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EFFECT OF USING FULL INVERSION TILLAGE AT PASTURE RENEWAL ON
SOIL AND PLANT CADMIUM CONCENTRATIONS

A thesis presented in partial fulfilment of the requirements for the degree of

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Abstract

Cadmium (Cd) accumulation in New Zealand (NZ) agricultural soils has been recognised as a potential concern for food safety, which can limit the exports of some agricultural products. In NZ, elevated soil Cd concentrations in long-term pastures is mainly because of the historic application of Cd-rich phosphate fertiliser. Similar to the strong vertical stratification of soil organic carbon (SOC), total soil Cd concentration also shows a decreasing trend with soil depth. Recently, one-off full inversion tillage (FIT, or deeper ploughing below 25 cm soil depth) at pasture renewal is being investigated in NZ, due to the potential positive impact of this cultivation method on long-term soil C storage. By burying topsoil under the 10–25 cm soil depth, FIT potentially influences soil Cd vertical stratification, but there is no previous research that quantifies the impacts of this practice on soil and plant Cd. Hence, the aim of the current study was to assess the effect of using FIT at pasture renewal on soil and plant Cd concentrations in two contrasting grazed pasture soils.

The current study involved the analysis of Cd in soil and plant samples taken from two on-going field trials in the North Island of NZ (Trial 1: Pallic Soil; Trial 2: Allophanic Soil). At both trial sites, three contrasting tillage treatments (i.e. FIT, shallow tillage-ST and no tillage-NT) were used in spring to establish a summer forage crop (leafy turnip), followed by sowing new ryegrass/white clover pasture in autumn. Soil cores were collected to a soil depth of 40 cm before the establishment of tillage treatments (i.e. pre-tillage: PT) and again at the end of the grazing of leafy turnip (i.e. post-tillage: FIT, ST and NT). Changes in soil total Cd (0–40 cm soil depth) and extractable Cd (0–15 cm soil depth) concentrations and soil pH (0–15 cm soil depth) were analysed. In addition, Cd concentration in herbage samples was monitored during both the summer crop and early new pasture growth phases.

At both trial sites, FIT modified the vertical stratification of total soil Cd, thus helping reduce topsoil (0–5 cm soil depth) Cd concentration, without changing the total mass of soil Cd to 40 cm soil depth. However, the extent of its effect was different between the two field trials, which was influenced by the pre-tillage total soil Cd concentrations, and its degree of vertical stratification above the 25 cm soil depth. At the Trial 1 site, average total soil Cd concentration in the 0–5 cm soil depth for the FIT treatment was about 24% lower (0.16 mg Cd/kg) than the pre-tillage value (0.21 mg Cd/kg); however, at the Trial 2 site, the average total soil Cd concentration in this soil

depth for the FIT treatment was about 40% lower (0.25 mg Cd/kg) than the pre-tillage value (0.42 mg Cd/kg). In terms of extractable Cd concentration, FIT also resulted in a different influence between the two trial sites, because of the contrasting pre-tillage extractable Cd distribution with soil depth. At the Trial 1 site, the FIT treatment had about 52% higher (0.024 mg Cd/kg) average extractable Cd concentration in the 0–5 cm soil depth than the pre-tillage value (0.016 mg Cd/kg), while it had about 57% lower (0.013 mg Cd/kg) average extractable Cd in this soil depth at the Trial 2 site than the pre-tillage value (0.031 mg Cd/kg).

Tillage treatments caused contrasting effects on plant Cd concentrations between the two trial sites. In addition, there was also a strong plant species influence on herbage Cd concentrations. In general, the new pasture Cd concentrations were less than 10% of the summer turnip crop at both trial sites. At the Trial 1 site, tillage practices did not significantly ($P > 0.05$) affect tissue Cd concentrations in either turnip leaves (on average: 0.92, 0.79 and 0.95 mg Cd/kg DM for the FIT, ST and NT treatment, respectively) or new grass (on average: 0.05 mg Cd/kg DM for all tillage treatments). In contrast, at the Trial 2 site, the FIT treatment resulted in lower Cd concentrations for both summer forage crop (on average: 0.69, 0.76 and 0.80 mg Cd/kg DM for the FIT, ST and NT treatment, respectively) and new pasture (on average: 0.04, 0.06 and 0.05 mg Cd/kg DM for the FIT, ST and NT treatment, respectively). Lower Cd uptake by plants sampled for the FIT treatment is likely to be the result of FIT-induced lower total soil Cd and extractable Cd concentrations in the topsoil at this trial site.

This field study demonstrated that the use of FIT during pasture renewal can be effective at decreasing total topsoil Cd concentrations in NZ pasture soils, particularly in those soils where there is a high degree of stratification in total soil Cd with soil depth. However, other management practices may also further reduce soil Cd bioavailability after tillage. In particular, any future accumulation of soil organic matter under the new pasture is expected to improve the topsoil's capacity to bind and immobilise Cd. Further work is required to evaluate the long-term influence of tillage treatments on soil chemical properties (e.g. soil Cd, organic matter and pH), and their effects on Cd bioavailability and uptake by plants.

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Chapter 1: Introduction

1.1 Reasons for this study

Livestock production from mostly pasture-based farming systems underpin New Zealand's (NZ) export earnings. For example, in 2019, annual exports of dairy commodities (milk powder, butter and cheese; \$ 15,782 million), meat and edible offal (\$ 8,048 million) and wool (\$ 519 million) accounted for approximately 41% of total exported goods value (Stats NZ, 2019a). Preserving this economic return largely depends on ensuring that the agricultural sector continues to produce and export high-quality products, and that the potential for non-tariff barriers to these exports are minimised. Historically, certain offal products in NZ, particularly kidneys of older grazing animals, have exceeded the permissible value for the trace metal cadmium (Cd) for human consumption (Roberts et al., 1994; Reiser et al., 2014). Cadmium is a bio-toxic metal that can be taken up by plants and then be incorporated into above-ground plant tissues (Bramley, 1990), resulting in the increased Cd bioaccumulation in the tissues and organs of grazing animals in the order kidney > liver > muscle (Solly et al., 1981; Lee et al., 1994) and, therefore, can pose a food safety concern.

The natural background concentration of Cd in soils is low, being typically < 0.15 mg Cd/kg (Adriano, 2013). However, in many countries, its level can be elevated due to intensive agricultural and industrial activities, including phosphate fertiliser application, mining and smelting industries (entering into soil through atmospheric deposition), and sewage effluent irrigation (Alloway & Steinnes, 1999). For example, between the period of 2004–2012, total soil Cd concentration increased from a range of 0.15–0.40 to 0.53–5.92 mg Cd/kg, when the local ceramic factories were established in Jiangsu, China (Liao et al., 2015). In contrast, industry is not an important contributor to the elevated soil Cd concentrations in NZ.

In NZ, Cd has been unintentionally added to pasture soils, due to the long-term and continuous application of phosphate fertiliser. Particularly, the historic applications of Cd-rich phosphate fertiliser, which was manufactured using Nauru phosphate rock containing 450–600 mg Cd/ kg P (Syers et al., 1986). It has been widely accepted that there is a significant positive relationship between pasture soil Cd concentration and phosphate fertiliser history (e.g. Salmanzadeh et al., 2016a; Stafford et al., 2018a). Based a survey of 26 pastures ranging from high-intensity dairy farm to low-intensity hill country grazing, the average NZ pasture total soil Cd concentration was about 0.23 mg Cd/kg, with a range from 0.06 to 0.85 mg Cd/kg (Wakelin et al., 2016). While the average

Cd level of NZ pasture soils is relatively low, there are some farms with moderate to high Cd levels. This is supported by other studies that identified some sites in the central North Island with soil Cd concentrations exceeding 1.8 mg Cd/kg (Abraham, 2020), and in the Waikato region where about 11% of pasture soils sampled contain more than 1 mg Cd/kg (Kim, 2008).

Total soil Cd concentration in permanent pasture soils shows a strong vertical stratification within the soil profile, with higher Cd concentration in the topsoil and declining with soil depth. More than 80% of the Cd added through phosphate fertiliser remains in the topsoil (Taylor, 1997). In a long-term pasture farm, topsoil (0–7.5 cm soil depth) contained as much as 3–10 times more Cd than the subsoil (Stafford et al., 2018b). This is a consequence of unwanted Cd inputs from past application of phosphate fertiliser increasing its concentration in the soil surface, and also due to Cd being relatively immobile in soils. Though total topsoil Cd concentration cannot completely reflect its concentration in plant tissues, its high concentration can impair the growth of rhizobia (Cavanagh et al., 2016), which can reduce herbage yield (Wakelin et al., 2016). Furthermore, the higher soil Cd concentration causes higher Cd uptake of pasture herbage grown in these soils (Roberts & Longhurst, 2002). Reducing total soil Cd concentration in topsoil, thereby, can help minimise any possible adverse impacts, including the ingestion of plant Cd by grazing animals.

