiourea method according to Blakemore et al. (1987) [188]. A 0.01 M silver thiourea solution was prepared by dissolving thiourea (BDH thiourea) and silver nitrate (Merck silver nitrate) in Milli Q. A soil sample of 0.7 g was weighed into 50 ml centrifuge tubes and 35 ml silver thiurea solution was added. The slurries were shaken overnight on an end-over-end shaker, subsequently centrifuged for 10 min at 2000 rpm and filtered through Whatman 40 filter into plastic vials. Solution concentrations of silver and the major basic cations (Mg, Ca, Na, K) were measured by ICP-OES. A reagent blank was carried throughout the procedure. The CEC and BS were finally calculated from solution concentrations of silver and major cations (formulas in Appendix A2).

Grain size distribution

The grain size distribution of the Soils 2 - 6 was determined using the pipette method according to the reference methods of the Swiss federal agricultural research stations [189]. Aliquots of hydrogen peroxide (30%) were added to 50 g of soil on a sand bath (100˚C) to degrade the organic matter. After completion of the reaction, soils were dried in the oven at 105˚C. Subsequently, 5 g dried material was dispersed in 0.2% Calgon solution (2g/l) in an ultrasonic bath and filled in a graduated cylinder of a volume of 500 ml. Cylinder was than filled to the mark with 0.2% Calgon solution and slurry was mixed. After 84 seconds a sample of a volume of 10 ml was taken in a depth of 19 cm

using a pipette. After two hours a second sample of the same volume was taken in a depth of 2.6 cm. Timekeeping began when all visible turbulence was dissipated. The samples were evaporated at 105˚C and dry weight was determined. The mass of blanks (cup with Calgon) were determined. Soil texture was calculated from the weight difference between samples and blanks (formula in Appendix A3).

3.4 Data analysis

Solid-solution distribution coefficients K_d were calculated from batch experiment results considering the fate of the spiked Cd according to Equation 1 which was derived as described in Appendix A5. $C_{Cd\ Y/pH\ X}$ is the Cd solution concentration in the treatment in which the sorption is assessed. $C_{no\ Cd/pH\ X}$ is the Cd solution concentration measure in the treatment with the corresponding pH, but without Cd spiking and $C_{Cd\ Y/SO}$ is the Cd solution concentration in the corresponding spiked treatment without addition of sorbent. This K_d value might describe the labile pool of Cd in the system if the concentration of labile Cd originating from soil or lignite is small compared to the spiked Cd and/or the system is far away from saturation (K_d not a function of concentration). For details about K_d values and metal pools see review by Degryse et al. (2009) [67]. The calculated K_d values can be considered unitless as 1 l of aqueous solution equals approximately 1 kg thereof.

$$K_d = \frac{\text{Cd adsorbed (mg/kg)}}{\text{Cd in solution (mg/l)}} = \frac{\left(C_{Cd\ Y/\ SO} - \left(C_{Cd\ Y/pH\ X} - C_{no\ Cd/pH\ X}\right)\right)\ (\text{mg/l}) * \frac{0.03\ \text{l}}{0.005\ \text{kg}}}{\left(C_{Cd\ Y/pH\ X} - C_{no\ Cd/pH\ X}\right)\ (\text{mg/l})} \quad (1)$$

Microsoft Excel 2007 was used for general data analysis and visualisation. (Log-)linear regressions including their statistical evaluation (R^2), Fisher's least significant difference tests (LSD-test) and analysis of variance (ANOVA) based on a generalised linear model (F-test based on type III sums of square) were computed using the statistical software R (http://www.r-project.org/). For Fisher's test the R package agricolae was used (http://tarwi.lamolina.edu.pe/~fmendiburu).

4. Results

4.1 Batch sorption experiments

Figure 7 shows the solid-solution distribution coefficient K_d for Cd as a function of solution pH as observed for the two sorbents (lignite and Soil 1) with 4 spiked Cd concentrations. The K_d for Soil 1 increased with increasing pH for all concentrations of spiked Cd. The K_d values for the spiked concentrations 0.12 mg/l, 0.39 mg/l and 1.26 mg/l were comparable at a comparable pH. The logarithm of K_d positively correlated with pH (R^2 = 0.99).

The K_d for lignite increased with increasing pH between pH 3.4 and 6.8. In this range, the K_d for different spiked concentrations were comparable at a comparable pH and the logarithm of K_d was positively correlated with pH (R^2 = 0.98). Above pH 6.8, K_d decreased. In the series with 1.26 mg/l spiked Cd, the K_d at pH 8.4 was lower by a factor of 18 compared to the corresponding one at pH 6.8 (1242 and 22066 respectively). In the series with 3.75 mg/l spiked Cd, the K_d at pH 8 was 89 fold lower than at pH 6.8 (212 and 18783 respectively). At pH ca. 4.4 the K_d value for sorption onto lignite was ca. 13 times higher than the corresponding value for Soil 1. The fitted log-linear regression lines (formulas given in Figure 7) showed slopes of 0.59 and 0.74 for Soil 1 and lignite respectively. The relative increase of K_d per pH unit was therefore higher for sorption onto lignite than onto soil. For pH 5 and pH 6 the K_d for adsorption on lignite was calculated to be ca. 17 and 23 times higher than at the corresponding pHs for Soil 1.[13]

Figure 8 shows the calculated fraction of spiked Cd adsorbed onto lignite and Soil 1 as a function of pH. The difference between the percentages adsorbed onto lignite and that adsorbed onto Soil 1 is highest at low pH (48%) and decreases with increasing pH. Figure 9 shows the calculated difference in percentage adsorbed assuming the solid/solution ratio used in the batch experiments (1:6) and solid/solution ratios that may represent an agricultural soil at field capacity (1:1) or below (1:0.25). The calculated difference for all three solid/solution ratios showed decreasing progression with increasing pH, but were smaller for greater solid/solution ratio or lower moisture content respectively.

[13] Please Note: A fitted log-linear line ($\log K_d$ ~ pH) to the observations with lignite excluding observations with a pH > 5.4 has a slope of 0.62 which is lower than the one given in Figure 7. Nevertheless, it is greater than the corresponding one (also excluding observations with pH > 5.4) calculated for Soil 1 of 0.50. Excluding these data points would therefore not change the discussion in a qualitative sense.

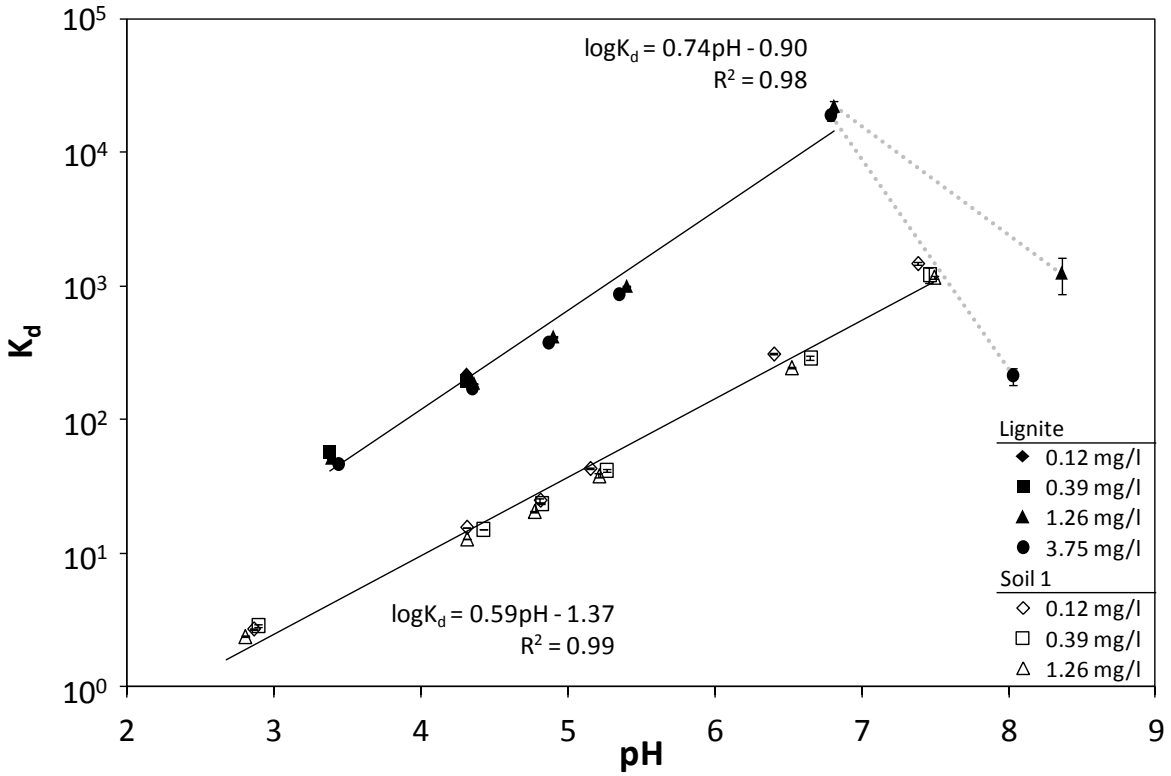


Figure 7: K_d for Cd adsorption onto lignite and Soil 1 as a function of solution pH and different spiked Cd solution concentrations as measured in Batch Experiment 1 (mean ± SE, N = 3). Lines represent fitted log-linear model (formula and R^2 given in figure). Training set included all observations for Soil 1 and observations in the pH range ≤ pH 6.8 for lignite.

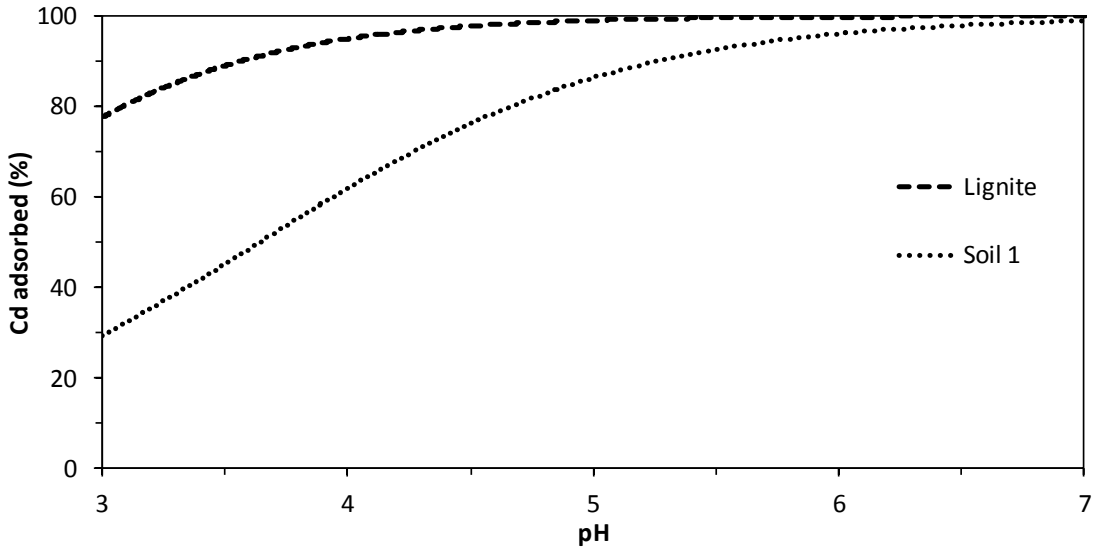


Figure 8: Percentage of Cd adsorbed as a function of pH for a solid/solution ratio of 1:6 and K_d values calculated using the formulas given in Figure 7.

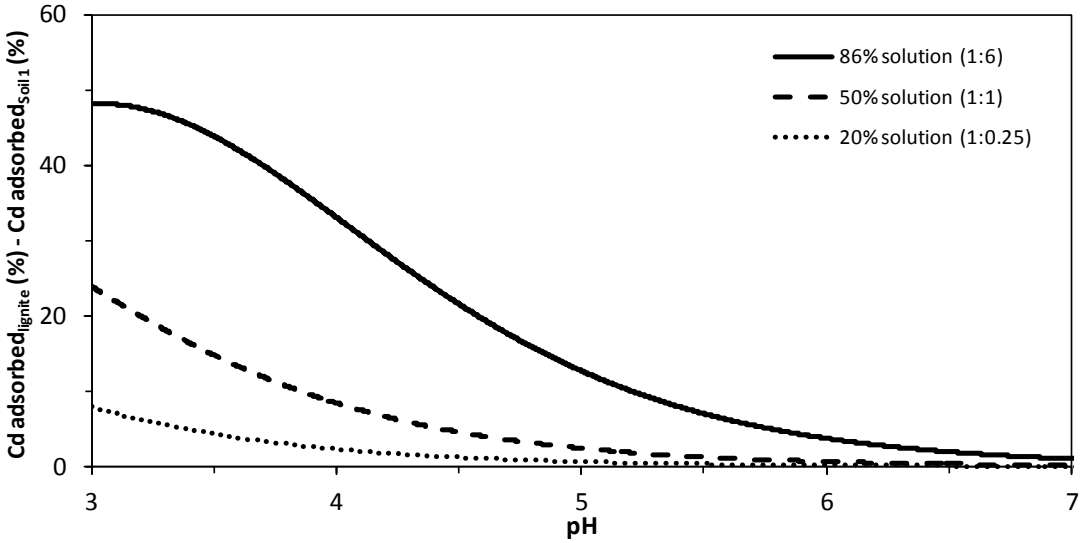


Figure 9: Difference in percentage Cd adsorbed on lignite and Soil 1 as a function of pH for three solid/solution ratios. Underlying K_d values were calculated using the formulas given in Figure 7.

Figure 10 shows the concentration of dissolved organic carbon (DOC) as a function of pH (measured in the treatments without Cd spiking). For Soil 1, the concentration of DOC for the pH range 4.3 to 7.5 varied within the narrow range of 104 to 129 mg/l. No clear trend was observed. For lignite, the concentration of DOC increased exponentially with increasing pH over the whole pH range investigated (pH 3.4 to 8.2). At pH ca. 4.3 and 7.5 the released concentration of DOC from Soil 1 was 6 and ca. 1.7 times that released from lignite respectively (formula in Figure 10 used).