Pasture renewal is a common practice in NZ permanent pasture to restore or improve its productivity (Whitehead et al., 2018). In NZ, permanent pastures mostly consist of perennial ryegrass and white clover. These pasture species can grow well throughout the year in most regions of NZ (Crush et al., 2005; Pembleton et al., 2015). However, biomass production may decline because of a decrease of productivity in seasonally dry periods, an increase of pests or weeds over time, or following physical damage caused by livestock grazing during wet soil conditions (Whitehead et al., 2018). An important aspect of maintaining pasture performance is the renewal of pastures, typically once every 7–10 years on dairy farms. Pasture renewal practices commonly involve spraying out the old pasture with herbicide in either spring or late summer-autumn followed by different tillage practices (e.g. full cultivation, shallow cultivation, and/or direct drill or no tillage) to prepare a new seedbed for forage establishment, or alternatively establish a summer or winter forage crop, before sowing new pasture (Hanly et al., 2017). The annual pasture renewal rate on dairy farms can reach to about 10% of a farm's area, which is approximately twice as high as for drystock farms on average (Bewsell et al., 2008).

Recent field-based research, both in the North Island (Calvelo Pereira et al., 2019, 2020; Beare et al., 2020) and the South Island (McNally et al., 2019) of NZ, are studying the use of infrequent full inversion tillage (FIT) at the time of pasture renewal, to improve the long-term storage of soil organic carbon (SOC) in permanent pasture soils. The hypothesis is that FIT, ploughing a deeper soil depth than usual cultivation (i.e. < 25 cm soil depth), can bury topsoil with high-C in an area of low degradation, while simultaneously exposing subsoil with low-C and, thereby, creating a C-unsaturated topsoil that could accumulate and stabilise new C input from the pasture (Whitehead et al., 2018), thus, increasing the soil C stock for the entire profile in the long term. However, FIT has the potential to not only redistribute C in the soil, but also other elementals, such as Cd, that accumulate in the topsoil of pastures. Moreover, FIT may influence other soil properties that can influence the bioavailability of Cd in the soil (e.g. soil organic matter and pH). Therefore, research is required to assess the effects of FIT on Cd redistribution in soils and its bioavailability for plant uptake under field conditions.

1.2 Research focus and objectives

This study involved two contrasting pasture soils (Trial 1: Pallic Soil; Trial 2: Allophanic Soil), which are part of on-going field trials in the Manawatū-Wanganui Region, North Island of NZ, as reported by Calvelo Pereira et al. (2019, 2020). In order to better understand the influence of FIT on soil and plant Cd concentrations, the objectives of the current study were to:

- 1) Assess the impact of using FIT at pasture renewal on the vertical stratification of soil Cd concentrations in two contrasting pastoral soils, namely, the profile changes of total soil Cd (0–40 cm soil depth) and extractable Cd concentrations (0–15 cm soil depth) after FIT, which were compared with shallow tillage (i.e. ST; approximately 5 cm soil depth) and no tillage (NT) treatments;
- 2) Determine the influence of using FIT at pasture renewal on plant Cd concentrations, grown in above-mentioned soils, by quantifying plant Cd concentrations and uptake for both summer turnip crop and new pasture phases, which were compared with ST and NT treatments.

Chapter 2: Literature Review

2.1 Cadmium in New Zealand pasture systems

2.1.1 Cadmium in phosphate fertiliser

The relatively low background cadmium (Cd) concentrations in soil, air and water can be increased due to anthropogenic influences. In countries with intensive anthropogenic activities, there can be a number of different sources that contribute to the elevated Cd concentrations in soils. For example, in China, irrigation, phosphate fertilisers, organic manures and atmospheric deposition are all sources of Cd, with the latter contributing 0.4–25 g/ha/yr Cd (Zhao et al., 2015), whereas atmospheric Cd deposition from industrial processes in 7 pasture cultivation sites across New Zealand (NZ) was extremely low, ranging from 0.09 to 0.36 g/ha/yr Cd (Gray et al., 2003a). However, long-term historical phosphate fertiliser application to pasture soils to increase livestock production has been recognised as the main source of the unintended Cd accumulation in NZ soils (Williams & David, 1973; Stafford et al., 2018a).

Cadmium exists naturally in phosphate rock sourced from sedimentary, igneous and island deposits (guano phosphate deposits). It has been estimated that more than 80% of phosphate fertilisers are manufactured from sedimentary deposits (Van Kauwenbergh, 2001). The average Cd concentration of sedimentary phosphate rock deposits is about 21 mg Cd/kg fertiliser with a range of < 1–150 mg Cd/kg fertiliser (Roberts, 2014). This wide range is related to the origin of sedimentary phosphate rock deposits, for example, phosphate rock from Nauru Island contains high average Cd concentration of 100 mg Cd/kg fertiliser (Table 2.1).

Table 2.1 Cadmium concentrations (mg Cd/kg fertiliser) of sedimentary phosphate rocks (compiled data presented in ^a Van Kauwenbergh, 2001, and ^b Syers et al., 1986).

Country	Deposit	Average Cd	Range
China ^a	Kaiyang	<2	-
Israel ^a	Zin	31	20–40
	Undifferentiated	24	20–28
	Arad	14	12–17
	Oron	5	-
Jordan ^a	El-Hasa	5	3–12
	Shidyia	6	-
Morocco ^a	Undifferentiated	26	10–45
	Bou Craa	38	32–43
	Khouribga	15	3–27
	Youssoufia	23	4–15
Senegal ^a	Taiba	87	60–115
Syria ^a	Khneifiss	3	-
Togo ^a		58	48–67
Tunisia ^a		40	30–56
United States ^a	Central Florida	9	3–20
	North Florida	6	3–10
	Idaho	92	40–150
	North Carolina	38	20–51
Peru ^b	Sechura Desert	11	-
Mexico ^b		8	-
Nauru Island ^b		100	-
Makatea Island ^b		10	-
New Zealand ^b	Chatham Rise	2	-

In addition to the origin of phosphate rock, fertiliser manufacture process can impact the Cd contents in phosphate fertilisers. Virtually, all of Cd in the original phosphate rock is retained in single superphosphate fertilisers during the manufacturing process, while 55–90% of Cd in the phosphate rock is transferred to ammonium phosphate fertilisers (Roberts, 2014). These two factors largely result in varying amounts of Cd in different phosphate fertilisers (Table 2.2). The application of phosphate fertiliser with high Cd concentration may cause high Cd accumulation in soils. For example, total soil Cd concentration was about twice higher for superphosphate treatments than that of diammonium phosphate treatment in the 0–7.5 cm soil depth, in a long-term grazing farm trial site, at Manawatū region (Loganathan et al., 1997).

Table 2.2 Cadmium concentrations in different phosphate fertilisers (Bureau of Resource Sciences, 1997).

Fertiliser type	Cadmium content (mg Cd/kg fertiliser)
Single superphosphate	16–26
Double superphosphate	< 0.6–12
Triple superphosphate	0.8–7.0
Mono-ammonium phosphate	1.8–8.1
Di-ammonium phosphate	4.3–6.6

In NZ, there are three different units to express Cd concentration of phosphate fertiliser: mg Cd/kg fertiliser, mg Cd/kg P, and mg Cd/kg P₂O₅. The conversions among the three units and the voluntary cadmium limit in NZ superphosphate fertiliser are shown in Table 2.3. Currently, 280 mg Cd/kg P has been the voluntary cadmium limit; however, the historical Cd contents of phosphate fertiliser greatly exceeds this standard.

Table 2.3 Voluntary cadmium limit in New Zealand superphosphate fertiliser (Kim, 2008).

Voluntary Cd limit	Single/double superphosphate	Triple superphosphate
Expressed as mg Cd/kg P	280	280
Expressed as mg Cd/kg P ₂ O ₅	122	122
Expressed as mg Cd/kg fertiliser	24.4	55

Historically, the NZ fertiliser industries utilised Cd-rich phosphate rock from Nauru Island (Syers et al, 1986), accounted for 40% of phosphate fertilisers manufactured during the mid-1980s in NZ and Australia (Kim, 2008). Since the 1990s, the NZ fertiliser industries discontinued using Nauru phosphate rock to manufacture fertilisers, and started using low Cd phosphate rocks sourced from other countries, such as Morocco (Salmanzadeh et al., 2016b).

As the origin of phosphate rocks has changed, the standard of Cd concentration of phosphate fertiliser has been correspondingly improved. In 1995, fertiliser industries established 420 mg Cd/kg P as the maximum value of Cd concentration in phosphate fertiliser, which was reduced to 280 mg Cd/kg P in 1997. This value was implemented as a voluntary limit for Cd concentration of phosphate fertiliser in 2001. The Cd concentration of phosphate fertiliser used in a long-term research farm (Winchmore farm was located in Canterbury and established in 1949) illustrated that the decrease of Cd contents in NZ phosphate fertilisers used since 1980s (Figure 2.1). Furthermore, the average Cd concentration in phosphate fertilisers from 2003 to 2019 was approximately 177 mg Cd/kg P. About 95% of the 3188 samples had Cd concentrations less than 242 mg Cd/kg P, while 5% of

samples had concentrations less than 109 mg Cd/kg P (<http://www.fertiliser.org.nz>).

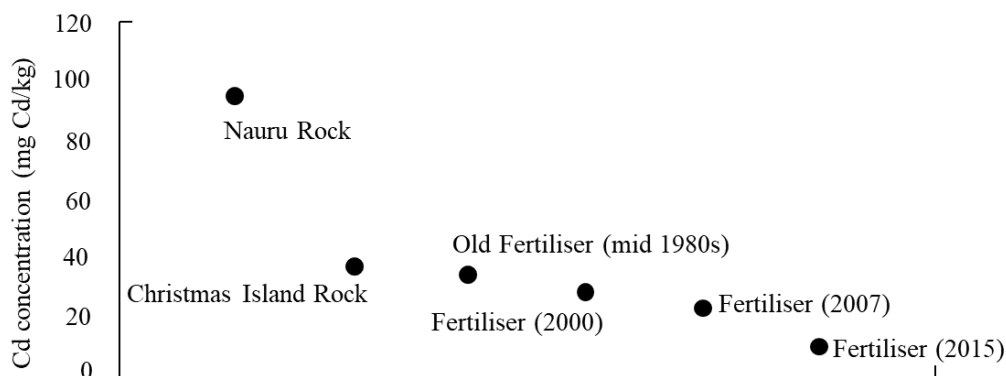


Figure 2.1 Cadmium concentration (mg Cd/kg) in phosphate rock and phosphate fertilisers in New Zealand (adapted from Salmanzadeh et al., 2016b).

The decrease in the Cd concentrations of phosphate fertilisers has contributed to the slowing Cd accumulation rate in NZ pasture soils. For example, in the Winchmore farm (Canterbury), the Cd accumulation rate significantly decreased since 1997, because of the lower Cd concentration in phosphate fertiliser applied (Salmanzadeh et al., 2016b). Moreover, pasture soils from a 23 yr phosphate fertiliser trial had different Cd accumulation rates, due to the change of phosphate fertiliser type, at Whatawhata Hill Country Research Station, in the North Island of NZ (Schipper et al., 2011). They found that single superphosphate applied in the hill farm soils led to soil Cd accumulation rate increased 0.036 and 0.045 mg Cd/kg/yr, at annual phosphate fertiliser loading rate of 50 and 100 kg P/ha/yr, respectively, between 1983 and 1989; however, from 1989 to 2006, at the same rates of phosphate fertiliser, the accumulation rate of Cd declined to 0.005 and 0.015 mg Cd/kg/yr, respectively, due to the change of phosphate fertiliser application to triple superphosphate (Schipper et al., 2011). Additionally, the annual Cd upload in NZ soils through phosphate fertiliser application peaked around 40 tonnes in 2005, which then decreased to an input of approximately 30 tonnes each year in more recent years (Figure 2.2). These changes incorporate not only the changes in phosphate fertiliser Cd concentration, but also changes in the fertiliser use.

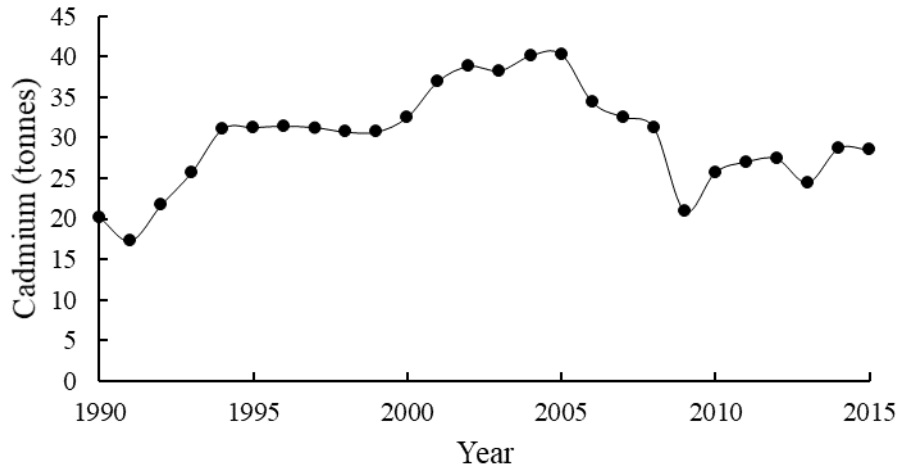


Figure 2.2 Cadmium added into soils through phosphorus fertiliser on a whole country basis for New Zealand (1990–2015).

Note: The data were estimated using the equation: Cd (tonne) = Phosphorous (tonne) * 184 mg Cd/ kg P * 10^{-6} (Abraham, 2020). The data on phosphorous in fertilisers was downloaded from Stats NZ ‘Nitrogen and phosphorous in fertilisers, 1990–2015’ (Stats NZ, 2019b)

2.1.2 Cadmium in pasture soils

Agricultural soils contain greater Cd concentrations than native soils because of the anthropogenic Cd inputs (Table 2.4). For example, agricultural soils in NZ have 2–7 times higher Cd than background Cd level due to the long-term history of phosphate fertiliser application (Roberts et al., 1994; Table 2.4). Loganathan & Hedley (1997) have highlighted that about 90% of added Cd through fertiliser was recovered in a pasture soil over 10 years, and approximately 93% of this Cd was accumulated within the top 12 cm soil depth, indicating a strong vertical stratification of Cd concentration. The low rate in the downward movement of Cd is caused by its adsorption into soil organic matter (Adriano, 2013). Thus, the historical accumulation of Cd promoted to commence intensive monitoring programs of Cd levels in NZ agricultural soils (Loganathan et al., 2003).

Table 2.4 Mean and range of soil cadmium concentrations in agricultural and non-agricultural sites in selected countries.

Land use	Soil depth (cm)	Country	No. of samples	Mean and range concentration (mg Cd/kg)	References
Agricultural	0–5	Australia	516	0.18 (0.01–0.73)	Merry & Tiller (1991)
	0–15	Ecuador	560	0.44 (0.02–6.90)	Argüello et al. (2019)
	0–20	Denmark	51	0.26	Tjell & Hovmand (1978)
	0–20	USA	3305	0.27 (<0.01–2.40)	Holmgren et al. (1993)
	0–20	China	92	0.17 (<0.01–0.69)	Chang et al. (2014)
	0–7.5	New Zealand	398	0.44 (0.04–1.53)	Roberts et al. (1994)
	0–20	New Zealand	466	0.71 (0.01–2.00)	Taylor & Kim (2009)
	0–10	New Zealand	939	0.32 (<0.01–2.70)	McDowell et al. (2013)
Non-agricultural	0–5	Australia	69	0.11 (0.01–0.29)	Merry & Tiller (1991)
	-	China	2989	0.03–0.24	Chen et al. (1991)
	0–7.5	New Zealand	86	0.20 (0.02–0.77)	Roberts et al. (1994)
	0–20	New Zealand	39	0.11 (0.03–0.30)	Taylor et al. (2010)
	0–10	New Zealand	289	0.14 (<0.01–0.67)	McDowell et al. (2013)

Since the early 1990s, researchers commenced on the national investigation of agricultural soil Cd levels in NZ, and reported their updated database, as shown in Figure 2.3. The main results from these reports demonstrated that:

- 1) The mean soil Cd concentration remained about 0.45 mg Cd/kg in NZ agricultural soils (Abraham et al., 2016), but the highest individual soil Cd concentration increased from 1.53 to 3.05 mg Cd/kg (Roberts, et al., 1994; Abraham et al., 2016);
- 2) The agricultural soil Cd level was relatively higher in Waikato, Taranaki and Bay of Plenty regions, and their mean soil Cd concentrations increased slightly from Taylor et al. (2007) to Cavanagh (2014);
- 3) Soil type and land use significantly impacted on soil Cd concentrations. Generally, Volcanic and Peat Soil Orders had higher soil Cd concentrations, compared to Pumice and Sedimentary Soils. In addition, the dairying land use had the highest mean soil Cd concentration (0.59 mg Cd/kg), followed by orchards, drystock and arable soils (Cavanagh, 2014). These findings were consistent with the recent study carried out by Abraham (2020), who selected 5459 samples to explore the relationship between soil Cd

concentrations and soil type/land use.