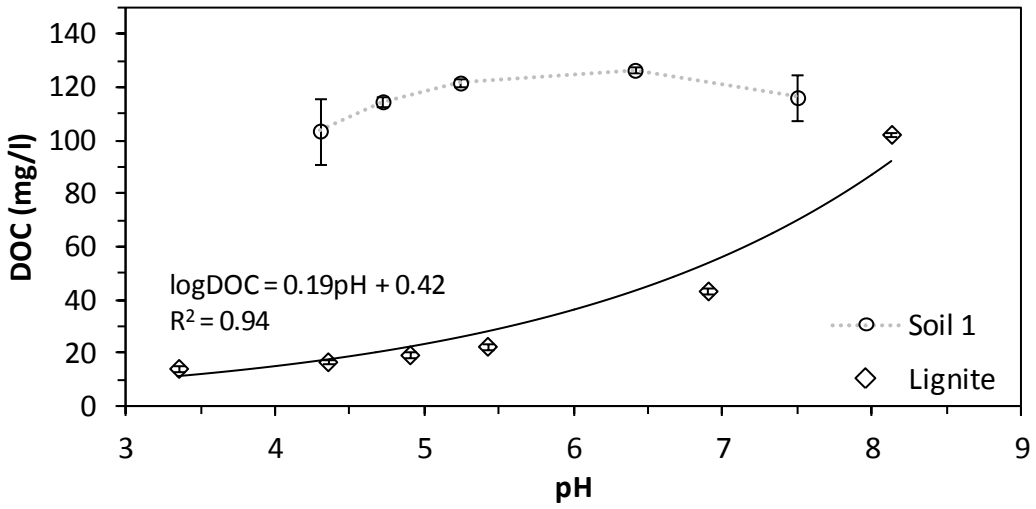


Figure 10: Dissolved organic carbon (released from lignite and Soil 1) versus pH as measured in the treatments without Cd addition in Batch Experiment 1 (mean ± SE, N = 3). Solid line represents fitted model (formula and R^2 given in figure).

Figure 11 shows K_d and pH in Batch Experiment 2. The measured pH for soils without lignite addition was significantly correlated (R^2 = 0.98) with the corresponding pH (H_2O) given in Table 7 but on average 0.93 pH units (SE = 0.08) lower. They ranged from pH 3.8 for Soil 4 to 6.1 for Soil 5. The K_d measured ranged from 6.0 for Soil 3 to 76.0 for Soil 5. The effect of lignite addition on K_d and pH was strongly dependent on the soil type. The soils with the lowest pH values (Soil 3 and Soil 4) showed an increase in pH whereas all other soils showed a decrease in pH when 5 wt% lignite was blended with the soil. Significant decrease in K_d was observed for Soil 5 and a significant increase in K_d was found for Soil 3. The K_d values significantly correlated with the pH values (R^2 = 0.91). No correlation was found between the K_d values and the total carbon content (calculated from carbon content of soils and lignite).

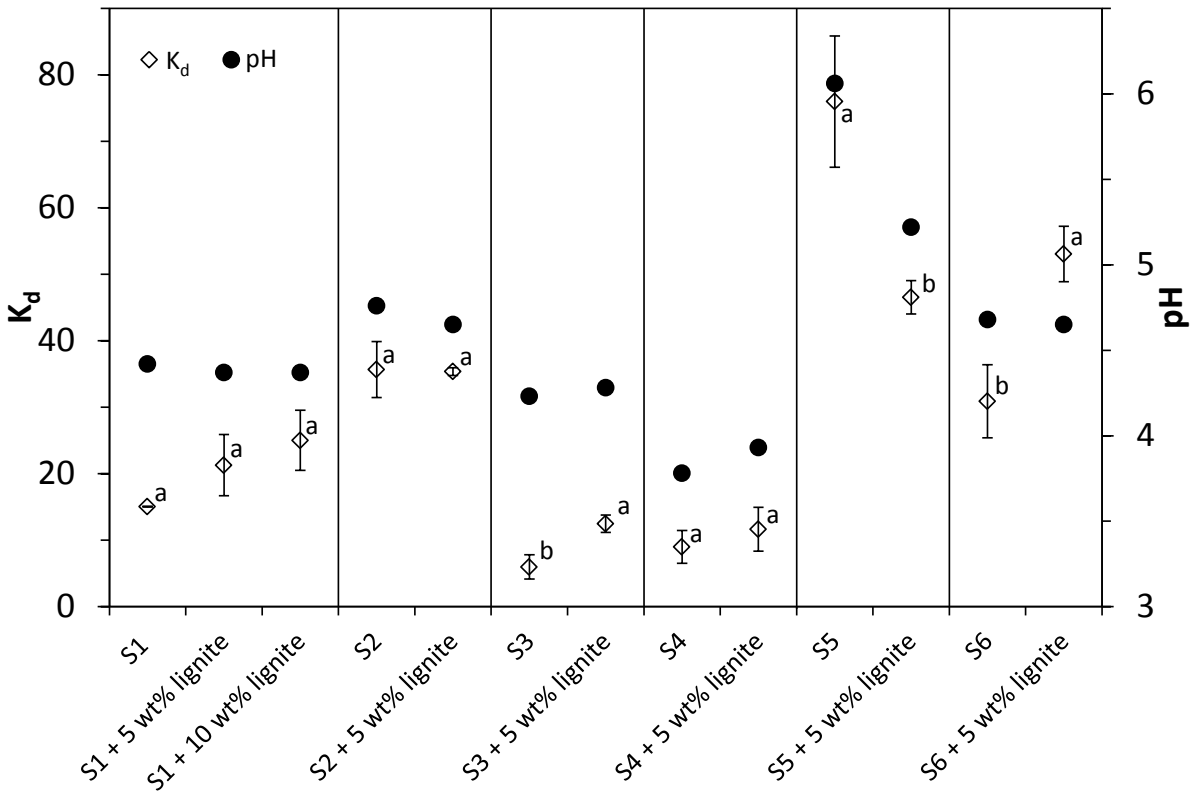


Figure 11: K_d and pH values as a function of sorbent type (Soil 1 - 6 with 0, 5 or 10 wt% lignite addition) as measured in Batch Experiment 2 (K_d: mean ± SE, N = 3, pH: no replicate). Means with the same letter are not significantly different.

4.2 Pot experiment

Cd solubility and plant uptake

Figure 12 shows the concentration of soluble Cd versus wt% lignite blended with the soils. Graph A and B refer to the treatment series without and with lime addition respectively. In the treatment series without lime addition (Graph A), there was a significant decrease in soluble Cd concentrations when soils were amended with 3.4 or 7.1 wt% lignite. The effect was greatest for the soils spiked with Cd; 3.4 wt% lignite decreased the soluble concentration significantly ($LSD_{0.05}$ = 0.108). In the treatments with biosolids addition the decrease was less pronounced but significant for 7.1 wt% lignite addition ($LSD_{0.05}$ = 0.010). For the unspiked treatments a significant decrease for 3.4 wt% lignite addition was observed ($LSD_{0.05}$ = 0.011). No significant decrease in the unspiked ($LSD_{0.05}$ = 0.004), the spiked ($LSD_{0.05}$ = 0.048) and the biosolids ($LSD_{0.05}$ = 0.008) treatments was observed in the treatment series with lime addition (Graph B). ANOVA based on a generalised linear model revealed that both lignite addition and liming had a significant negative effect on soluble Cd concentrations when soil was spiked with Cd or blended with biosolids (Table 9). In the unspiked soil the effect was just significant for lime[14].

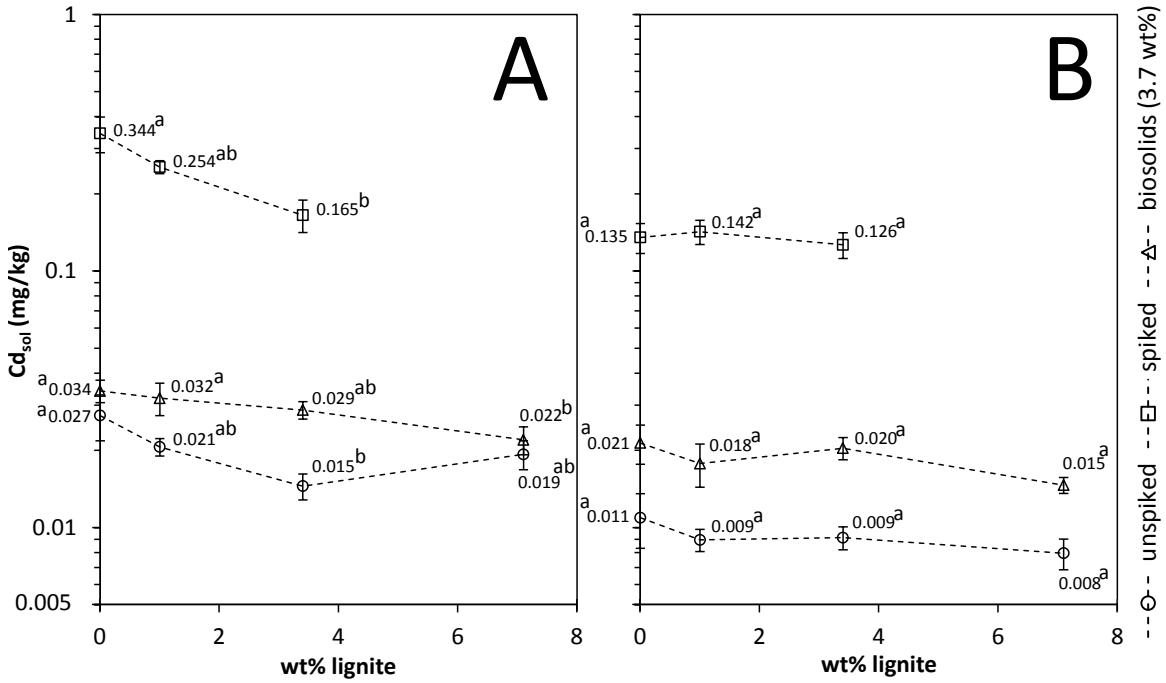


Figure 12: Concentration of soluble Cd in soil (Cd_{sol}) as a function of wt% lignite addition (mean ± SE, N = 5). Means with the same letter are not significantly different. The graphs A and B refer to the treatment series without and with lime addition respectively.

[14] Excluding the highest lignite treatment of 7.1 wt% resulted in significant effect of both lime and lignite. The interaction does not become significant by excluding these observations.

Table 9: Effect of lignite and lime addition on soluble soil Cd concentration, Cd_{sol}, and Cd concentration in *Lolium perenne*, Cd_{plant} (- negative effect, + positive effect). ANOVA based on a generalised linear model with interaction in the form X ~ lignite + lime + lignite:lime (F-test using type III sums of square). Lignite was treated as a continuous variable and lime as a categorical factor with values "Yes" and "No". Significance codes: 'ns' > 0.05 > '*' > 0.01 > '' > 0.001 > '***'**

	Factor	pH	Cd_{sol} (mg/kg)	Cd_{plant} (mg /kg dw)
unspiked	lignite	ns	ns	- (**)
	lime	+ (***)	- (***)	ns
	lignite:lime	- (***)	ns	ns
spiked	lignite	- (**)	- (***)	- (***)
	lime	+ (***)	- (***)	- (***)
	lignite:lime	- (*)	+ (**)	+ (**)
biosolids	lignite	ns	- (**)	- (***)
	lime	+ (***)	- (***)	ns
	lignite:lime	- (***)	ns	ns

Figure 13 shows the plant Cd concentration as measured in above-ground biomass of *Lolium perenne*. Graph A and B refer to the treatment series without and with lime addition respectively. In both treatment series, with and without lime addition, there was a significant decrease in plant Cd concentrations when 1.0 or 3.4 wt% lignite was amended. In the series without lime addition (Graph A) this decrease was greatest for the treatments spiked with Cd where the plant concentration decreased significantly for 1.0 and 3.4 wt% ($LSD_{0.05}$ = 0.11). In the treatments with biosolids, the decrease was less pronounced but significant for 3.4 and 7.1 wt% lignite addition ($LSD_{0.05}$ = 0.03). In the unspiked treatments a significant decrease for 1.0, 3.4 and 7.1 wt% lignite amendment was observed ($LSD_{0.05}$ = 0.03). In the treatment series with lime addition (Graph B), a significant decrease for 3.4 wt% lignite was observed for the spiked treatments ($LSD_{0.05}$ = 0.08), the biosolids amended treatments ($LSD_{0.05}$ = 0.02) and the unspiked treatments ($LSD_{0.05}$ = 0.02). ANOVA based on a generalised linear model revealed that lignite addition significantly decreased plant Cd concentrations independent of whether the soil was unspiked, spiked with Cd or amended with biosolids (Table 9). Liming had a significant effect in the spiked but not in the unspiked and biosolids treatments.

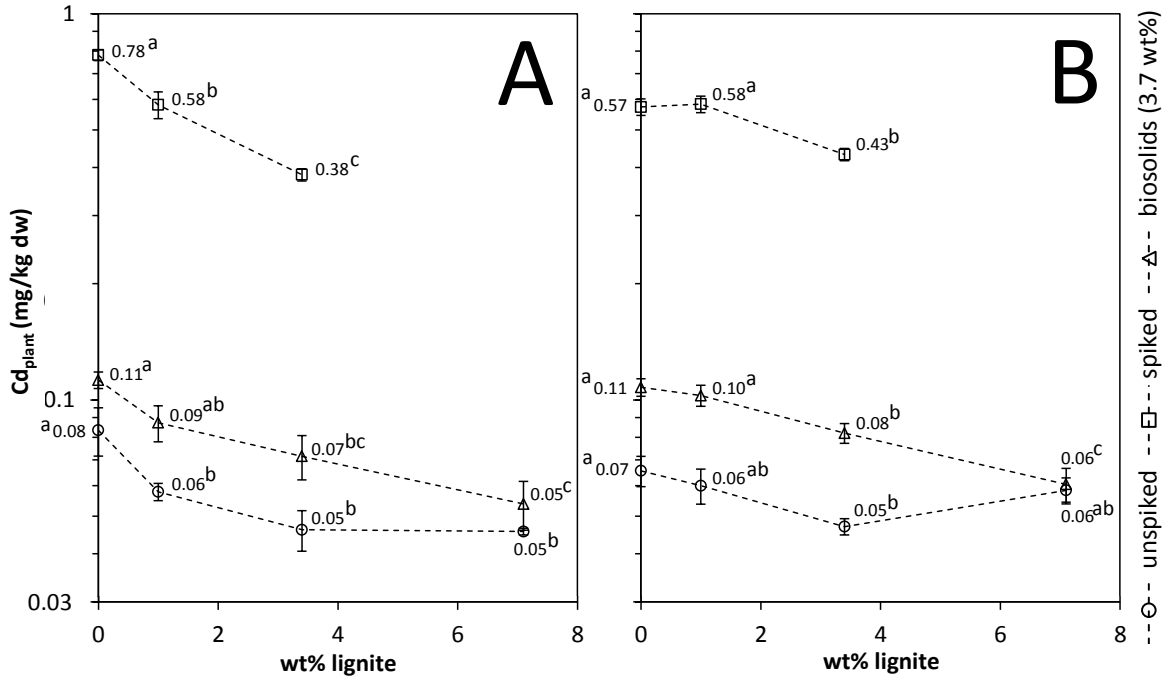


Figure 13: Concentration of Cd in *Lolium perenne* (Cd_{plant}) as a function of wt% lignite addition (mean ± SE, N = 5). Means with the same letter are not significantly different. The graphs A and B refer to the treatment series without and with lime addition respectively.

Figure 14 shows the changes in soluble Cd versus the changes in plant Cd as observed relative to the concentrations in the corresponding treatments without lignite and lime addition. Graph A and B refer to the treatment series without and with lime addition respectively. Note that their axes are scaled identically as the reference samples are the same. In the series without lime addition (Graph A), the maximal relative reduction in soluble Cd of 52% was observed in the spiked treatment with 3.4 wt% lignite addition. The treatments with the maximal reduction in plant Cd are the spiked soil amended with 3.4 wt% lignite and the biosolids with 7.1 wt% lignite (51 and 52% reduction respectively). The ratio between percentage change in plant and soluble Cd was generally close to, or greater than, 1. For the spiked treatments, the relative change in plant and soluble Cd are of similar value (data points close to 1:1 line). For the biosolids treatments, the relative change in plant Cd was, in order of increasing lignite addition, 1.5, 2.3 and 3.5 times greater than the corresponding change in soluble Cd (data points right of 1:1 line). For the unspiked treatments, there was no distinct pattern regarding the ratio of reduction in plant and reduction in soluble Cd

All treatments with lime addition (Graph B) showed relative reduction in soluble Cd of > 30%. The greatest relative reduction in soluble Cd of ca. 71% was observed for the unspiked treatment with 7.1 wt% lignite addition. The unspiked and spiked treatments with 3.4 wt% lignite addition and the biosolids treatment with 7.1 wt% lignite addition showed relative reduction in plant Cd of ca. 45%; all other treatments showed ≤ 30% reduction. Most of the treatments showed smaller change in plant Cd as compared to the corresponding treatments without lime addition. The relative change in soluble Cd was greater than the change in plant Cd for all treatments with lime addition (data points left of 1:1 line). The average ratio of relative change in plant Cd to relative change in soluble Cd was significantly different compared to the series without lime addition (1.6 without lime, 0.5 with lime, $LSD_{0.05}$ = 0.7) but no clear patterns were visible.

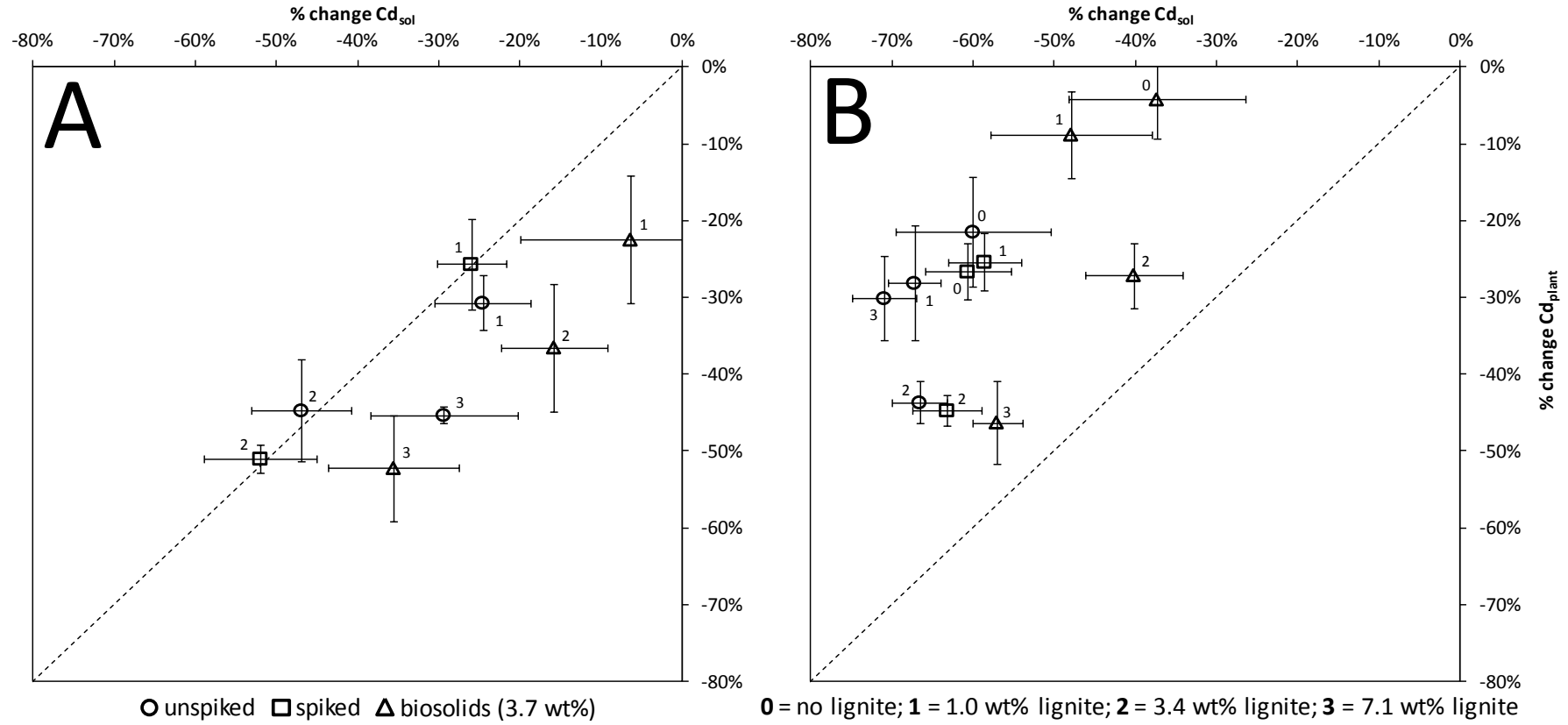


Figure 14: Change in soluble Cd versus changes in plant Cd as observed relative to the concentrations in the corresponding unlimed treatments without lignite addition (mean ± SE, N = 5). The Graphs A and B refer to the treatment series without and with lime addition respectively. Note that the treatments without lignite addition in Graph A fall onto the origin as they are the reference treatments.

Solubility and plant uptake of micro- and macronutrients

Soil pH and solubility of macronutrients - Table 10 shows the influence of lignite addition on the soil pH and on the soluble soil concentrations of the macronutrients P and S. Although within a small pH range, the soil pH significantly decreased with addition of 1.0 wt% and/or greater lignite addition (3.4 and 7.1 wt%). The only exceptions were the treatments with biosolids in the series without lime addition where there were no significant changes for all three lignite additions. These treatments were the most acidic in the whole experiment (ca. pH 4.9). The lignite-induced pH decrease was greater when lime was applied. Decreases of 0.1 and 0.6 pH units were observed in the unlimed and limed treatments respectively. ANOVA revealed a significant interaction between lime and lignite treatment (Table 9). The soluble P concentration significantly increased for 3.4 and/or 7.1 wt% lignite amendment in the unspiked treatments and in the biosolids treatments with lime addition. Apart from the unspiked treatments, lignite addition did not increase soluble S concentration.

Solubility of micronutrients - Table 11 shows the influence of lignite addition on the soluble soil concentrations of the micronutrients Zn, Cu, Fe and Mn. With one exception in each case, there were no significant differences in soluble Cu and Zn. Apart from the unspiked treatments with lime addition, a significant increase in soluble Fe concentration with 1.0, 3.4 and/or 7.1 wt% lignite addition was observed. A significant increase in soluble Mn was observed in the unspiked treatments and the biosolids treatments with lime addition for 3.4 and/or 7.1 wt% lignite amendments.

Biomass and plant uptake of macronutrients - Table 12 shows the influence of lignite addition on the above-ground biomass and on the concentrations of a range of macronutrients in *Lolium perenne.* Apart from one exception, no significant change in biomass was observed when 1.0 or 3.4 wt% lignite was amended. The addition of 7.1 wt% lignite decreased biomass significantly in the biosolids treatments in the series without liming and the unspiked and biosolids treatments in the series with lime addition.

In general, no significant change of plant P with lignite addition was observed. The only exceptions were the unspiked treatments without lime addition where the highest lignite addition (7.1 wt%) decreased plant P significantly. No consistent pattern in plant S concentration with increasing lignite addition was observed. In the spiked treatments without lime addition the concentration increased significantly for 3.4 wt% lignite addition. Significant differences were also observed in the biosolids treatments without lime and in the unspiked treatments with lime addition, but no consistent trend with increasing lignite addition was apparent. In general, no significant changes in plant N were observed. The only exceptions were the biosolids treatments without lime addition where 1 wt%, but not 3.4 and 7.1 wt%, lignite addition lead to a significant decrease in plant N. Apart from the spiked treatments, a decrease in plant Ca with lignite addition was observed (significant for 3.4 wt% and/or 7.1 wt% lignite addition). With exception of the unspiked treatments without lime and the spiked treatments with lime addition, a decrease in plant Mg with lignite addition was observed (significant for 3.4 and/or 7.1 wt% lignite addition). No apparent and significant effect of lignite addition on K plant concentration was observed (only significant change between 3.4 and 7.1 wt% lignite addition in the treatments with biosolids and lime addition).

Apart from Mg, all measured plant concentrations of the macronutrients were above the NZ average in pasture grass (see last row in Table 12). For Mg, some values were below the mean but within the

standard deviation range. With few exceptions for P, concentrations of P, N and K were above the standard deviation range.

Plant uptake of micronutrients - Table 13 shows the influence of lignite addition on the concentrations of a range of micronutrients in *Lolium perenne*. Plant concentrations of Zn decreased with increasing lignite addition in the biosolids treatments with and without lime addition (significant for 3.4 wt% and/or 7.1 wt% lignite addition). In contrast, a significant increase in Zn plant concentrations was observed for 7.1 wt% lignite amendment in the unspiked treatments with lime addition. Apart from the biosolids treatments without liming for Cu and the spiked treatments without liming for Mo, a significant decrease throughout the experiment at least for the highest lignite addition was observed for both micronutrients. Plant B concentrations significantly increased with increasing lignite addition. For addition of 7.1 wt% lignite, the B plant concentration was more than double that of the corresponding treatment without lignite addition. No influence of lignite addition on plant Fe concentration was observed. An increase in plant Mn concentration with lignite addition was observed throughout the experiment (significant for 3.4 and/or 7.1 wt% lignite addition).

All measured Zn concentrations were above the NZ average (see last row in Table 13); all treatments with biosolids amendment exceeded the standard deviation range. Apart from the biosolids treatments, the measured Cu concentrations were below the NZ average. Some treatments with lignite addition were below the standard deviation range. For B, all treatments with lignite addition were above the average and exceeded the standard deviation range when 3.4 or 7.1 wt% lignite was applied. Some treatments without lignite addition were below the national average but within the standard deviation range. Most Mn concentrations measured were below the NZ average; most limed treatments were below the standard deviation range. Apart from exceptions for iron, measured concentrations of Fe, Mo and Co were within the standard deviation range reported for NZ pasture.

Appendix D contains additional analysis of pH, soluble nutrient concentrations, biomass and nutrient concentrations in plant using ANOVA. This appendix is especially recommended for the reader who is interested in the effect of liming.

Effect on nutrient uptake as compared to effect on Cd uptake - Figure 15 shows the change in element concentrations in *Lolium perenne* for the treatments with 1.0 wt% lignite addition relative to the corresponding treatment without lignite addition. In the treatment series without lime addition (Graphs A1 - A3), the relative decrease in Cd concentration in plant was greater than for the nutrients studied independent of whether Cd was indigenous (31%), spiked as Cd solution (22%) or elevated by biosolids amendment (26%). In the series with lime addition (Graphs B1 - B3), the relative decrease was greater for concentrations of some nutrients than for the Cd concentration. In the unspiked treatment (Graph B1), the Mo concentration in plant was reduced by 20% whereas Cd concentration was reduced by 8%. In the series with spiking (Graph B2), plant concentrations of S, N, P, Mg, K, Cu and Ca where decreased to a greater extent (5 - 22%) than the Cd concentration (3%). In the biosolids treatments (Graph B3), Zn concentration was reduced by 9% whereas Cd concentration was reduced by 5%. Similar observations regarding the relative importance of effect on Cd as compared to effects on nutrients was also observed for 3.4 wt% lignite addition (see Appendix D3).

Table 10: Influence of lignite addition on soil pH and soluble concentrations of the macronutrients P and S. Mean (SE), N = 5. Means with the same letter are not significantly different.

Treatment					
	Soil	Lignite (wt%)	pH (H_2O)	P (mg/kg)	S (mg/kg)
unlimed	unspiked	0	5.08[a]	4.4 (0.5)[b]	28 (5)[b]
		1.0	5.01[b]	5.2 (0.3)[ab]	32 (2)[b]
		3.4	5.02[b]	4.3 (0.5)[b]	30 (4)[b]
		7.1	4.98[b]	6.8 (0.9)[a]	59 (8)[a]
	LSD (α = 0.05)		0.06	1.8	16
	spiked	0	5.05[a]	4.1 (0.5)[a]	27 (3)[a]
		1.0	5.06[a]	4.8 (0.1)[a]	33 (1)[a]
		3.4	4.98[b]	5.1 (0.9)[a]	38 (7)[a]
	LSD (α = 0.05)		0.04	1.8	13
	biosolids	0	4.87[a]	4.3 (0.5)[a]	74 (18)[a]
		1.0	4.88[a]	5.7 (0.7)[a]	58 (10)[a]
		3.4	4.90[a]	5.8 (0.6)[a]	63 (5)[a]
		7.1	4.88[a]	5.4 (0.6)[a]	74 (10)[a]
	LSD (α = 0.05)		0.05	1.8	34
limed	unspiked	0	5.90[a]	2.8 (0.4)[b]	23 (3)[c]
		1.0	5.75[a]	3.6 (0.4)[ab]	31 (4)[bc]
		3.4	5.42[b]	4.2 (0.6)[a]	38 (5)[ab]
		7.1	5.32[b]	4.3 (0.5)[a]	47 (5)[a]
	LSD (α = 0.05)		0.16	1.4	13
	spiked	0	5.64[a]	3.8 (0.5)[a]	30 (4)[ab]
		1.0	5.58[a]	3.4 (0.22)[a]	29 (2)[b]
		3.4	5.47[b]	4.2 (0.4)[a]	39 (3)[a]
	LSD (α = 0.05)		0.06	1.2	10
	biosolids	0	5.51[ab]	2.8 (0.4)[b]	61 (16)[a]
		1.0	5.56[a]	4.6 (0.6)[ab]	66 (12)[a]
		3.4	5.41[bc]	5.3 (0.3)[a]	68 (10)[a]
		7.1	5.28[c]	4.8 (0.7)[a]	75 (8)[a]
	LSD (α = 0.05)		0.12	1.9	33

Table 11: Influence of lignite addition on soluble concentrations of the micronutrients Zn, Cu, Fe and Mn. Mean (SE), N = 5. Means with the same letter are not significantly different.