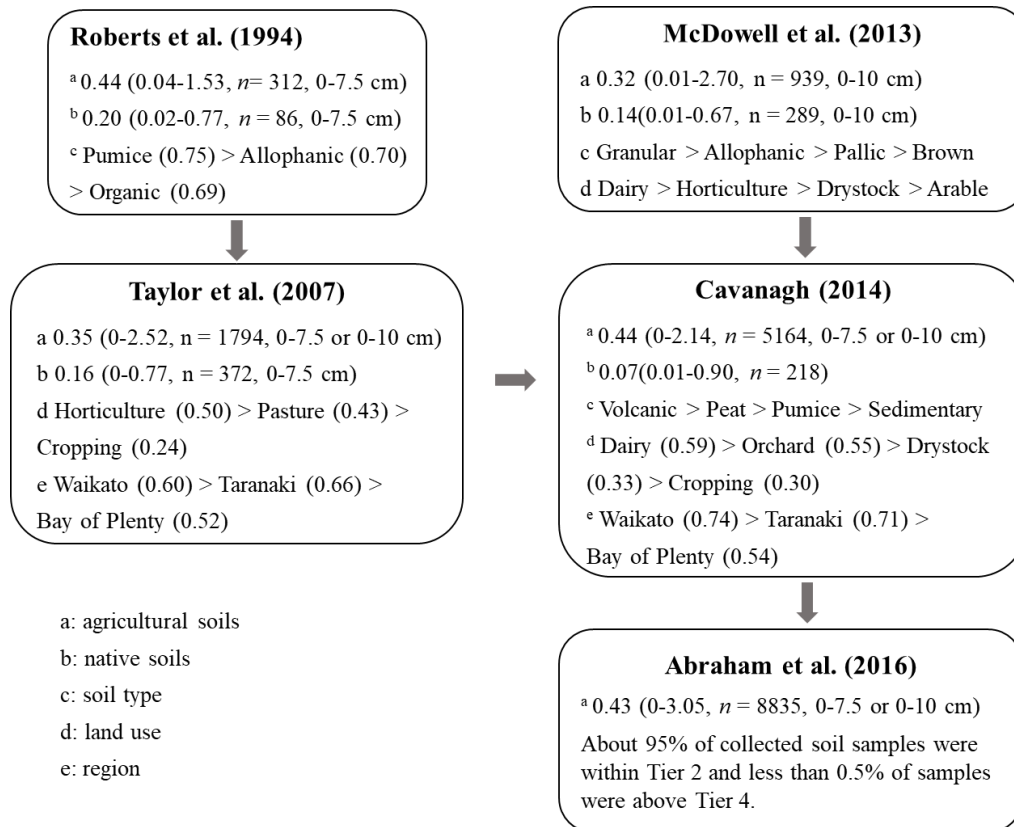


Figure 2.3 Summary of selected national surveys of cadmium concentrations (mg Cd/kg) in agricultural soils in the soil depth of 0–7.5 or 0–10 cm, in New Zealand. The grey arrow means that part of the database in the former study were incorporated into the following one.

A Cadmium Working Group (CWG) was established in 2006, and this group has released the Tiered Fertiliser Management System (TFMS), which is a current recommended standard for NZ soil Cd concentration (see section 2.4.1). Thus, Cavanagh (2014) and Abraham et al. (2016) both assessed the national soil Cd levels according to the TFMS. They revealed that most soil samples fell into the Tier 0 or Tier 1 (< 1 mg Cd/kg), but few individual samples exceeded the Tier 4 (>1.8 mg Cd/kg).

However, Cavanagh (2014) claimed that sampling depth could impact on total soil Cd concentrations and the ability to make comparisons with the Tiers within the TFMS. The author reported that samples collected in the 0–10 cm soil depth in pastoral farms had approximately 10% lower Cd contents than that of samples collected in the soil depth of 0–7.5 cm (Cavanagh, 2014). Similarly, Taylor et al. (2007) mentioned that the lower Cd contents in crop soils, compared to pastoral soils, was probably attributed to the deeper soil depth of samples, alongside the tillage

practices which can dilute soil Cd concentrations.

While the mean Cd concentration (0.45 mg Cd/kg) in NZ agricultural soils remains within the Tier 0 (< 0.6 mg Cd/kg), a few other sites are above the Tier 1, especially amongst pastoral farms on Volcanic and Peat Soils. Although Cd can be reduced through losses (e.g. leaching and erosion) and removal by plants and animals (Grant, 2011), only < 0.25% of total soil Cd contents were lost from pasture soils via leaching losses in NZ (Gray et al., 2003b), as Cd is relatively immobile in most pastoral soils. However, Cd can be accumulated in the soil-plant system via plant uptake (Nedjimi & Daoud, 2009), which can impose a serious risk to both ecosystem and human beings in the long-term. This transfer is affected by a number of factors associated with plant species and soil properties, which will be discussed in the following sections.

2.1.3 Cadmium in herbage and grazing animal offal

The herbage Cd concentration in NZ is relatively low in grazing systems with a mean of < 0.3 mg Cd/kg DM (Stafford et al., 2016). Roberts et al. (1994) reported that the mean grass Cd concentration of 312 NZ pasture farms was < 0.1 mg Cd/kg DM. However, based on the same database, the variation of herbage Cd concentration was wide, ranging from 0.03 to 0.30 mg Cd/kg DM (Longhurst et al., 2004). Similarly, Reiser et al. (2014) reported that 90% of pasture samples collected from 69 sites contained mean Cd concentration of 0.13 mg Cd/kg DM, with a broad range of 0.01–1.55 mg Cd/kg DM. Although the mean herbage Cd level is not high in NZ pasture systems, continuous supply of trace Cd through grazing can cause Cd toxicity in the animal's kidney and liver (Solly et al., 1981). For example, a national survey of grazing animals during 1988 and 1992 in NZ reported that 22–28% of ovine kidneys and 14–20% of cattle kidneys exceeded Maximum Residue Level (MRL) of 1 mg Cd/kg (Roberts et al., 1994).

The age of grazing animal also significantly contributes Cd level in offal through its effect on the time for exposure to Cd intake. For example, there was a 22% increase in lamb kidney Cd accumulation rate per month, when animal's age increased from 3 to 15 months (Roberts & Longhurst, 2002). This study also found that the mean kidney Cd concentration of 30 months old sheep was higher than the MRL of 1 mg Cd/kg. This offered further evidence to support the NZ Meat Industry policy to discard kidneys of slaughtered animals exceeding 30 months of age, to minimise Cd risk through the food chain. However, in 2002, NZ and Australia jointly established

the Australia New Zealand Food Authority (ANZFA), which increased the MRL of Cd for NZ meat products from 1 to 2.5 mg Cd/kg for kidneys, to 1.25 mg Cd/kg for livers and to 0.05 mg Cd/kg for muscle. Such increase of MRL in offal products may result in reducing of the amounts of NZ animals' offal meat exceeding the food standard of Cd. For example, Reiser et al. (2014) estimated daily intake of Cd for cows and sheep, and found that only 2.9% of kidneys from cows, and 1.4% of kidneys and 2.9% of livers from sheep exceeded the new food standards of ANZFA.

2.2 Factors affecting herbage cadmium level

Soil cadmium concentration

Plant cadmium (Cd) concentration is most likely to be affected by specific factors, including soil plant-available Cd concentration, pasture composition (forage species and weeds), individual plant characteristics (e.g. growth rate), the history of application of phosphate fertiliser and the slope (Table 2.5). Soil Cd concentration may impact plant Cd concentration by its influence on the plant-available Cd concentration in soils. A long-term pasture research at Manawatū, New Zealand (NZ) demonstrated that there was a strong positive relationship between the grass/clover Cd concentration and the 0.01 M CaCl₂ extractable Cd concentration (Loganathan et al., 1997). For example, the soil treatment with the highest CaCl₂ -Cd concentration (0–3 cm soil depth: 0.026 mg Cd/kg; 3–7.5 cm soil depth: 0.040 mg Cd/kg) had the highest Cd uptake by grass (1081 mg Cd/ha) and grass plus clover (1144 mg Cd/ha), in comparison with other treatments (Loganathan et al., 1997). Similarly, Roberts et al. (1994) reported that herbages grown in a Pumice Soil had the highest Cd concentration (average: 0.2 mg Cd/kg DM), because of the high total soil Cd concentration of 0.75 mg Cd /kg, on average, with a rang of 0.30–1.47 mg Cd/kg.

Table 2.5 Factors affecting plant cadmium uptake in New Zealand pasture systems.

Factor	Description	References
Plant-available Cd	High plant-available Cd can result in high Cd uptake by grasses.	Loganathan et al. (1997)
Weeds	Weed species can accumulate higher Cd than grass species.	Roberts et al. (1994)
Plant species	Broad leaf forage plant species (e.g. chicory, plantain and turnips) have higher Cd concentration.	Stafford et al. (2016)
Grass cultivar	Short-rotation ryegrass varieties have lower Cd concentration.	Gray & McLaren (2005)
Growth rate	High growth rate can dilute herbage Cd concentration, resulting in highest Cd concentration in autumn but lowest in spring.	Loganathan et al. (1997)
Phosphate fertiliser	High inputs of phosphate fertiliser can enhance herbage Cd level.	Loganathan et al. (1995)
Slope	Increase of slope on the farm can increase plant Cd concentration.	Roberts & Longhurst (2002)

Weeds

Pasture composition is another essential factor determining plant Cd uptake in pasture systems. In NZ, the typical plant composition of pasture is about 70% ryegrass, 20% white clover, and 10% weeds (Roberts & Longhurst, 2002). Previous findings demonstrated that weeds can accumulate greater Cd than grasses; for example, mean Cd concentration in the grasses (0.10 mg Cd/kg DM) was significantly lower than in the weeds (0.28 mg Cd/kg DM) (Roberts et al., 1994). Another study also indicated that a high fraction of weeds in pasture systems can result in the higher total forage Cd uptake (Roberts & Longhurst, 2002). Thus, reducing weed productivity is important for decreasing Cd level in pasture systems (Lee et al., 1996).

Plant species

In recent years, the influence of pasture plant species on Cd uptake has received increased attention. In the early of 2000s, winter and summer brassica crops, such as kale, swede and turnip, and herbs (e.g. chicory and plantain) were introduced to NZ pasture systems, to enhance pasture biomass (Stafford et al., 2016), as well as improve grazing animals' production (Somasiri et al., 2015). A comprehensive research was implemented by Stafford et al. (2016) who compared Cd

concentration of 12 forage species in NZ livestock grazing systems. They concluded that chicory (average: 1.64 mg Cd/kg DM) and plantain (average: 0.73 mg Cd/kg DM), turnip leaf (average: 0.53 mg Cd/kg DM) had significantly higher Cd than perennial ryegrass (average: 0.10 mg Cd/kg DM) and white clover (average: 0.04 mg Cd/kg DM) in the glasshouse trial, as well as in the field survey (1.82, 0.80, 0.11 and 0.08 mg Cd/kg DM for chicory, plantain, ryegrass and white clover, respectively, on average). They also stated that forage brassica crops had moderate tissue Cd concentrations; for example, turnip leaf had about 0.53 mg Cd/kg DM, on average. This result was in agreement with Cavanagh et al. (2016), who reported that chicory and plantain had significantly higher Cd concentration, compare to other pasture species. In this study, leaf of all tested forage crops (e.g. maize, foodebeet, kale and sunflower) with higher Cd concentrations than their other components of plants (i.e. bulb/stem and head) was disclosed.

Grass cultivar

There are also intraspecies differences regarding on plant Cd concentration. For example, within ryegrass cultivars, the mean Cd concentration was 0.05 mg Cd/kg DM, ranging between 0.03 and 0.12 mg Cd/kg DM (Longhurst et al., 2004). In general, the short-rotation ryegrass cultivars, such as 'Tabu', 'Archie' and 'Flanker', have relatively low Cd concentrations (Gray & McLaren, 2005), because of their higher growth rate, compared to other ryegrass cultivars. In addition, seasonal differentials in plant Cd concentrations (higher in autumn and lower in spring) are largely caused by changes in growth rate (lower in autumn and higher in spring), alongside the higher proportion of weeds in autumn, in NZ pasture soils (Loganathan et al., 1997).

Other factors: phosphate fertiliser and slope

Plant Cd concentration can be increased when more phosphate fertilisers were applied into pasture soils (Roberts & Longhurst, 2002). Especially, the application of single superphosphate, historically had considerably higher Cd, compared to the diammonium phosphate and Jordan phosphate (Loganathan et al., 1997). In addition, Roberts & Longhurst (2002) explored the effect of paddock position (slope) on plant Cd concentration in a sheep-razed hill-country pasture, and found that plant Cd concentration increased with the increase of slope, as a result of a rise in the biomass of weeds. This is in agreement with Loganathan et al. (1995) who also reported that plant

Cd concentration increased from 0.14 to 0.49 mg Cd/kg DM due to the increased slope.

2.3 Soil factors affecting cadmium bioavailability

2.3.1 Fate of cadmium in soil

An illustration of cadmium (Cd) fate in pasture systems is presented in Figure 2.4. The long-term phosphate fertiliser application mainly contributes to the elevated soil Cd concentration in New Zealand (NZ) agricultural system (Syers et al., 1986; Salmanzadeh et al., 2017; Figure 2.4-I). There is a 2–30 times greater soil Cd load in the top 30 cm soil depth of fertilised NZ pasture soils, in comparison with unfertilised soils (Zanders et al., 1999). The soil Cd originating from phosphate fertilisers is fairly immobile (Gray et al., 2003b), and therefore, approximately 75% of the fertiliser-derived Cd has accumulated in the 0–7.5 cm soil depth (Zanders et al., 1999), suggesting that the vertical stratification of soil Cd concentration is common in pastoral soils. In addition, negligible fertiliser-applied Cd is transferred below the 50 cm soil depths (Kelliher et al., 2017).

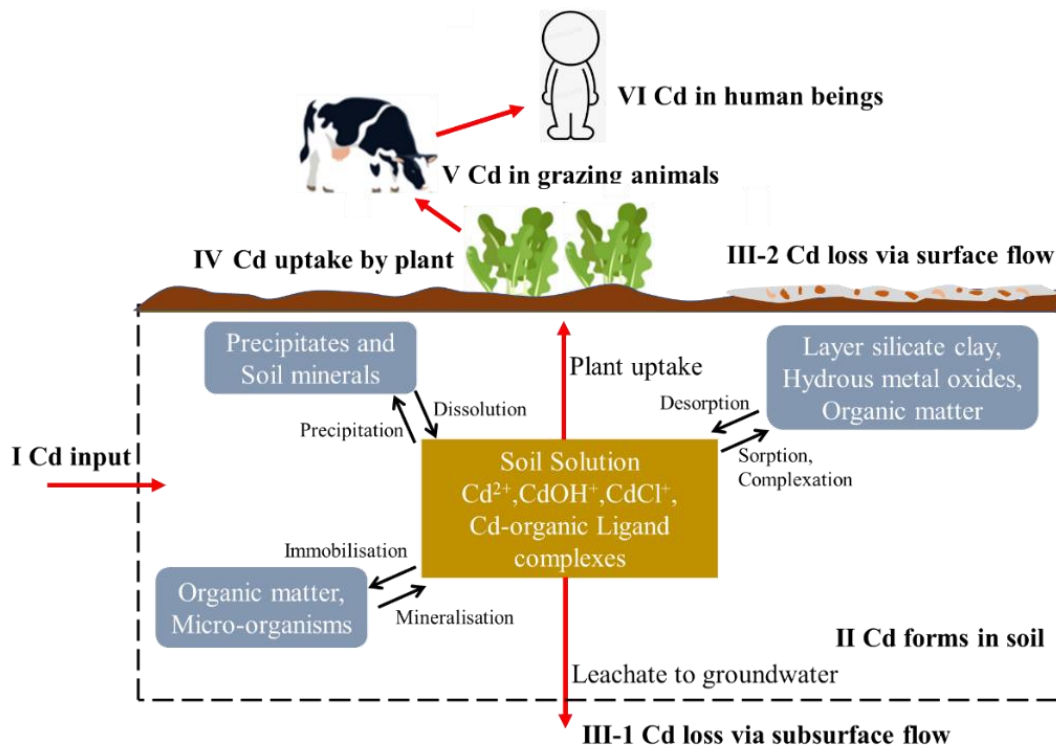


Figure 2.4 The cadmium fate in pasture systems (adapted from Loganathan et al., 2012). (I) cadmium added to soils through natural and anthropogenic activities, (II) the behaviours of cadmium in soils, (III-1 and III-2) cadmium loss via subsurface/surface flow, (IV) cadmium uptake by plants, (V) cadmium in grazing animals, (VI) cadmium accumulation in human beings.