Treatment						
	Soil	Lignite (wt%)	Zn (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
unlimed	unspiked	0	2.0 (0.4)^{a}	0.021 (0.006)^{a}	3.0 (0.2)^{b}	35 (4)^{b}
		1.0	1.8 (0.1)^{a}	0.018 (0.003)^{a}	4.0 (0.27)^{b}	39 (2)^{ab}
		3.4	1.4 (0.2)^{a}	0.011 (0.003)^{a}	4.1 (0.4)^{b}	34 (4)^{b}
		7.1	2.0 (0.5)^{a}	0.023 (0.006)^{a}	9.0 (1.0)^{a}	49 (6)^{a}
	LSD (α = 0.05)		1.0	0.014	1.8	13
	spiked	0	1.4 (0.2)^{a}	0.013 (0.004)^{a}	3.0 (0.4)^{b}	30 (4)^{a}
		1.0	1.6 (0.0)^{a}	0.016 (0.000)^{a}	4.2 (0.2)^{b}	38 (1)^{a}
		3.4	1.3 (0.2)^{a}	0.013 (0.004)^{a}	6.1 (0.9)^{a}	35 (5)^{a}
	LSD (α = 0.05)		0.5	0.009	1.6	12
	biosolids	0	11.1 (1.6)^{a}	0.073 (0.011)^{a}	3.6 (0.4)^{c}	31 (3)^{a}
		1.0	10.0 (2.1)^{a}	0.062 (0.012)^{ab}	5.9 (0.6)^{b}	36 (4)^{a}
		3.4	9.8 (0.7)^{a}	0.054 (0.005)^{ab}	6.8 (0.7)^{ab}	40 (4)^{a}
		7.1	7.5 (1.0)^{a}	0.043 (0.007)^{b}	8.7 (0.8)^{a}	40 (4)^{a}
	LSD (α = 0.05)		4.0	0.026	2.0	11
limed	unspiked	0	0.6 (0.1)^{a}	0.016 (0.006)^{a}	3.5 (2.2)^{a}	20 (2)^{b}
		1.0	0.6 (0.1)^{a}	0.017 (0.002)^{a}	1.7 (0.2)^{a}	25 (2)^{ab}
		3.4	0.7 (0.1)^{a}	0.010 (0.003)^{a}	2.9 (0.4)^{a}	27 (4)^{ab}
		7.1	0.6 (0.1)^{a}	0.012 (0.002)^{a}	4.3 (0.3)^{a}	31 (3)^{a}
	LSD (α = 0.05)		0.3	0.010	3.3	8.5
	spiked	0	0.6 (0.1)^{ab}	0.017 (0.004)^{a}	1.7 (0.2)^{b}	24 (3)^{a}
		1.0	0.6 (0.0)^{b}	0.012 (0.002)^{a}	1.9 (0.1)^{b}	24 (2)^{a}
		3.4	0.8 (0.1)^{a}	0.019 (0.006)^{a}	3.1 (0.3)^{a}	31 (2)^{a}
	LSD (α = 0.05)		0.2	0.013	0.6	7
	biosolids	0	7.5 (1.8)^{a}	0.068 (0.022)^{a}	1.6 (0.2)^{c}	21 (3)^{b}
		1.0	5.7 (1.4)^{a}	0.053 (0.012)^{a}	2.3 (0.3)^{bc}	28 (4)^{ab}
		3.4	4.3 (1.2)^{a}	0.043 (0.009)^{a}	3.1 (0.3)^{b}	34 (2)^{a}
		7.1	4.8 (0.6)^{a}	0.037 (0.005)^{a}	4.8 (0.7)^{a}	36 (3)^{a}
	LSD (α = 0.05)		3.9	0.038	1.2	10

Table 12: Influence of lignite addition on biomass and concentrations of macronutrients in *Lolium perenne*. Mean (SE), N = 5. Means with the same letter are not significantly different. Last row contains NZ reference values for pasture grass reported as geometric mean (SD range) for log distributed data or mean ± SD for normal distributed data as determined by Reiser (2012) in a soil survey (N = 69) [190].

Treatment			Biomass (g dw)	P (mg/kg)	S (mg/kg)	N (%)	Ca (mg/kg)	Mg (mg/kg)	K (mg/kg)
	Soil	Lignite (wt%)							
unlimed	unspiked	0	3.9 (0.2)^{a}	5597 (191)^{a}	3874 (161)^{a}	2.7 (0.2)^{a}	7013 (107)^{a}	2304 (46)^{a}	41143 (1853)^{a}
		1.0	4.0 (0.3)^{a}	5286 (298)^{a}	3855 (166)^{a}	2.6 (0.2)^{a}	6695 (161)^{ab}	2311 (35)^{a}	39794 (1504)^{a}
		3.4	3.8 (0.2)^{a}	5182 (287)^{ab}	4014 (249)^{a}	2.3 (0.1)^{a}	6559 (91)^{bc}	2211 (127)^{a}	37037 (1469)^{a}
		7.1	3.5 (0.3)^{a}	4554 (188)^{b}	3748 (123)^{a}	2.4 (0.1)^{a}	6301 (120)^{c}	1785 (25)^{b}	37561 (1126)^{a}
	LSD (α = 0.05)		0.7	701	519	0.4	370	210	4495
	spiked	0	4.2 (0.2)^{a}	4930 (254)^{a}	3274 (144)^{b}	2.8 (0.1)^{a}	6455 (59)^{a}	1729 (8)^{b}	38376 (1192)^{a}
		1.0	3.9 (0.1)^{a}	5140 (214)^{a}	3576 (159)^{ab}	2.8 (0.1)^{a}	6719 (198)^{a}	1744 (31)^{ab}	40368 (1351)^{a}
		3.4	3.8 (0.2)^{a}	4938 (175)^{a}	3770 (89)^{a}	2.7 (0.1)^{a}	6360 (62)^{a}	1795 (15)^{a}	39365 (1015)^{a}
	LSD (α = 0.05)		0.5	652	411	0.3	412	61	3691
	biosolids	0	6.5 (0.2)^{a}	3896 (185)^{a}	4602 (129)^{ab}	3.4 (0.1)^{a}	7700 (116)^{a}	1774 (21)^{b}	37702 (1117)^{a}
		1.0	6.2 (0.3)^{ab}	4375 (137)^{a}	4731 (151)^{a}	2.9 (0.1)^{b}	7218 (139)^{ab}	1749 (20)^{b}	36500 (1222)^{a}
		3.4	5.7 (0.2)^{bc}	4019 (211)^{a}	4173 (181)^{b}	3.3 (0.2)^{ab}	7006 (198)^{bc}	1789 (19)^{b}	38953 (640)^{a}
		7.1	5.3 (0.2)^{c}	4184 (205)^{a}	4192 (137)^{b}	3.4 (0.1)^{ab}	6665 (156)^{c}	1906 (24)^{a}	39351 (1478)^{a}
	LSD (α = 0.05)		0.6	579	473	0.4	487	64	3370

Treatment			Biomass (g dw)	P (mg/kg)	S (mg/kg)	N (%)	Ca (mg/kg)	Mg (mg/kg)	K (mg/kg)
	Soil	Lignite (wt%)							
limed	unspiked	0	4.2 (0.2)^{a}	4401 (200)^{a}	3340 (191)^{ab}	2.6 (0.2)^{a}	7656 (219)^{a}	1624 (46)^{c}	38466 (1523)^{a}
		1.0	4.3 (0.2)^{a}	4347 (81)^{a}	3238 (51)^{b}	2.5 (0.1)^{a}	7366 (94)^{ab}	1628 (17)^{bc}	37065 (710)^{a}
		3.4	3.8 (0.1)^{ab}	4548 (282)^{a}	3561 (189)^{ab}	2.4 (0.1)^{a}	7076 (108)^{bc}	1699 (16)^{b}	36452 (1239)^{a}
		7.1	3.4 (0.2)^{b}	4165 (334)^{a}	3673 (126)^{a}	2.4 (0.1)^{a}	6720 (79)^{c}	1815 (14)^{a}	36359 (482)^{a}
	LSD (α = 0.05)		0.6	700	435	0.3	405	75	3101
	spiked	0	3.9 (0.2)^{a}	4857 (174)^{a}	3598 (166)^{a}	2.9 (0.2)^{a}	7523 (213)^{a}	1660 (34)^{a}	39734 (1475)^{a}
		3.4	4.2 (0.2)^{a}	4583 (389)^{a}	3571 (242)^{a}	2.7 (0.1)^{a}	7326 (131)^{a}	1645 (30)^{a}	38967 (1290)^{a}
		7.1	3.6 (0.2)^{a}	4826 (256)^{a}	3833 (189)^{a}	2.7 (0.2)^{a}	7094 (173)^{a}	1692 (37)^{a}	40571 (1194)^{a}
	LSD (α = 0.05)		0.7	860	595	0.5	519	101	3943
	biosolids	0	6.1 (0.1)^{a}	3642 (112)^{a}	4082 (136)^{a}	3.2 (0.1)^{a}	8737 (189)^{a}	1664 (27)^{c}	39366 (727)^{ab}
		1.0	5.7 (0.2)^{ab}	4120 (138)^{a}	4374 (183)^{a}	3.3 (0.1)^{a}	8820 (174)^{a}	1702 (28)^{bc}	39947 (514)^{ab}
		3.4	5.5 (0.2)^{ab}	4191 (168)^{a}	4045 (115)^{a}	3.3 (0.2)^{a}	7617 (62)^{b}	1757 (23)^{ab}	40638 (626)^{a}
		7.1	5.2 (0.3)^{b}	4184 (269)^{a}	4192 (175)^{a}	3.2 (0.1)^{a}	6665 (164)^{b}	1906 (18)^{a}	39351 (810)^{b}
	LSD (α = 0.05)		0.6	594	467	0.4	570	72	2151
NZ average				**2806 ± 1165**	**2114 (1315 - 3398)**	**0.48 (0.32 - 0.73)**	**5509 ± 1875**	**1654 ± 412**	**17550 ± 9503**

Table 13: Influence of lignite addition on the concentrations of micronutrients in *Lolium perenne*. Mean (SE), N = 5. Means with the same letter are not significantly different. Last row contains NZ reference values for pasture grass reported as geometric mean (SD range) as determined by Reiser (2012) in a soil survey (N = 69) [190].

Treatment			Zn (mg/kg)	Cu (mg/kg)	Mo (mg/kg)	Co (mg/kg)	B (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
	Soil	Lignite (wt%)							
unlimed	unspiked	0	39 (2)^{a}	5.5 (0.2)^{a}	1.1 (0.1)^{a}	0.21 (0.04)^{a}	7.0 (0.8)^{c}	231 (85)^{a}	146 (3)^{b}
		1.0	39 (1)^{a}	5.1 (0.1)^{a}	0.9 (0.1)^{ab}	0.21 (0.03)^{a}	8.1 (0.7)^{c}	234 (46)^{a}	154 (4)^{ab}
		3.4	39 (2)^{a}	4.5 (0.2)^{b}	0.9 (0.1)^{b}	0.20 (0.02)^{a}	15.6 (2.3)^{b}	145 (19)^{a}	172 (12)^{ab}
		7.1	35 (1)^{a}	3.8 (0.1)^{c}	0.6 (0.0)^{c}	0.20 (0.02)^{a}	21.5 (1.6)^{a}	99 (2)^{a}	168 (6)^{a}
	LSD (α = 0.05)		5	0.6	0.2	0.08	4.5	140	22
	spiked	0	35 (1)^{a}	5.1 (0.2)^{a}	0.7 (0.1)^{a}	0.08 (0.02)^{a}	8.8 (0.1)^{c}	86 (7)^{a}	101 (2)^{b}
		1.0	34 (1)^{a}	5.2 (0.2)^{a}	0.8 (0.1)^{a}	0.10 (0.04)^{a}	10.8 (0.2)^{b}	128 (43)^{a}	104 (2)^{b}
		3.4	34 (1)^{a}	4.6 (0.1)^{b}	0.7 (0.0)^{a}	0.08 (0.01)^{a}	16.7 (0.6)^{a}	88 (5)^{a}	119 (1)^{a}
	LSD (α = 0.05)		3	0.5	0.2	0.07	1.2	79	5
	biosolids	0	102 (8)^{a}	8.5 (0.1)^{a}	1.3 (0.1)^{a}	0.13 (0.03)^{a}	8.5 (0.3)^{c}	155 (69)^{a}	96 (2)^{c}
		1.0	87 (7)^{ab}	8.1 (0.3)^{a}	1.6 (0.1)^{a}	0.10 (0.01)^{a}	9.7 (0.5)^{c}	81 (6)^{a}	97 (3)^{c}
		3.4	73 (4)^{bc}	8.1 (0.5)^{a}	0.9 (0.0)^{b}	0.12 (0.02)^{a}	13.9 (0.5)^{b}	100 (16)^{a}	111 (3)^{b}
		7.1	64 (3)^{c}	7.7 (0.6)^{a}	0.9 (0.0)^{b}	0.16 (0.01)^{a}	20.9 (1.7)^{a}	136 (41)^{a}	137 (2)^{a}
	LSD (α = 0.05)		18	1.2	0.3	0.05	2.6	122	8

Treatment			Zn (mg/kg)	Cu (mg/kg)	Mo (mg/kg)	Co (mg/kg)	B (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
	Soil	Lignite (wt%)							
limed	unspiked	0	28 (2)^{b}	5.1 (0.3)^{a}	1.6 (0.3)^{a}	0.13 (0.06)^{a}	7.5 (0.3)^{c}	252 (147)^{a}	58 (5)^{c}
		1.0	29 (1)^{b}	4.7 (0.2)^{ab}	1.3 (0.1)^{ab}	0.14 (0.03)^{a}	9.4 (0.3)^{c}	195 (58)^{a}	63 (4)^{c}
		3.4	32 (1)^{b}	4.2 (0.2)^{bc}	1.0 (0.1)^{bc}	0.13 (0.01)^{a}	13.4 (0.7)^{b}	108 (9)^{a}	87 (1)^{b}
		7.1	37 (2)^{a}	3.7 (0.2)^{c}	0.8 (0.1)^{c}	0.20 (0.03)^{a}	20.1 (1.1)^{a}	164 (45)^{a}	128 (2)^{a}
	LSD (α = 0.05)		4	0.6	0.5	0.10	1.9	238	10
	spiked	0	33 (1)^{a}	5.5 (0.2)^{a}	1.2 (0.1)^{a}	0.11 (0.01)^{ab}	7.4 (0.4)^{c}	86 (10)^{a}	58 (2)^{b}
		1.0	32 (1)^{a}	5.0 (0.3)^{ab}	1.0 (0.1)^{ab}	0.08 (0.01)^{b}	8.5 (0.3)^{b}	68 (3)^{a}	59 (3)^{b}
		3.4	34 (1)^{a}	4.6 (0.2)^{b}	0.9 (0.1)^{b}	0.14 (0.01)^{a}	13.1 (0.4)^{a}	79 (3)^{a}	73 (3)^{a}
	LSD (α = 0.05)		4	0.7	0.2	0.04	1.0	22	8
	biosolids	0	83 (3)^{a}	8.2 (0.1)^{a}	2.2 (0.3)^{a}	0.10 (0.01)^{a}	7.5 (0.2)^{c}	91 (8)^{a}	50 (3)^{c}
		1.0	76 (6)^{ab}	8.1 (0.1)^{ab}	2.3 (0.2)^{a}	0.12 (0.04)^{a}	8.6 (0.5)^{c}	165 (65)^{a}	57 (5)^{c}
		3.4	69 (5)^{bc}	7.7 (0.2)^{b}	1.6 (0.1)^{b}	0.10 (0.01)^{a}	13.9 (0.5)^{b}	105 (20)^{a}	72 (7)^{b}
		7.1	64 (3)^{c}	7.7 (0.1)^{c}	0.9 (0.1)^{b}	0.16 (0.01)^{a}	20.9 (0.6)^{a}	136 (18)^{a}	137 (3)^{a}
	LSD (α = 0.05)		13	0.4	0.5	0.06	1.7	107	14
NZ average			**26 (19 - 37)**	**7.0 (4.9 - 10.0)**	**0.7 (0.3 - 1.6)**	**0.12 (0.06 - 0.25)**	**8.2 (5.5 - 12.2)**	**118 (68 - 207)**	**164 (78 - 347)**