The fertiliser-derived Cd entering into soils is transformed to different forms by various reactions, such as adsorption/desorption, precipitation/dissolution, and Cd-ligand complex formation (Loganathan et al., 2012; Figure 2.4-II). These chemical reactions cause soil Cd to be present as a free or complex ion in soil solution, specifically or non-specifically adsorbed onto clay, hydrous oxides and organic matter, as well as insoluble precipitates and soil minerals (Figure 2.4-II). Chemical fractionation techniques have been used to identify soil Cd fractions, which can be categorized as follows: exchangeable Cd, organic bound Cd, hydrated oxides bound Cd, carbonate fraction and residual fraction (Hooda, 2010). Such classification of the soil Cd chemical forms can help assess the plant-available Cd concentration, which is a key factor impacting on the uptake of Cd by plants.

The plant-available Cd concentration mainly depends on the percentage of the soluble Cd fraction in soils. It has been estimated that 55–99% of Cd in soil solution exists in the form of Cd^{2+} (Kabata-Pendias, 1993), which is available for plant uptake. Currently, the extractable Cd concentration by chemical extractants, such as $Ca(NO_3)_2$, $CaCl_2$, NH_4NO_3 , NH_4OAc and EDTA, has been considered as a common and effective indicator of plant-available Cd concentration (Gray et al., 1999a). However, soil Cd concentration extracted by different reagents varies greatly. The buffered, chelate-linked extractants, including EDTA (pH 6.0) and AAAC-EDTA (pH 4.65), can extract considerably greater soil Cd contents than unbuffered neutral acid extractants, such as 0.01 M $CaCl_2$ and 1 M NH_4NO_3 (Gray et al., 1999a). Andrews et al. (1996) used 5 common extractants to estimate plant-available Cd concentration, and recommended 0.01 M $CaCl_2$ as the best extractant to quantify the bioavailable Cd concentration in NZ soils. This chemical reagent also was suggested by Gray et al. (1999a), although it extracted the smallest value of phytoavailable Cd concentration, compared to the other 7 chemical extractants, such as 0.05 M $Ca(NO_3)_2$, 1 M NH_4NO_3 , 0.05 M $CaCl_2$, 1 M NH_4OAc (pH 7.0), 1 M NH_4Cl , 0.04 M EDTA (pH 6.0) and 0.05 M AAAC-EDTA (pH 4.65).

It has been demonstrated that some Cd can be removed from pasture soils by subsurface and surface flow (Figure 2.4-III). For example, Gray et al. (2003b) investigated 6 pasture sites representing 4 NZ Soil Orders (i.e. Pumice, Allophanic, Brown and Pallic Soil), and found that the annual Cd losses in subsurface flow ranged between 0.27 and 0.86 g Cd/ha, equivalent to 5–15% of annual added Cd from single superphosphate (200 kg/ha fertiliser with 280 mg Cd/kg P, on average),

and 0.07–0.23% of total soil Cd that was in the 0–25 cm soil depth. However, irrigation practice enhanced annual Cd losses via leaching up to about 2.3 g Cd/ha in the 0–10 cm soil depth and approximately 7.2 g Cd/ha in the 0–40 cm soil depth, compared to the unirrigated soil in NZ dairy cattle farms, which equated to about 7% and 10% of the total fertiliser-linked Cd from these soil depths, respectively (Salmanzadeh et al., 2017). Compared to Cd downward movement to groundwater, Cd losses by surface flow appeared to be lower at 0.04 g Cd/ha from NZ pasturelands, representing < 1% of new Cd inputs from phosphate fertilisers (Gray et al., 2017).

In addition, herbage also can remove Cd from soil by uptake, which can then enter into grazing animals through herbage ingestion (Figure 2.4-IV and V). As discussed in section 2.1.3, the mean herbage Cd concentration was about 0.13 mg Cd/kg DM in NZ (Reiser et al., 2014). Yi (2019) used this herbage Cd concentration to estimate annual Cd uptake in a ryegrass/clover pasture (annual dry matter yield of 10 t/ha) at about 1.3 g Cd/ha. This aligns with an earlier study conducted in a Manawatū trial site, over 10 years of application of single superphosphate (30 kg P/ha/yr), and reported that Cd uptake by herbage was approximately 1g Cd/ha (Loganathan et al., 1997). Furthermore, Lee et al. (1996) reported that net retention of Cd in the fleece-free body of sheep only represented for 0.05–0.35 % of daily Cd intake. The majority of Cd ingested by grazing animals is returned to pasture soils via the excreted Cd in the faeces (Grace et al., 1993). Therefore, most of this Cd removed by herbage returns via faeces, and then contributes to the soil's Cd stock.

In a recent analysis, based on the annual fertiliser application of 30 kg P/ha/yr with 184 mg Cd/kg P, the average amount of fertiliser-derived Cd in soils is estimated to be 5.5 g Cd/ha/yr in NZ as the cumulative Cd inputs (Abraham, 2020). Assuming leaching and surface runoff is about 1 g Cd/ha/yr (most of ingested herbage Cd is returned in pastoral soils by the grazing animals' faeces), the annual Cd accumulation rate is likely at about 4.5 g Cd/ha/yr from the application of 30 kg P/ha/yr. This value was smaller than the result of Gray et al. (1999b), who estimated that the mean Cd accumulation rate was about 7.8 g Cd/ha/yr in the Winchmore long-term phosphate trial (376 kg SSP/ha/yr) between 1952–1996. When directly comparing the Cd accumulation rate, the difference may be caused by sampling depth, soil types, the amounts of phosphate fertilisers from different rock sources as well as the measurement for soil Cd concentration in soil profile and leachate (Gray et al., 1999b; Salmanzadeh et al., 2017). The average fertiliser Cd concentration had decreased to 184 mg Cd/kg P (Abraham, 2020), which was about 34% lower than that in 2000 (280 mg Cd/ kg P) and

about 59% lower than that before 1990s (450 mg Cd/kg P). This may contribute to the slowdown of Cd accumulation in NZ soils. Moreover, Gray et al. (2020) reported that there were negligible reductions in total and labile soil Cd concentrations (1 M CaCl₂ extractable), and Cd plant uptake in NZ pasture system, even after 22 years without fertiliser Cd inputs. These studies imply that Cd concentrations through phosphate fertilisers as well as its application rate and type choice are the crucial factors determining Cd accumulation in NZ soils, while leaching is the main process governing Cd removal in NZ pasture system.

The minimal Cd reduction via leaching, outwash, or plant uptake is probably connected with the relatively low Cd solubility in NZ soils (Yi, 2019). Pasture soils with relatively high amounts of soil C that are likely to help prevent Cd removal via leaching or plant uptake, as a result of high amounts of complexed or occluded Cd with organic matter through adsorption. Gray et al. (2000) analysed the soil Cd fractionation in 12 different NZ pasture soils, and found that the greatest proportion of Cd in soil was in the organic fraction (35%, on average), whereas the smallest was in the exchangeable fraction (3%, on average). A long-term NZ trial site has demonstrated that that soil C increased by about 35% and 41% from 1994 to 2016 in soil without and with the application of N fertiliser (50 k N/ha), respectively (Gray et al., 2020). The elevated soil C content may increase the proportion of soil Cd adsorption on soil organic matter, rising soil organic bound Cd concentration (Kelliher et al., 2017), and then reduce the plant-available Cd concentration.