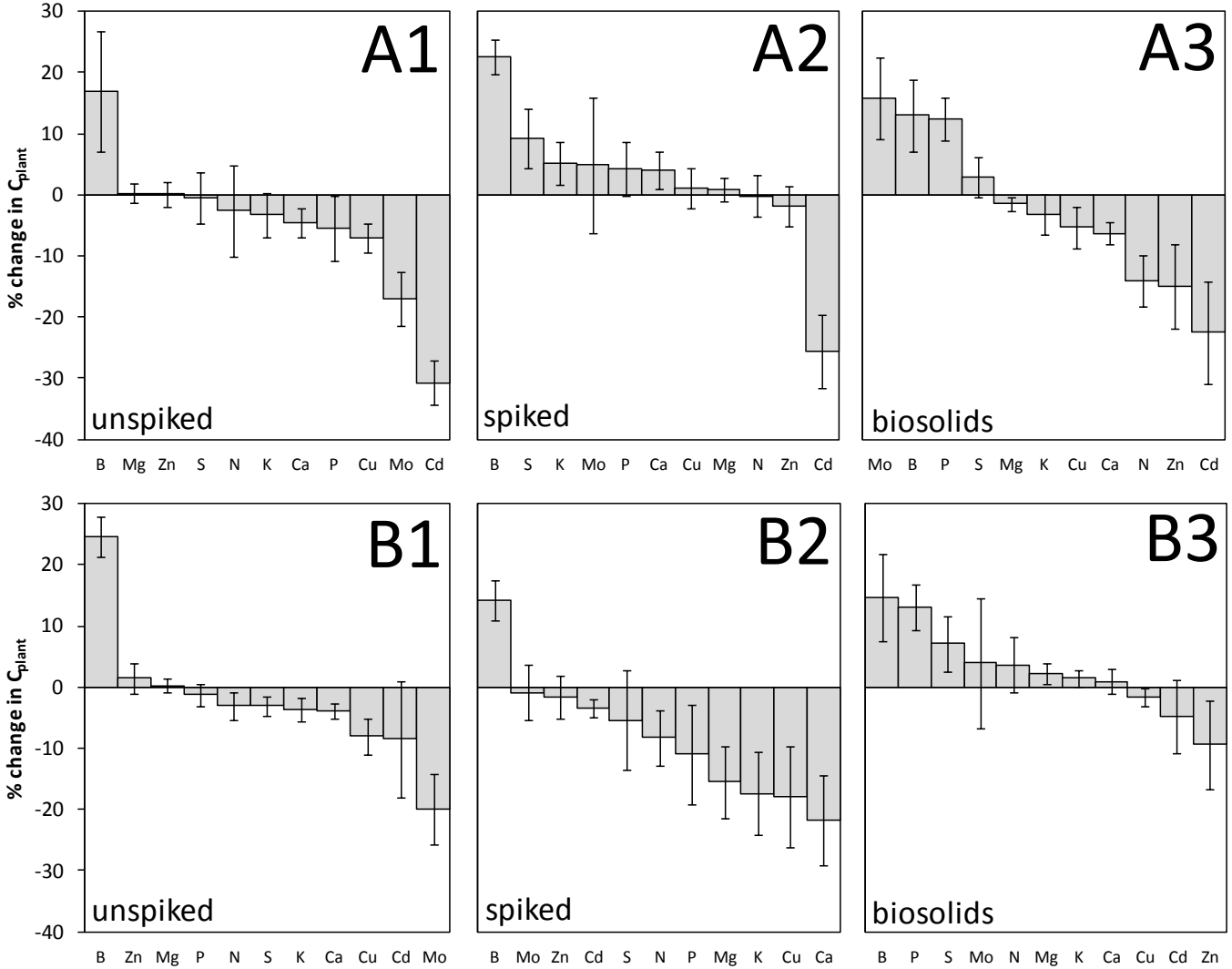


Figure 15: Difference in element concentrations in *Lolium perenne* for the treatments with 1.0 wt% lignite addition relative to the corresponding treatments without lignite addition (Mean ± SE). A1 - A3 refer to the unspiked, spiked and biosolids treatment in the series without lime addition. B1 - B3 refer to the unspiked, spiked and biosolids treatment in the series with lime addition. Note the difference in normalisation of plot B1 - B3 as compared to Figure 14 B.

5. Discussion

5.1 Cd adsorption as function of pH and Cd loading

In the pH range of 3.4 to 6.8 and biologically relevant Cd concentrations, Cd sorption from solution was significantly higher for lignite compared to a typical New Zealand agricultural soil (Figure 7). Amendment of lignite to a NZ soil is therefore likely to increase the soils' ability to sorb Cd. The Cd loading had no influence on the K_d value for sorption on soil (Soil 1) and lignite. This indicates that in this concentrations range, the adsorbed Cd bound to sites which are well below saturation and that the average affinity of the sites contributing to adsorption did not change with increasing concentrations.

The observed increase in K_d in this pH range is a well-known phenomenon for soil and was also reported for lignite [33, 39]. The log-linear increase of K_d with increasing pH indicates that the mechanism accounting for the increase in sorption is dominated by a competition reaction with H^+ following the law of mass action rather than being a result of coagulation and flocculation of colloids. Colloid-stability does not show such continuous pH behaviour and an increase rather than a decrease would be expected as the majority of soil and lignite particles are negatively charged and therefore expected to increasingly disperse with increasing pH (increase in Gouy-Chapman layer leads to increasing repulsive forces between particles and therefore colloid stability) [66]. The competitive metal association reaction can be written according to Equation 2 where L is the deprotonated ligand and y is the coefficient indicating the number of dissociable protons bonded to the ligand.

$$\mathrm{Cd} + \mathrm{LH_y} \leftrightarrow \mathrm{LCd} + \mathrm{yH^+} \tag{2}$$

L might be of variably or permanently charged type and no binding mechanism is implied. The competition coefficient $\mathrm{K_p}$ is written according to Equation 3 where square brackets denote concentrations in the sorbent and round brackets activities in solution.

$$\mathrm{K_p} = \frac{[\mathrm{LCd}](\mathrm{H^+})^{\mathrm{y}}}{(\mathrm{Cd})[\mathrm{LH_y}]} \tag{3}$$

Taking the logarithm (and rearrangement) of Equation 3 gives:

$$\log\left(\frac{[\mathrm{LCd}]}{(\mathrm{Cd})}\right) = -\mathrm{y}\log(\mathrm{H^+}) + \log\mathrm{K_p} + \log[\mathrm{LH_y}] \tag{4}$$

Inserting the definition of pH and a solid-solution distribution coefficient defined as $\mathrm{K_d} = [\mathrm{LCd}]/(\mathrm{Cd})$ gives:

$$\log \mathrm{K_d} = \mathrm{ypH} + \left(\log \mathrm{K_p} + \log\left[\mathrm{LH_y}\right]\right) \quad (5)$$

In case most of the sites are protonated ($\log[\mathrm{LHy}] \approx \log[\mathrm{L}_{total}] = \mathrm{const}$) Equation 5 can be approximated as:

$$\log \mathrm{K_d} = \mathrm{ypH} + \left(\log \mathrm{K_p} + \log[\mathrm{L_{total}}]\right) \quad (6)$$

Equation 6 is a function of the form $\log \mathrm{K_d} \sim \mathrm{m} * \mathrm{pH} + \mathrm{b}$ and might therefore be a reasonable model to explain the pH dependency of soil and lignite in Figure 7. Given the model describes a real phenomenon, the slope of the regression line quantifies y, the number of protons exchanged with one Cd at a binding site. The slopes being 0.74 (lignite) and 0.59 (Soil 1) might therefore indicate that the reaction is more complex than simple ion exchange involving Cd^{2+} as for reasons of charge balance we would expect $\mathrm{y} = 2$ (one Cd^{2+} replacing two protons) or that the assumption of $\log \mathrm{K_p} + \log\left[\mathrm{LH_y}\right]$ being constant does not hold. Soluble complexes (e.g. with Cl^-) or competing cations (e.g. Ca^{2+}) might have played a role.

Dissociation of variably charged sites is expected to account for the observed pH effect on Cd sorption of lignite. Carboxylic groups might have been the main functional groups which dissociated. Phenolic and thiol groups have typically a pK_a above pH 8 [33, 82] and are therefore not expected to deprotonate in great quantities in the pH range studied. Adsorption onto charged COO^- groups may have accounted for the increase in Cd adsorption onto lignite with increasing pH. The change of pH of the lignite slurry with acid and base addition respectively was gradual over the whole pH range and did not result in distinct titration edges (see Appendix C2). This indicates that the lignite from the New Vale Mine contains functional groups with a relatively broad range of pK_a values in the region typical for carboxylic groups [41]. These observations do not exclude specific sorption onto other functional groups, possibly S groups. Despite the chalcophilic nature of Cd, which would indicate a strong interaction with reduced organic S, experimental evidence showing that Cd complexes with S groups in natural organic matter is scarce and in case of lignite absent. Karlsson et al. (2005) stated that studies on sorption mechanisms of Cd to natural organic matter e.g. Otto et al. (2001) [191] or Li et al. (1998) [192] used high Cd concentration in relation to organic C at which possible contribution of S groups might be difficult to detect [193]. Karlsson et al. (2007) found that complexation with S groups might be the dominant mechanism of Cd binding in soils with a concentration of < 5 mg Cd/g organic C [82]. Organic S in lignite is present as aromatic S (thiophenic structures, aryl sulphides, aryl sulphones) and aliphatic S. A rule-of-thumb estimate for lignite suggests that aliphatic sulphide typically account for 40 - 50% and S in thiophene structures for ca. 30% of the total organic S. But this fractions are quite variable between lignites from different origins; for some lignites thiophene S is the dominant form of organic S [194]. The main form of S in the lignite investigated in this work is heterocyclic S in dibenzothiophene like structures [181].

Dibenzothiophen S is considered a soft base [195] and is therefore expected to form specific complexes with the soft acid Cd [196]. Several authors found that dibenzothiophene is more effectively adsorbed by a sorbent impregnated with the soft metal Ag(I) as compared to a sorbent impregnated with the borderline metals Ni(II), Cu(II) or Zn(II) [197, 198]. The organic S content of the lignite studied is 0.65 wt% or 0.2 mmol/g respectively (S in inorganic form is negligible [181]). In comparison to the number of carboxylic and phenolic groups of typical lignite of 5 - 7 mmol/g [33], the number of organic S groups is small. However, given that the affinity to reduced S groups might be much higher than to oxygen groups [82], sorption to the organic S in lignite might potentially have been of great importance. The highest Cd concentration spiked in the experiment was 2×10^{-4} mmol/g lignite (treatment spiked with 3.75 mg/l). Even assuming that each Cd ion coordinated with several S groups [193] and that a part of the groups were already occupied by Cd originating from the coal (0.06 mg/kg = 5×10^{-7} mmol/g), the lignite contains a sufficient number of S groups that could have played an important role in Cd binding at these biologically relevant concentrations. Ca. 80% of spiked Cd was adsorbed onto lignite at pH 3 (Figure 8). A major part of this fraction might potentially have been bound to S groups as the amount of Cd bound to reduced S is expected to be approximately constant over the pH range investigated (see model calculations by Karlsson et al. (2007) [82]). In contrast to sorption on carboxylic groups, Cd is usually more competitive than Zn at reduced S groups [199]. Lignite might therefore be a more efficient sorbent for Cd than for Zn at biologically relevant concentrations. Martinez et al. (2002) found that peat had a higher affinity for Cd than for Zn and concluded that this might indicate high importance of S groups in the binding of Cd in peat [199].

The increase in K_d with increasing pH was greater for lignite than for Soil 1 (Figure 7). Nevertheless, the superiority of lignite regarding efficiency in terms of percentage adsorbed was highest at lower pH and diminishes with increasing pH (Figure 8). As shown in Figure 9, this might also hold for solid-solution ratios more realistic for soils. The calculated difference in efficiency decreased with increasing solid-solution ratio or decreasing moisture content respectively. Therefore, lignite addition to soil might be most effective in soils with low pH and high moisture content.

At pH ≥ 8 the K_d for sorption of Cd onto lignite was significantly lower than at around neutral pH. This decrease at high pH might be caused by dissolution of lignite humic acids. An increase of such organic ligands in solution increases the solution concentration of Cd by forming soluble Cd-humic acid complexes. The dissolved organic carbon (DOC) concentration released from lignite approached an approximately constant level for low pH values (Figure 10). DOC at these low pH values were largely fulvic acids which remain by definition in solution even at pH < 2. With increasing solution pH increasing concentrations of humic acids, which are by definition not soluble at pH < 2 but increasingly soluble at higher pH, were dissolved. This observation is consistent with the fact that lignite contains usually higher concentrations of humic than fulvic acids [32]. A fraction of these dissolved fulvic and humic acids may be in submicron colloidal form and not truly dissolved. However, such colloids are usually included in the operationally defined extracted fractions humic or fulvic acids as this acids tend to form colloidal aggregates [200]. At alkaline pH, the effectiveness of lignite to immobilise Cd might be lower than for an agricultural soil itself. Although no K_d value for Soil 1 above neutral pH was measured, it may be higher than for lignite. The dissolved organic carbon released from Soil 1 was dominated by fulvic acids as it did not significantly change with increasing pH. Therefore, no dramatic decrease in K_d at pH > 7 is expected. Whether lignite addition to calcareous soil might fail to lower plant Cd concentrations finally depends on whether or not

humic acid-Cd complexes contribute to the plant's Cd uptake. Antoniadis & Alloway (2002) found that the application of dissolved organic matter (DOM) significantly increased the uptake of Cd by *Lolium perenne* [101]. Evangelou et al. (2004) observed that humic acid amendment to soil increase Cd uptake by *Nicotiana tabacum* [201].