2.3.2 Total soil cadmium concentration

Total soil Cd concentration has been referred to as an important factor influencing plant-available Cd concentration (e.g. Loganathan et al., 1997; Gray et al., 1999c). Soil with high total soil Cd concentration may also contain higher bioavailable Cd concentration. For example, when total soil Cd concentration increased from about 0.04 to 0.42 mg Cd/kg between 1952–1996 with the constant phosphate fertiliser application, the EDTA-extractable Cd concentration correspondently increased from about 0.02 to 0.24 mg Cd/kg (Gray et al., 1999b). Gray et al. (1999c) also used total soil Cd concentration to estimate the Cd concentration in the 0.01 M Ca(NO₃)₂ extract, and found that total soil Cd concentration, soil pH and soil organic matter could explain approximately 76% of the variation in the soluble Cd concentration in NZ pasture topsoil (0–7.5 cm).

Due to the impact of the soil Cd concentration on Cd in plant tissues, total soil Cd concentration has been employed to assess Cd uptake by crops (McBride, 2002). This also can be used to statistically predicate Cd uptake by onions and spinach in NZ (Cavanagh et al., 2019). Based on a wide survey of horticultural crops and farms carried out during 2016–2017, total soil Cd concentration and soil pH explained about 38% of the variation of onion Cd concentration. However, Yi et al. (2020) analysed the same database, and discovered that extractable Cd concentration using 0.05 M $\text{Ca}(\text{NO}_3)_2$ was a better predictor than total soil Cd concentration to estimate Cd in crops.

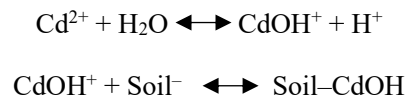
2.3.3 Soil properties

Soil pH

Soil pH can have an impact on Cd adsorption/desorption processes in soils, which is an important determinant of forage Cd concentration in NZ pasture soils. Cavanagh et al. (2016) suggested that the significant difference in chicory Cd concentration at two field sites (one was about 0.18 mg Cd/kg DM; another was about 0.06 mg Cd/kg DM) in Waikato was because of differences in soil pH (data not given in this study). Many previous studies have shown that Cd adsorption in soils increases with an increase in soil pH (e.g. Naidu et al., 1994; Gray et al., 1999c; Ardestani & van Gestel, 2016). Xian & Shokohifard (1989) reported that soil Cd in the exchangeable fraction increased approximately 26%, when soil pH decreased from 7.0 to 4.5. There is a sharp increase of Cd adsorption with a change in soil pH within a range of 4–7, recognised as the ‘sorption edge’ by Loganathan et al. (2012). Within this soil pH range, the proportion of adsorbed Cd increased 2–4 times with unit increase of soil pH, and the extent of Cd adsorption at low soluble Cd concentration was significantly greater than at high soluble Cd concentration (Naidu et al., 1994). As a consequence, the decrease of plant Cd concentration has been reported with increasing soil pH. Singh et al. (1995) reported that Cd concentration in wheat grain and carrot root reduced about 55% and 62%, respectively, with the rise of soil pH from 5.5 to 6.5. This finding was consistent with the result in a NZ pasture study, indicating that Cd concentration in ryegrass and clover reduced by about 50% and 76%, respectively, with the increase of soil pH from 5.5 to 7.0 (Gray et al., 1999a).

The effects of soil pH on Cd adsorption in soils, from a number of studies, are summarised in Table 2.6. Soil surfaces become increasingly negative with increasing soil pH, which increases Cd adsorption on soil surface negative charge (Naidu et al., 1997; Gray et al., 1998). Another effect is

linked to the formation of hydroxyl species of Cd in soil solution (Naidu et al., 1994). The metal hydrolysis model has been suggested by Hodgson et al. (1964) to understand the metal adsorption mechanism. Based on this model, the hydrolysis of Cd ions can cause the formation of hydroxy species, for example, CdOH^+ , which is the dominant Cd species controlling the Cd adsorption on oxide surfaces, as the following equations:



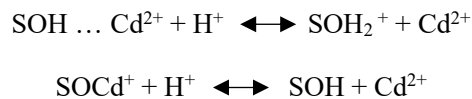
However, Naidu et al. (1994) detected the effects of soil pH on the proportion of Cd^{2+} and CdOH^+ species in soil solution, and found that the significant increase of CdOH^+ ions only occurred at soil pH exceeding 8.

Table 2.6 Previous studies about the effects of soil pH on cadmium adsorption in soils.

Sample site	Soil type	pH range	Results and explanation	Reference
Denmak	Loamy Sand, Sandy Loam	4–7	Soil Cd adsorption capacity increased about 3 times with pH increase of one unit, and Sandy Loam had a greater adsorption capacity than the Loamy Sand at a pH range of 6–7.	Christensen (1984)
New Zealand	Orthic Granular Soil, Orthic Allophanic Soil, Recent Soil	5.5–7.0	Increasing soil pH decreased Cd concentration in clover, lettuce, carrot and ryegrass. When soil pH increased, Cd adsorption onto soil components such as clay, organic matter and soil oxides increased.	Gray et al. (1999a)
Australia New Zealand	Oxisols (Mena and Malanda) Xeralf, Xerert, Andept (Patua), Fragiaqualf (Tokomaru)	3–8	The adsorption of Cd increased with an increase of pH value. The affinity of the hydroxy species (e.g. CdOH ⁺) for adsorption sites increased with the increase of soil pH. Moreover, the increase of soil pH can result in the soil surface becoming more negative.	Naidu et al. (1994)
New Zealand	Orthic gley Soil, Orthic podzol, Humin Organic Soil, Mesic Organic Soil, Yellow Ultic Soil	4.9, 5.1, 5.3, 5.8, 6.1	The increase of soil pH caused a significant increase in Cd adsorption. The net charge on soil colloids become increasingly negative with the increase of soil pH, resulting in increases of Cd being bound to organic matter.	Gray et al. (1998)
Germany	LUFA2.2 Natural Soil	4.5, 5.5, 6.5	Cd concentrations in soil pore water decreased to 5–16% with increasing pH, whereas the percentage of dissolved organic matter bound Cd increased to 94%. At low pH, the higher H ⁺ concentration forces both Cd ²⁺ and Ca ²⁺ into the soil solution, then the higher Ca ²⁺ concentration results in the replacement of Cd ²⁺ with Ca ²⁺ at the sorption sites on the soil surface.	Ardestani & van Gestel (2016)

The third mechanism is associated with Ca competition for adsorption site (Ardestani & van Gestel, 2016). When soil pH is low, the high amounts of H⁺ can replace both Ca²⁺ and Cd²⁺ into the soil solution, then Ca ions (Ca²⁺) can compete with Cd ions (Cd²⁺) for uptake sites on soil surfaces, improving Cd concentration in soil solution (Ardestani & van Gestel, 2016). For example, Ca competition decreased Cd adsorption by 60–80%, and a decrease of soil pH unit reduced Cd adsorption of about 75% (Temminghoff et al., 1995). However, the increase of soil pH from 4.5 to 6.5, Cd adsorption in the pore water increased approximately 16 times higher in the Freundlich sorption constants k_f (Ardestani & van Gestel, 2016).

It is noteworthy that soil pH also can impact on Cd desorption. More than 80% Cd could be released into soil solution with a low soil pH level, especially when soil pH is below 5 (Wang et al., 2009). However, only a small part of Cd (< 1.25%) was desorbed from soil surfaces with high soil pH (Gray et al., 1999c). The desorption of Cd is probably because H⁺ ion can be adsorbed on the mineral surface, and then cause the desorption of Cd, as the following reactions (Wang et al., 2009):



A national survey found that NZ soil pH ranged from 4.1 to 7.4, and pasture soils had on average lower pH, compared to arable soils (Sparling & Schipper, 2002). Therefore, the application of lime to improve NZ soil pH has been recommend to reduce Cd bioavailability, which will be discussed in more detail in section 2.4.2.

Soil organic matter

Soil organic matter (SOM) is another edaphic factor impacting on plant-available Cd concentration in soils (Loganathan et al., 2012). A strong positive relationship between SOM and total soil Cd concentration ($P < 0.0001$, $R^2 > 0.7$) has been demonstrated in two long-term NZ pasture farms (Stafford et al, 2018a). For example, Te Kuiti Soil (Orthic Allophanic Soil) contained the highest organic carbon contents (13%) with total soil Cd concentration at about 1.34 mg Cd /kg, whereas total soil Cd concentration was 0.07 mg Cd/kg in Waimakariri Soil (Recent Soil) with the lowest organic carbon value of 2.4% (Gray et al., 2000). However, this positive relationship between SOM and total soil Cd concentration cannot represent the influence of SOM on bioavailable Cd concentration. Previous studies have shown that the addition of SOM can decrease the plant-

available Cd concentration through improving the fraction of Cd bound to organic matter (see section 2.4.2).