5.2 Cd sorption of various soils amended with lignite

The capacity of lignite to decrease the solubility of Cd in soil varied strongly with soil type (Figure 11). Lignite addition may affect the affinity of a soil to sorb Cd directly by changing the density and composition of sorption sites as well as by changing conditions that affect sorption indirectly, in particular pH. Given that Cd sorption was stronger in lignite than in soil, an increase in Cd sorption should be expected upon lignite addition as long as this direct effect was not outmatched by Cd solubilisation due to decrease in pH. In case of decreasing pH, the overall effect of lignite addition on the soils ability to immobilise Cd might become negative as observed for Soil 5. For Soil 6 an increase in K_d was observed although the pH slightly decreased. This might indicate that the negative effect of decreasing pH was too small to compensate the positive effect. For Soil 3 an increase in K_d was observed. This is consistent with the expectation that both effects are suspected to be positive. Lignite addition to Soil 2, which resembles Soil 6 with regard to pH and K_d, did not decrease the Cd solubility. Assuming lignite addition does not change pH and that lignite's K_d at the corresponding pH can be predicted using the regression function in Figure 7, blending 5 wt% lignite with Soil 2 and Soil 6 is expected to increase their sorption affinity by ca. 55%. The observed increase in K_d for Soil 6 was with 72% higher than expected, whereas lignite addition to Soil 2 was without effect. As the drop in pH for both soils was small (0.11 and 0.03 pH units respectively) this discrepancy might not be fully explained by differences in pH dependency of Cd sorption as it would imply extreme pH dependency of Cd sorption for Soil 2 (see Figure 7 for comparison with pH dependency of Soil 1 and lignite). Nevertheless, it cannot be ruled out from the results presented and as the drop in pH was greater for Soil 2 it does not violate the aforementioned rationale. Differences in pH dependency of Cd adsorption might arise from the fact that different pH buffering systems are active, involving groups with different importance with regard to Cd sorption. Another plausible explanation is that interactions of lignite with soil constituents determining the amount of additional sorption sites accounted for the difference. According to Christensen & Haung (1999), humified organic matter is intimately bound to mineral colloids in most organic soils and the extend and mechanism of association of minerals with organic matter influences Cd adsorption [68]. Lignite is therefore suspected to interact with mineral soil constituents, creating organo-mineral associates which work more as a unit than as separate entities. Comparing Soil 2 and 6 reveals that they differ remarkable with regard to their clay fraction, carbon content and concentrations of the (hydr)oxide forming metals Fe and Mn (Table 7). Therefore, interactions of lignite with Soil 2 are likely to be significantly different from those observed in Soil 6.

The efficacy of lignite to reduce the solubility of Cd in soil is dependent on 1) the pH of soil and lignite, 2) the pH buffering capacity of soil as compared to lignite, 3) the type of functional groups involved in pH buffering, 4) the proportion of the quality and quantity of sorption sites in the specific soil as compared to lignite and 5) interactions of lignite with soil constituents other than acid-base

reactions. Factors 1 to 3 determine the pH effect of lignite addition. Factor 4 and 5 determine whether and how strong lignite amendment increases the quantity and/or quality of sorption sites.

Lignite alone equilibrated with the $Ca(NO_3)_2$ solution at pH 4.3 (see Chapter 4.1). As Soil 1 came to equilibrium at approximately the same pH, no change in pH is expected when Soil 1 is blended with lignite. For a soil that equilibrates with the solution above pH 4.3, a decrease in pH is expected when this soil is blended with lignite. Analogous, an increase in pH is expected for a soil equilibrating with the solution below pH 4.3. The data in Figure 11 confirm these expectations. The critical pH value is a function of the lignite type and pre-treatment. It might be variable between different lignites as it depends on the acidic properties of the functional groups and the base saturation of the specific lignite.

Assuming that other interactions of lignite with soil constituents than acid-base type are not of relevance, lignite addition is suspected to fail to immobilise Cd for some soils with a $pH(H_2O)$ of > 4.5 (pH of lignite in H_2O). For a soil with a $pH(H_2O)$ < 4.5 we would expect decreasing solubility of Cd when lignite is applied. The lab findings confirm these expectations (Figure 11). But, lab findings must be transferred conservatively as their relevance for field conditions is limited. Formation of organo-mineral associates might be slow as compared to the Cd adsorption processes with regard to which the batch system seems to be in equilibrium within 2 hours (see Appendix C1). Therefore, longer equilibration times (days to weeks) might potentially have changed the results significantly.

5.3 Effect of lignite addition on the plant uptake of Cd

Lignite addition effectively reduced Cd concentration in soil solution and accumulation in ryegrass. Solubility and plant uptake was significantly reduced by up to 52% and 51% when *Lolium perenne* was grown on Soil 1 without liming (Figure 14). The reduction in Cd concentration was greater than the reduction in Zn and Cu concentration (Figure 15 and Appendix D3). Assuming bioavailability of these metals follows their solubility, this observation is surprising as Zn and especially Cu are often cited to show higher affinity to soil organic matter than Cd [74]. It might indicate the importance of S groups in complexation of metals by lignite as Cd binds more strongly to S groups than Zn and Cu [199]. However, the assumption that the bioavailability of these three metals follows their solubility might be violated as the solubility data in Table 11 is not consistent with the pattern in Figure 15 for all treatments.

When lime was applied prior to lignite addition the efficiency was reduced (see Figure 13 and Figure 14). This observation is consistent with the findings from the lab experiments. Under the assumption that lignite addition would not change the soil pH value, lower efficiency of lignite addition to immobilise Cd is expected at higher pH according to the results in Figure 8 discussed in Chapter 5.1. However, in agreement with the findings discussed in Chapter 5.2 (pH > 4.5), a decrease in pH was observed in both the limed and the unlimed treatments. As the pH decrease was more pronounced in the limed treatments we expect a stronger negative effect on Cd adsorption. As demonstrated by the significant interaction between lime and lignite in the spiked treatments (Table 9), this may be responsible for the differences in efficiency of lignite addition in reducing Cd solubility and plant uptake between unlimed and limed soil.

Potentially, lignite could be blended with a sufficient amount of lime to buffer the pH drop. Several authors recommended reducing soil acidity by liming as a suitable measure to reduce Cd plant uptake [8, 146]. Therefore, the application of a combination of lignite and lime is expected to be more effective in reducing Cd plant uptake than lignite alone. In this study, treatments with lime addition did not show reduced plant uptake as compared to their corresponding treatments without lime addition (Figure 14). Lack of effect of liming on Cd plant uptake under certain conditions was described by several authors [106, 202, 203]. Loganathan et al. (2012) mentions that the large amount of Ca added via lime might compete with Cd for sorption if the pH is not sufficiently increased by the lime application to specifically sorb and immobilise Cd [106]. This would imply that outer sphere complexation is an important Cd sorption mechanism in this soil as Ca binds via ion exchange mechanism and is not expected to compete in inner sphere sorption. The importance of outer and inner sphere sorption in soil at biologically relevant concentrations is debated. Experimental evidence is scarce as most of the studies investigated sorption mechanisms to soil constituents at high concentrations not relevant for agricultural soils. At low Cd loadings, the effect of pH on Cd sorption is much lower and Cd tends to bind increasingly inner sphere [106]. Harter and Naidu (2001) suggested this lack of pH effect in high affinity soils at low Cd loading might explain the absence of effect of liming on plant uptake [203]. Both, Ca competition and lack of pH effect on Cd sorption in high affinity soils, is unlikely to explain the lack of liming effect on plant uptake in this study as the solubility of Cd was significantly reduced. Other possible reasons more consistent with the results documented in this paper are that lime increases root growth by supplying Ca and ameliorating soil acidity; lime decreases Zn availability, thereby reducing Zn competition with Cd for plant uptake; and Ca from lime increases root cell permeability, thereby facilitating root Cd uptake [202]. Due to plant and/or microbial activity the pH values in the rhizosphere between the treatments with and without lime addition might potentially be much similar than the pH values observed in the bulk soil. *Lolium perenne* and/or associated microorganisms are known to change the pH value in the rhizosphere compared to the bulk soil [204-207]. Blossfeld et al. (2010) studied rhizosphere changes using a recently developed, non-invasive 2D imaging technique. They observed that *Lolium perenne* alkalinised the rhizosphere up to 1.5 pH units compared to the bulk soil [204]. Depending on the nutrition, of N, it was observed that *Lolium perenne* might also acidify the rhizosphere [207]. Local buffering of the pH in the rhizosphere by biological activity might explain the lack of effect of lime addition on Cd plant uptake. Whether and how *Lolium perenne* changed the pH value in our experiments cannot be deduced from these results.

5.4 Effect of lignite on pasture quantity and quality

Lignite addition to soil improved the fodder quality with regard to the Cd concentration but did also influence the concentration of other elements in pasture. This might result in improvement or decline of A) plant health and pasture quantity and/or B) fodder quality or livestock health respectively. Results regarding biomass and nutrients are discussed in the following paragraphs. The discussion is either focused on plant health or fodder quality according to their major concern for pastoral farming in New Zealand. Please note that all of these elements can be a concern for plant and animal health under certain circumstances.

Biomass - Apart from detrimental effects for the highest lignite addition (7.1 wt%), no significant effect on biomass was observed. In contrast, other authors showed significant increase in plant biomass when lignite was applied [24, 26]. In these studies, soil was highly contaminated with heavy metals. Lignite addition might have eased phytotoxic effects by rendering metals at toxic levels unavailable to the plant, which in turn might have caused the increase in biomass. The decrease in biomass observed in this study might be caused by toxicity arising from lignite addition or by locking up limiting plant nutrients. The measured trace elements concentrations in soil and grass were in a typically non-toxic range but the results do not allow ruling out any toxic effects caused through lignite addition, e.g. by soluble organic compounds released from lignite. The decrease in biomass was most pronounced for the treatments fertilised with biosolids. Therefore lignite might have locked up plant nutritions which were released from biosolids.

Phosphorus, sulphur, nitrogen - Pasture growth in New Zealand is commonly limited by S and P. The two macronutrients are therefore commonly added via fertilisation (mainly via superphosphate). Lignite is compared to Soil 1 rich in S and poor in P. Although there was an increase in soluble S with lignite addition in some treatments, the main fraction of S in lignite is not suspected to be plant-available in short term as it is present as heterocyclic S and might be well protected against mineralisation. Pasture concentrations of P as well as S were not significantly influenced by lignite addition. The same was true for N.

Calcium, magnesium and potassium - Lignite addition decreased the concentrations of Ca and increased the concentration of Mg in *Lolium perenne* in most treatments. This must be due to a change in bioavailability and not a change in total concentration of these two elements in soil. Lignite had higher total Ca concentrations but lower concentrations of Mg than Soil 1 and therefore lignite amendment elevates the total soil Ca concentration but dilutes the total Mg concentration. The concentration of K was unaffected by lignite addition in most treatments. The ratio between K and the sum of Ca and Mg affects the quality of the grass when used as fodder. The ratio should not be greater than 2.5:1 [208]. The ratio K/(Ca+Mg) in this study was > 2.5 for all treatments and lignite addition tended to increase the ratio.

Zinc - Zinc levels in pasture were significantly reduced in the treatments with biosolids addition which showed elevated Zn concentrations but not in the rest of the treatments. The pasture Zn concentrations in all treatments were adequate regarding the requirements for sheep and cattle [209]. Lignite did not decrease pasture Zn concentrations below 30 mg/kg dw. Therefore, the lignite amendment at rates used in this study is not expected exacerbate any Zn deficiencies in livestock.

Copper and molybdenum - Lignite addition reduced the pasture concentration of the two essential elements Cu and Mo. Copper deficiency is one of the major element deficiencies limiting livestock performance in New Zealand [210]. Plants require extremely low concentrations of Mo [209]. Many New Zealand soils are naturally deficient in Cu and/or high in Mo [210]. High Mo has adverse effects on livestock with marginal Cu supply due to its antagonistic effect lowering the absorptivity of Cu by farm animals [209]. Whether the decrease in Cu in *Lolium perenne* observed in this study would result in lower Cu absorption by livestock is unclear. Lower antagonistic effects due to lower Mo levels may compensate for the lower pasture Cu concentrations but such predictions are speculative as Cu absorption in livestock is also influenced by other pasture factors such as Cd, Fe, Ca, and S [209], which were also affected by lignite addition.

Cobalt - Lignite addition did not significantly influence the Co concentration of *Lolium perenne*. Many New Zealand soils are naturally deficient in Co resulting in Co deficiency in grazing animals. Nowadays, Co deficiency is mainly confined to lambs because areas where severe Co deficiencies were observed in adult sheep or cattle received Co fertiliser over decades [210].

Boron - Lignite addition significantly increased B concentration in pasture. Boron deficiency in plants is widespread in New Zealand but affects mainly brassica root crops [211] and exotic forest (*Pinus radiata*) [212, 213]. Pasture response to B application is rare and probably related to improved growth of clover which have higher B requirement than grasses [211, 214-216]. Lignite contains 36.3 mg/kg B whereas Soil 1 contains 7.3 g/kg B. The additional B in plant is suspected to originate from the added lignite. Due to its low retention as a non-ionic species (< pH 8 boric acid is the prevailing species) B is mobile in some soils and is therefore prone to leaching which in turn can limit its availability for plant uptake [6]. As soil organic matter adsorbs more B than mineral soil constituents [7], lignite addition might also increase the soils ability to hold and slowly release B amended via irrigation water.

Manganese - Lignite significantly increased the Mn concentration in *Lolium perenne* in most treatments. Lignite contains lower Mn total concentrations than Soil 1 but at least a part seems to be present in a comparably solubilisable and phytoavailable form. Lignite addition significantly increased soluble Mn concentrations (Table 11) in soil and significant Mn release from lignite was observed in the batch experiments (Appendix E). Manganese is generally not a direct issue for livestock or crop health in New Zealand but soil Mn was found to crucially influence the plant availability of Co which in turn is one of the major trace elements deficient in New Zealand's livestock [217].

5.5 Application rates and costs

Assuming that lignite would be applied to the top 7.5 cm of a pasture soil (ρ = 1.2 kg/dm^3) at equivalent rates than used in the pot experiment (1.0, 3.4, 7.1 dry wt%), the rates would account for 14.5, 49 and 103 t/ha wet lignite respectively (considering 38% moisture). For a presumable price of 500 NZ$/t [181] the material costs of these application rates would account for ca. 7'000, 24'000 and 72'000 NZ$/ha. Although the roots of pasture are likely to penetrate the soil to a greater depth than 20 cm, application to this relatively shallow depth might be reasonable as most Cd is expected to be concentrated in the top layer [8]. Diminishing marginal effectiveness was observed in the pot experiment. In the unlimed series, 1.0 wt% lignite amendment reduced the plant concentration by 22 - 31% depending on the source of Cd. When 3.4 wt% lignite was amended, the average wt% added reduced the Cd plant concentration by 10 - 15%. The corresponding reduction per wt% for the highest amendment (7.1 wt%) was with 6 - 7% the lowest. This indicates that the cost of an *in situ* fixation technology based on lignite addition increases disproportionally high with increasing reduction to fulfil, e.g. to comply with certain food standards. Rates of 103 t/ha might not be viable considering the transport cost and the fact that the pasture quantity or quality might be detrimentally affected (Chapter 5.4). Lower rates might be economically attractive. Further research on the technology is needed to conduct a realistic quantitative economic analysis.

6. Conclusions

Potentially, lignite is an effective soil amendment to reduce Cd solubility in some New Zealand pasture soils and reduce Cd uptake by *Lolium perenne*. Cadmium in a soil with a total Cd concentration in the range of the soil guideline for safe application of biosolids to land in New Zealand of 1 mg/kg [17] was rendered less phytoavailable when lignite was applied. Lignite addition did not significantly affect biomass production of *Lolium perenne*. Exceptions were some treatments with the highest lignite amendment of 7.1 wt% which are unlikely to be viable on pastureland (Chapter 5.5). Amendment of lignite significantly reduced the concentration of some nutrients in the plant, but these reductions were smaller than the reduction in Cd concentration. Lignite seems to have higher affinity to sorb Cd than geochemically similar elements such as Zn and Cu. This selectivity might be an advantage as compared to other *in situ* fixation technologies, e.g. application of liming agents.

The efficiency of lignite addition in fixing Cd was strongly dependent on the soil type. The results of this study indicate that lignite addition is generally more effective in rendering Cd unavailable to plants in soils with low pH values. Other soil factors that determine the effectiveness are the pH buffering properties and the quantity and quality of Cd sorption sites present in the soil. It is unclear whether the presence of soil constituents forming organo-mineral associates with lignite might also be important in this regard. The chemical properties of lignite, especially the acidic properties, the base saturation and the number and quality of Cd binding sites are expected to determine whether a specific lignite is effective in a given soil.

There is indication that in higher-pH soils, lignite addition may even elevate Cd solubility and potentially exacerbate plant Cd uptake. Evidence was found that in calcareous soils, lignite might release considerable amount of humic acids leading to enhanced solubility of Cd. Below circumneutral pH, potential Cd solubilisation and elevation of Cd plant uptake by lignite addition is expected to be mainly a result of a drop in soil pH due to the acidic properties of lignite. Contrarily to expectations, a combination of lignite and $CaCO_3$ did not improve the efficiency of lignite addition with regard to a reduction in plant uptake although a reduction in Cd solubility was observed. Several possible explanations for this lack of effect were found in the literature.

In this work I provided proof-of-concept for an *in situ* fixation technology able to render Cd in pasture soils less phytoavailable while maintaining pasture health and fodder usefulness. But, there is a need for further research to develop a technology ready for action. Recommendations for future research are given in the next chapter.

7. Further research

Follow-up research might work on the following aspects:

Field conditions - It must be proven that lignite addition can reduce the Cd concentration in pasture under field conditions. Furthermore, optimal rates and way of application (e.g. ploughing to a certain depth) should be determined considering the distribution of Cd in agricultural soils, practical handling aspects and cost-effectiveness.

Soil constraints - Soil pH was identified as an important soil property controlling the efficiency of lignite addition in reducing plant Cd uptake. It is suspected that, besides the pH value, other soil properties are also important in this respect. These factors should be identified and their influence studied. If possible, easily measurable indicators following the identified factors should be determined, e.g. CEC or organic carbon. Findings should be used to create a decision making tool which allows to evaluate the suitability of the technology for a specific soil based on a few easily measurable soil parameters. Further research might also focus on whether certain constrains can be overcome by blending the lignite with other soil amendments. Blending with a liming agent might help to avoid a drop in pH which is suspected to limit the efficiency in some soils. In this study, $CaCO_3$ did not improve the efficiency with regard to plant uptake. Whether this observation is restricted to certain soil conditions or generally observable should be investigated. As Ca released from $CaCO_3$ is suspected to be responsible for the lack of effect on plant uptake, other liming agents releasing other cation than Ca (e.g. $MgCO_3$, MgO) and/or with higher neutralisation value (e.g. CaO) might be tested.

Long-term effectiveness - Lignite added to the soil will be chemically altered over time. As it shows high degree of humification it is expected to be relative well protected against mineralisation but an unknown fraction of the organic matter in lignite will be mineralised in long term. Oxidation of the organic structure is expected to increase the density of oxygen groups over time while decreasing the number of reduced S groups. Mineralisation and oxidation of S groups might diminish and increase in O groups might elevate the Cd fixation efficiency of lignite in long term. Finally the efficiency will decrease but an increase over an unknown period of time might be observed after addition. Changes in the density of O and reduce S groups might furthermore influence the selectivity of lignite to adsorb different cations, e.g. Cd and Zn. This processes might also be crucially influenced by other soil constituents, e.g. oxides might occlude lignite particles and prevent their mineralisation and chemical alteration. Further research should investigate changes in Cd adsorption efficiency of lignite in soil in long term and elucidate whether soil type has a crucial influence hereon.

Effect on physical soil properties - Lignite addition might change aggregate stability, hydraulic conductivity, water holding capacity, soil temperature and other physical soil properties. Lignite amendment is expected to strengthen aggregate stability as organic matter in soil is known to do so [74]. The hydraulic conductivity might be increased if aggregate stability is enhanced or depressed as lignite may clog pore space and constrict water flow due to hydrophobic action. Water holding capacity is expected to increase as organic matter is important factor controlling the water holding

capacity of a soil [74]. At high rates, lignite addition might considerably lower the albedo of the soil which in turn might, given that the soil is partially bare, result in an increase in soil temperature. A change in soil colour was apparent in this study. Further research should elucidate whether and under which conditions (soil type, climate) lignite addition might improve or diminish soil fertility by altering the physical properties of the soil.

Phytoavailability of micro- and macronutrients - The results of this study indicate that lignite addition significantly influences the plant uptake of other elements than Cd. But, the range of trace elements commonly deficient in plants or livestock in New Zealand and worldwide was not studied exhaustively. Further research should comprehensively screen for changes in elemental composition. The work should aim to identify possible deficiencies or toxicities in plants and livestock which might results from lignite addition under certain conditions. Additionally, fertilising value of lignite could be studied, e.g. as B fertiliser (see Chapter 5.4). In this study, indication where found that lignite might have locked up limiting nutrients. Depending on the limiting nutrient, this might possibly be an advantage with other respect, e.g. assuming N was locked up, lignite may prevent leaching of excess N to waterways and buffer the plants supply.

Suitable lignite type - There is indication that S groups might play an important role in Cd binding to organic matter at typical Cd concentration in soil [82, 193]. Further research might therefore investigate whether high-S lignite is of particular value as a fixing additive of Cd at biologically relevant concentrations. This might be especially attractive as high-S coal is less suitable for heat production as elevated amount of SO_2 is emitted [218].

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Appendix

A Formulas

A1 Estimation of K_d at low equilibrium concentration from isotherm data

At low equilibrium concentrations, the system might be far away from saturation of the sites with the highest affinity. Given constant pH and ionic background conditions the solid-solution distribution coefficient K_d might be independent of the equilibrium concentration or approximately constant respectively.

K_d at low equilibrium solution concentration can be estimated from Freundlich, Langmuir or Langmuir-Freundlich isotherms by the following linear approximations:

Langmuir:

$$q = \frac{Q_{max} b C_e}{(1+bC_e)} \approx Q_{max} b C_e \rightarrow K_d = Q_{max} b * 1000 \frac{g}{kg}$$

Freundlich:

$$q = K_F C_e^{1/n} \approx K_F C_e \rightarrow K_d = K_F * 1000 \frac{g}{kg}$$

Langmuir-Freundlich:

$$q = \frac{Q_{max} K_{LF} C_e^n}{1+K_{LF} C_e^n} \approx Q_{max} K_{LF} C_e \rightarrow K_d = Q_{max} K_{LF} * 1000 \frac{g}{kg}$$

q	Cd sorbed (mg/g)
C_e	equilibrium Cd solution concentration (mg/g)
$Q_{max}, b, K_F, n, K_{LF}$	isotherm fitting parameters
K_d	solid-solution distribution coefficient (unites or l/kg respectively)

A2 Cation exchange capacity (CEC) / base saturation (BS)

$$\mathrm{CEC} = \left(1 - \mathrm{C_{Ag}}\right) * 50$$

$$\mathrm{BS} = \frac{(\mathrm{Mg} + \mathrm{Ca} + \mathrm{K} + \mathrm{Na}) * 100}{\mathrm{CEC}}$$

with

$$\mathrm{Mg} = \frac{(\mathrm{C_{Mg}} - \mathrm{C_{Mg,blank}}) * 0.29}{\mathrm{weigth\ [g]}}$$

$$\mathrm{Ca} = \frac{(\mathrm{C_{Ca}} - \mathrm{C_{Ca,blank}}) * 0.175}{\mathrm{weigth\ [g]}}$$

$$\mathrm{K} = \frac{\left(\mathrm{C_K} - \mathrm{C_{K,blank}}\right) * 0.09}{\mathrm{weigth\ [g]}}$$

$$\mathrm{Na} = \frac{(\mathrm{C_{Na}} - \mathrm{C_{Na,blank}}) * 0.15}{\mathrm{weigth\ [g]}}$$

BS	base saturation (%)
CEC	cation exchange capacity (meq/100g)
$\mathrm{C_{Ag}}, \mathrm{C_{Mg}}, \mathrm{C_{Ca}}, \mathrm{C_K}, \mathrm{C_{Na}}$	concentration of Ag, Mg, Ca, K, Na (mg/l)

A3 Grain size distribution

The fraction of particles with a diameter d is calculated as follows.

$$g(\%) = G_P * \frac{100 * V_T}{V_P * G_T}$$

V_T	content of the cylinder (ml)
V_P	removed sample quantity (ml)
G_T	weighed sample (g)
G_P	removed particle quantity (g)

G_p is calculated through evaporation of V_P, weighing und subtraction of the Calgon portion.

A4 Weight percentages of lignite and biosolids addition (pot experiment)

$$\text{lignite addition (wt\%)} = \frac{C_{\text{unspiked X wt\% lig}} - C_{\text{unspiked}}}{C_{\text{lig}}}$$

$$\text{biosolids addition (wt\%)} = \frac{C_{\text{biosolids}} - C_{\text{unspiked}}}{C_{\text{bio}}}$$

$C_{\text{unspiked X wt\% lig}}$	average (N = 5) carbon content in soils with lignite addition (%)
$C_{\text{biosolids}}$	average (N = 5) carbon content in soils with biosolids addition (%)
C_{unspiked}	average (N = 5) carbon content in pure soil (%)

Values in Appendix E.

C_{lig}	average (N = 3) carbon content in lignite (%)
C_{bio}	carbon content in biosolids (%)

Values in Table 7.

A5 Solid-solution distribution coefficient K_d considering spiked Cd

Rationale: In order to describe the equilibrium with regard to fast sorption processes, the fate of the labile pool of Cd should be followed (see Degryse et al. (2009) on metal pools of different lability [67]). The labile pool of Cd in the batch system is made up off the spiked Cd and labile Cd originating from the sorbent. Unfortunately, the fraction of Cd in the sorbent which must be considered labile is unknown. But, a K_d value describing the fate of the spiked Cd approximates the K_d value for the labile Cd given A) the system is well below saturation (K_d not a function of concentration) or B) the labile fraction originating from the sorbent is comparably small (spiked Cd ≈ labile Cd).

Derivation: The equilibrium concentration of spiked Cd in solution is calculated as measured solution concentration in the treatment in which the sorption is assessed ($C_{\mathrm{Cd\ Y/pH\ X}}$) minus the solution concentration which originates from the sorbent. The later was measured in the corresponding treatment without spiking ($C_{\mathrm{no\ Cd/pH\ X}}$).

$$\text{spiked Cd in solution (mg/l)} = \left(C_{\mathrm{Cd\ Y/pH\ X}} - C_{\mathrm{no\ Cd/pH\ X}}\right)\ \text{(mg/l)}$$

The adsorbed concentration of spiked Cd per mass sorbent is then calculated as the product of the difference between initial, $C_{\mathrm{Cd\ Y/SO}}$, and the equilibrium concentration of spiked Cd times the inverse of the solid-solution ratio.

$$\text{spiked Cd adsorbed (mg/kg)} = \left(C_{\mathrm{Cd\ Y/SO}} - \left(C_{\mathrm{Cd\ Y/pH\ X}} - C_{\mathrm{no\ Cd/pH\ X}}\right)\right)\ \text{(mg/l)} * \frac{0.03\ \mathrm{l}}{0.005\ \mathrm{kg}}$$

Building the ratio of spiked Cd adsorbed to spiked Cd in solution gives K_d in form of Equation 1 in Chapter 3.4.

B Instruments

- End-over-end shaker: Custom made
- Centrifuge: KUBOTA 8420
- Centrifugal mill: Retsch ZM200
- Microwave: CEM MarsXpress with 40 place rotor

  Soil samples were digested at 175˚C for 20 min. Plant samples were digested at 170˚C for 20 min. Time to ramp temperature was 20 min for both plant and soil samples.

- pH-electrode: METLER TOLEDO InLab 413 (connected to a METLER TOLEDO SevenEasy pH meter)

  A two-point calibration with standards pH 4 and 7 was used. Additional standards of pH 1.68 and 9 were used for verification of the linear range beyond the calibration range. Recalibration was done after 10 samples.

- Inductively coupled plasma optical emission spectrometer (ICP-OES): Varian 720-ES (axial, sea spray nebuliser, cyclonic spray chamber) with Varian SPS3 autosampler and Lytron chiller.

  Standard curves with three/four standards were used for calibration. The standards were prepared from Merck 1000 mg/l stock solutions. A Calibration curve for Cd consisting of the standards 0.1, 0.5 and 1 mg Cd/l respectively was used. Rescaling using the blank and a standard was done after every 20 samples. Continuing calibration verification was conducted using WaterChek reference samples. Yttrium and Tellurium were used as internal standards correcting for matrix effects. Cs was used as ionisation buffer.

- Total carbon analyser: Shimadzu TOC-5000A

  For total carbon, a calibration curve consisting of 10, 100, 200 and 200 mg/l standards was used. Inorganic carbon was calibrated using 2, 10, 20 mg/l standards. Total organic carbon is calculated as the difference between total carbon and inorganic carbon. Calibration was verified by measuring standards at the beginning and the end of a measurement series.

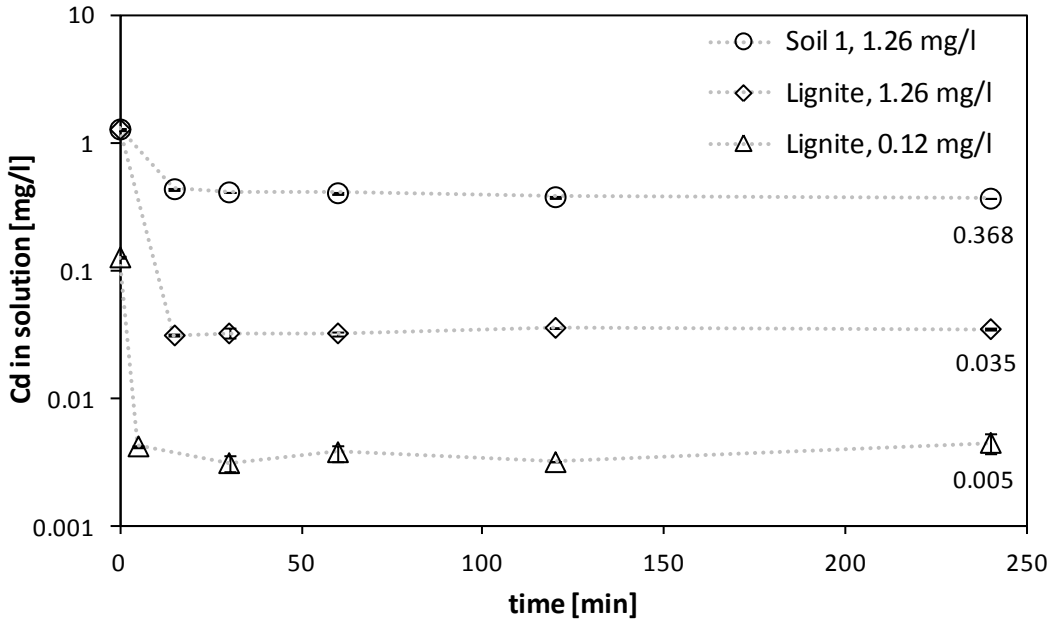
- C/N element analyser: Elementar vario MAX CN

  Build-in standard curves were adjusted using L-glutamic acid. For continuous verification of the calibration L-Glutamic acid was measured every 25 samples as a reference. For plant analysis a wheat flour reference (NIST durum wheat flour reference 8436) was additionally used to verify the accuracy. Sample duplicates were measured every 20 samples to monitor precision. The sample weight was adjusted considering the working range of 0.02 - 400 mg for C and 0.02 - 150 mg for N.

C Method development

C1 Determination of time to reach equilibrium (batch experiments)

The time to reach sorption equilibrium was investigated in a pre-experiment. Material was prepared as described for the batch experiments in Chapter 3.2. Five grams of lignite or Soil 1 was added to 30 ml 0.05 M $Ca(NO_3)_2$ solution spiked with 0.12 and/or 1.26 mg/l Cd (in 40 ml centrifuge tubes). The tubes were continuously agitated for different durations (5 - 240 min). Three replicates per treatment were prepared. Samples were prepared and the solution Cd concentration measured as described in Chapter 3.2. Initial concentrations (time = 0) were measured in separate treatments without addition of sorbent. The results are shown in the following figure.



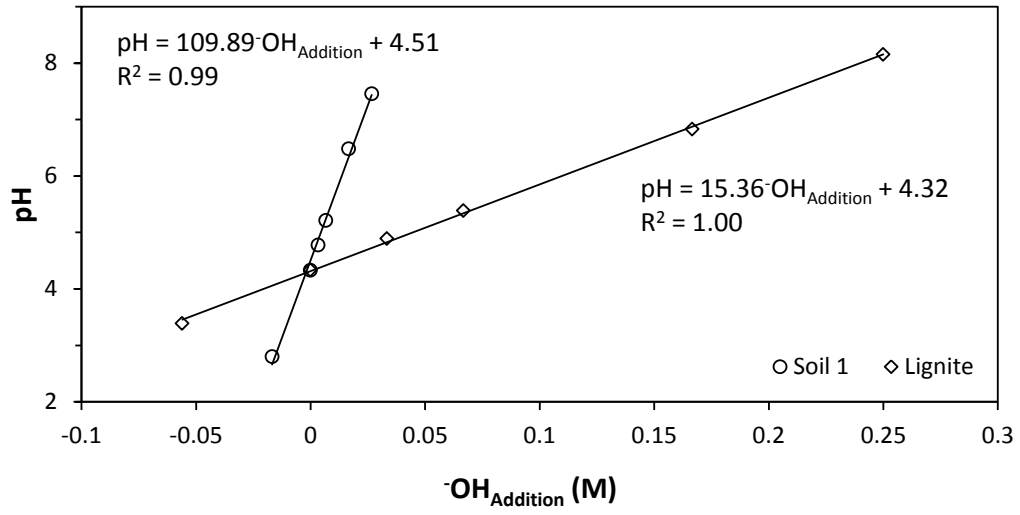
C1.1: Solution concentration of Cd as a function of contact time (mean ± SE, N = 3).

The solution concentration was stable after less than half an hour. Therefore equilibrium regarding fast sorption processes can be assumed after the two hours agitation time used in the batch method described in Chapter 3.

C2 pH adjustment (Batch Experiment 1)

C2.1: Treatments of Batch Experiment 1. The added Cd concentrations were measured in the corresponding spiked treatments without sorbent (mean ± SE, N = 3). The pH values were measured after 2 hours agitation (mean ± SE, N = 5, 4 or 3 according to the number of Cd levels).

Sorbent (5g in 30 ml)	Added Cd concentration (mg/l)	pH	Acid/base addition
no sorbent	0, 0.12 (0.00), 0.39 (0.001), 1.26 (0.001), 3.75 (0.003)	5.0 (0.05)	-
Soil 1	0, 0.12, 0.39, 1.26	2.8 (0.02)	300 µl HNO_3 1:10
	0, 0.12, 0.39, 1.26	4.3 (0.03)	-
	0, 0.12, 0.39, 1.26	4.8 (0.02)	50 µl 2 M KOH
	0, 0.12, 0.39, 1.26	5.2 (0.02)	100 µl 2 M KOH
	0, 0.12, 0.39, 1.26	6.5 (0.06)	250 µl 2 M KOH
	0, 0.12, 0.39, 1.26	7.5 (0.03)	400 µl 2 M KOH
Lignite	0, 0.12, 0.39, 1.26, 3.75	3.4 (0.01)	1 ml HNO3 1:10
	0, 0.12, 0.39, 1.26, 3.75	4.3 (0.01)	-
	0, 1.26, 3.75	4.9 (0.01)	100 µl 10 M KOH
	0, 1.26, 3.75	5.4 (0.02)	200 µl 10 M KOH
	0, 1.26, 3.75	6.8 (0.03)	500 µl 10 M KOH
	0, 1.26, 3.75	8.2 (0.1)	750 µl 10 M KOH



C2.2: pH as a function of acid/base addition represented by the corresponding $^{-}$OH equivalent. Lines represent fitted linear model (formula and R^2 given in figure).

D Complementary analysis

D1 Effect of lignite and lime on soil pH and solubility of nutrients

D1.1: Effect of lignite and lime addition on soluble soil concentrations of P, S, Zn, Cu, Fe and Mn. (- negative effect, + positive effect). ANOVA based on a generalised linear model with interaction in the form X ~ lignite + lime + lignite:lime (F-test using type III sums of square). Lignite was treated as a continuous variable and lime as a categorical factor with values "Yes" and "No". Significance codes: 'ns' > '0.05' > '*' > 0.01 '' > 0.001 > '***'**

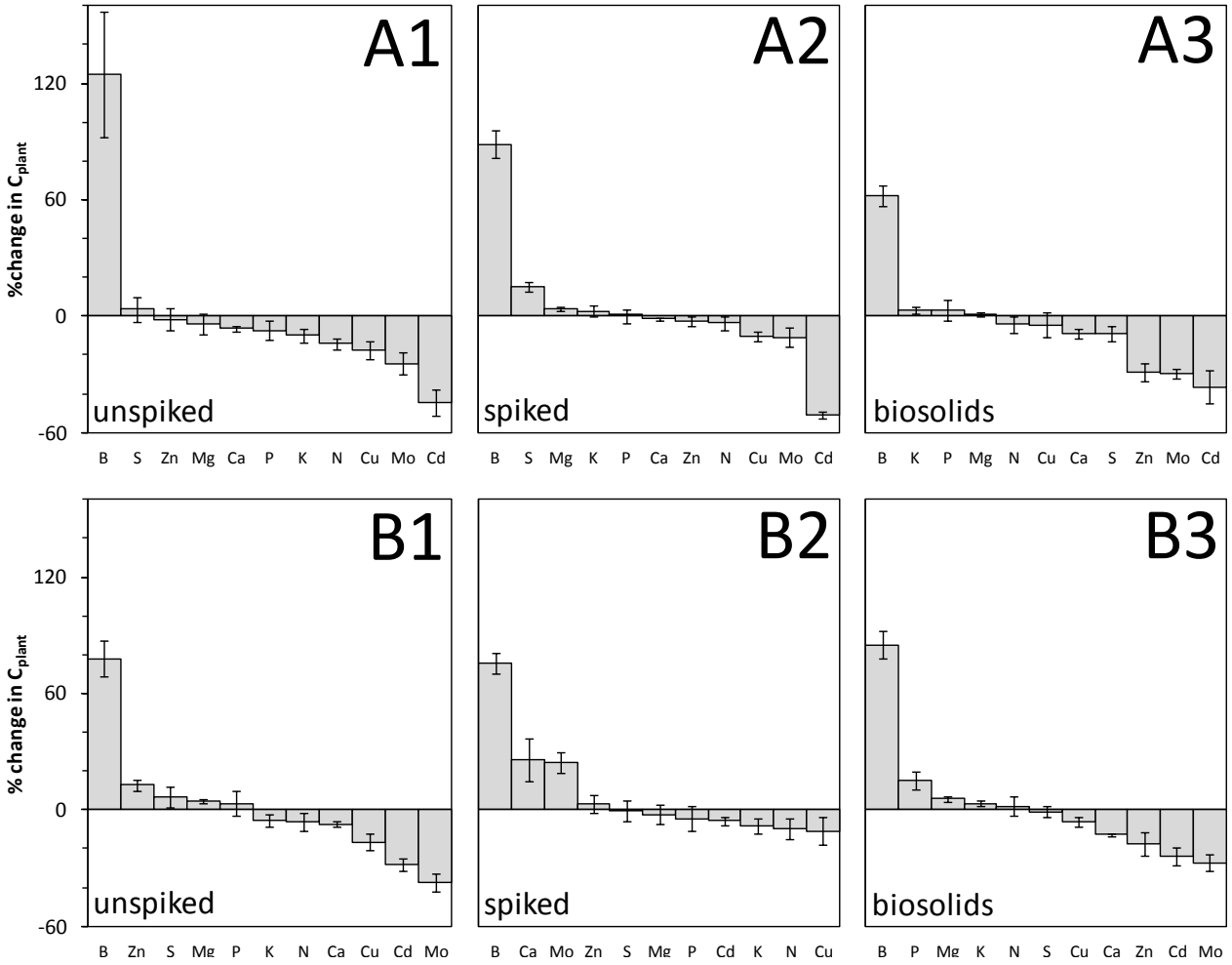
	Factor	P	S	Zn	Cu	Fe	Mn
unspiked	lignite	+ (**)	+ (***)	ns	ns	+ (***)	+ (*)
	lime	- (*)	ns	- (***)	ns	ns	- (**)
	lignite:lime	ns	ns	ns	ns	- (*)	ns
spiked	lignite	ns	ns	ns	ns	+ (***)	ns
	lime	ns	ns	- (***)	ns	- (**)	- (*)
	lignite:lime	ns	ns	ns	ns	- (*)	ns
biosolids	lignite	ns	ns	ns	ns	+ (***)	ns
	lime	ns	ns	- (**)	ns	- (***)	- (*)
	lignite:lime	ns	ns	ns	ns	ns	ns

D2 Effect of lignite and lime on biomass and plant nutrient concentrations

D2.1: Effect of lignite and lime addition on biomass and concentrations of various elements in *Lolium perenne* (- negative effect, + positive effect). ANOVA based on a generalised linear model with interaction in the form X ~ lignite + lime + lignite:lime (F-test using type III sums of square). Lignite was treated as a continuous variable and lime as a categorical factor with values "Yes" and "No". Significance codes: 'ns' > '0.05' > '*' > 0.01 '' > 0.001 > '***'**

	Factor	Biomass	Zn	Cu	Mo	Co	B	Ca	Mg	K	Fe	Mn	P	S	N
unspiked	lignite	ns	- (*)	- (***)	- (**)	ns	+ (***)	- (***)	- (***)	- (*)	ns	+ (**)	- (**)	ns	ns
	lime	ns	- (***)	- (*)	+ (**)	- (*)	ns	+ (***)	- (***)	ns	ns	- (***)	- (***)	- (***)	ns
	lignite:lime	ns	+ (***)	ns	ns	ns	ns	ns	+ (***)	ns	ns	+ (***)	ns	ns	ns
spiked	lignite	ns	ns	- (*)	ns	ns	+ (***)	ns	ns	ns	ns	+ (***)	ns	ns	ns
	lime	ns	ns	ns	+ (***)	ns	- (**)	+ (***)	- (*)	ns	ns	- (***)	ns	ns	ns
	lignite:lime	ns	ns	ns	ns	ns	- (**)	ns	ns	ns	ns	ns	ns	ns	ns
biosolids	lignite	- (***)	- (***)	ns	- (**)	ns	+ (***)	- (***)	+ (***)	ns	ns	+ (***)	ns	- (*)	ns
	lime	- (*)	- (**)	ns	+ (***)	- (*)	ns	+ (***)	- (**)	+ (**)	ns	- (***)	ns	- (**)	ns
	lignite:lime	ns	ns	ns	- (*)	ns	ns	- (*)	ns	- (*)	ns	ns	ns	ns	ns

D3 Effect on nutrient uptake as compared to effect on Cd uptake



D3.1: Difference in element concentration in *Lolium perenne* for the treatments with 3.4 wt% lignite addition relative to the corresponding treatments without lignite addition (Mean ± SE). A1 - A3 refer to the unspiked, spiked and biosolids treatment in series without lime addition. B1 - B3 refer to the unspiked, spiked and biosolids treatment in the series with lime addition. Note the difference in normalisation of plot B1 - B3 as compared to Figure 14 B.

E Data CD-ROM

The data analysed and reported in this paper plus data of additional experiments conducted in the context of this work can be found on the attached CD-ROM. The spreadsheet *data.xlsx* contains several worksheets which are described in the following table.

E1: Description of the worksheets in the spreadsheet *data.xlsx*

Worksheet	Description
"Pot Experiment"	Data from the pot experiment discussed in this paper.
"Batch Experiments 1&2"	Data from the Batch Experiments 1 and 2 discussed in this paper.
"Characterisation Lignite&Soil1"	Characterisation of Lignite and Soil 1. Contains values reported in Table 7 in Chapter 3.1.
"Characterisation Soil 2-6"	Characterisation of Soils 2 - 6. Contains values reported in Table 7 in Chapter 3.1.
"Kinetic Experiments"	Data from two kinetic experiments conducted as part of the method development. Notes on the methods as well as representation of the data can be found in Appendix C1.
"Pot Experiment Rep."	Data of a pot experiment which was conducted as a repetition of a part of the main pot experiment. The treatments and the analysis of the plant material correspond in large parts to the pot experiment described in this thesis. The element concentrations where measured with inductively coupled plasma mass spectrometry (ICP-MS) or graphite furnace atomic absorption spectrometry (GFAAS). Data is not discussed in this work.