The influence of SOM on Cd bioavailability is linked to its functional surface -OH groups, such as carboxyl (COOH-) and phenolic hydroxyl (-OH), and the presence of soft Lewis bases (e.g. -SH groups with high affinity for Cd²⁺), which can bind Cd through cation exchange or specific adsorption (Loganathan et al., 2012). For example, soils with similar pH values but differing in SOM content (i.e. 2.17 vs. 15.95% organic carbon), the Cd concentration in lettuce was markedly lower in the soil with the higher amount of OM (MacLean, 1976). In addition, SOM also influences other soil chemical properties, such as soil pH, CEC and Eh, which can affect Cd bioavailability. For example, the addition of 320 g/kg OM resulted in about 6-fold and 1.5-fold CEC values increase in the sand soil and the sandy/clay loam soil, respectively (He & Singh, 1993). Such significant increase of soil CEC increased Cd adsorption capacity in these soils, so that Cd concentration in the ryegrass decreased by about half in the sand soil and one-third in the sandy/clay loam soil. Similarly, Kashem & Singh (2001) found that the soluble Cd concentration was lower in the OM treated soils due to the decreased Eh and increased pH in the soil solution.

Other factors: essential metals, LMWOAs and rhizobacteria

The presence of essential metals, such as Fe²⁺, Ca²⁺, Zn²⁺, Cu²⁺ and Mg²⁺, have been known to inhibit Cd uptake by roots, because of the essential metal/non-essential metal (e.g. Cd) competition for ion transport specific channels. This is because the bioavailable Cd can be incorporated into plant tissues via the same transporters that are available for essential metal elements (Curie et al., 2008; Lux et al., 2010). They suggested that Cd (Cd²⁺) can be mediated by ZIP (Zinc-regulated transporter/Iron-regulated transporter-like Protein) or Cd-chelated through YSL (Yellow-Stripe1-Like) proteins at root level. Then, Cd can be loaded into the xylem by Heavy Metal ATPases HMA2 and HMA4 as root-to-shoot transporters (Mendoza-Cózatl et al., 2011). For example, Cd concentrations in maize roots increased 3-fold under Zn deficiency treatment; however, when Zn concentration in the incubation solution increased to 2.5, 100 and 250 µM, the Cd concentration was remarkably decreased to 87%, 38% and 30% of total Cd in the maize roots, respectively (Han et al., 2006).

At the plant root-soil interface, the existence of low molecular weight organic acids (LMWOAs)

released by plant roots, such as acetic, citric, oxalic, fumaric, malic and tartaric, can influence Cd uptake and root-to-shoot translocation. LMWOAs are capable of forming soluble complexes with metal cations, due to their chelating ability, thus promoting metal bioavailability (He et al., 2005). For example, Han et al. (2006) found that acetic and malic acids enhanced the uptake of Cd by maize (*Zea mays*) roots grown in hydroponic. The ability of LMWOAs to improve Cd uptake by plants suggests that LMWOAs can be used to enhance the phytoextraction of Cd (Agnello et al., 2014). A recent study demonstrated that tartaric acid increased Cd mobilisation and uptake in Cd-hyperaccumulator *Sedum alfredii* because of the formation of soluble Cd-tartrate complexes (Tao et al., 2020). In addition, some studies have observed that the effect of LMWOAs on Cd accumulation is related to the Cd translocation from plant roots to shoots (Chen et al., 2003; Ubeynarayana et al., 2021). Ubeynarayana et al. (2021) disclosed that chicory had about 3.4 greater shoot Cd concentration than plantain under the pot conditions with 1.6 mg Cd/kg. They suggested that Chicory had higher acetic acid (not detected for plantain) and lower fumaric acid excretion could explain the high Cd uptake by chicory.

Furthermore, rhizobacteria in soils also has been regarded as an important factor impacting on Cd bioavailability. Rhizobacteria can sequester Cd from soil solution in NZ pasture soils (Robinson et al., 2001). This finding was also supported by the study of Cavanagh et al. (2018), which showed that rhizobacteria had the ability of reducing the Cd toxicity to white clover in NZ pasture systems due to the existence of *Rhizobium leguminosarum* TA1. However, soil pH and the species of rhizobacteria can impact on the capabilities of Cd adsorption by rhizobacteria (Robinson et al., 2001). Moreover, the growth of rhizobia were restricted at high soil Cd concentration (Wakelin et al., 2016). These studies imply that rhizobacteria can mediate Cd bioavailability when total soil Cd concentration is within the tolerable concentration for rhizobacteria, but there is no standard value about this tolerable Cd concentration for rhizobacteria.

2.4 Mitigating the elevated cadmium concentrations in soils

2.4.1 Management of phosphate fertiliser application

Phosphate rocks naturally contain cadmium (Cd) that is a major contaminant in phosphate fertilisers (Table 2.1). However, there is no commercially efficient mechanism to eliminate Cd from these rocks. As mentioned above, in New Zealand (NZ), long-term and continuous application of

phosphate fertilisers to agricultural soils has caused the unintended consequence of increasing total soil Cd concentrations (Syers et al., 1986). Plants uptake of Cd from Cd contaminated soils can pose a risk to grazing animals and human beings through the food chain, and affect high value commercial food production (Roberts et al., 1994). Cadmium concentrations in plants can be minimised by using low Cd-accumulating species or cultivars or applying soil amendments, such as lime and organic matter (Cavanagh et al., 2016; Stafford et al 2016). However, it is of paramount importance to minimise Cd concentration in phosphate fertiliser and manage its application (e.g. the rate and the choice of phosphate fertiliser use), in order to reduce further accumulation of fertiliser-induced Cd in NZ soils.

In NZ, Cd concentrations in phosphate fertilisers have been regularly tested and monitored. In the late 1990s, the NZ fertiliser industry voluntarily limited Cd concentration in phosphate fertilisers to 280 mg Cd/kg P (see section 2.1.1). Since 2001, Cd concentrations in phosphate fertilisers have been monitored under the Fertmark programme (Abraham, 2020), which was established as an independent NZ fertiliser quality assurance programme, in 1996 (<https://fertqual.co.nz>). Since Jan. 2003, Cd concentrations in superphosphate fertilisers have been tested and monitored using samples from two largest fertiliser companies (i.e. Ballance and Ravensdown), which carry out sampling of their fertilisers on a weekly basis (Abraham, 2020).

To minimise the risk of unwanted Cd accumulation in soils and the subsequent transfer to plants and animals, the national Cadmium Management Strategy (CMS) was developed in 2011 (CMG, 2019). The Tiered Fertiliser Management System (TFMS) is an integral part of the CMS (MAF, 2011). This system includes 5 total soil Cd level tiers from Tier 0 (natural background level) to Tier 4 (the maximum threshold). The aim of the TFMS is to ensure that total soil Cd concentration remains below Tier 4 (1.8 mg Cd/kg) for at least the next 100 years. This can be achieved by controlling the choice and rate of phosphate fertiliser application, depending on the total soil Cd concentration in the land use (Table 2.7). When total soil Cd concentration is at or above 1.8 mg Cd/kg, some recommended steps can be taken to ensure no further net accumulation of Cd in this soil. The corresponding steps include withholding phosphate fertiliser, using P fertiliser with extremely low Cd concentration, changing land use and/or ploughing to a soil depth of more than 30 cm (FANZ, 2019).

Table 2.7 Cadmium management and tier boundary trigger values within the TFMS (Sneath, 2015).

Tier	Regulations on phosphate fertiliser application	Soil Cd concentration (mg Cd/kg)
Tier 0	Soil cadmium is within the range of natural background concentrations. No restriction on phosphate fertiliser type or application	< 0.6
Tier 1	Low level restriction on the rate of type and application of phosphate fertiliser. Implementation of appropriate management practices	> 0.6–1.0
Tier 2	Moderate restriction on phosphate fertiliser type and rate of application	> 1.0–1.4
Tier 3	High restriction on phosphate fertiliser type and rates of application	> 1.4–1.8
Tier 4	No further cadmium accumulation allowed unless a detailed site-specific investigation is undertaken to identify risks and pathways for potential harm	> 1.8

Moreover, the latest version of the TFMS has provided a rigorous system to specify the choice and recommended rate of average annual phosphate fertiliser application for soils at each soil Cd tier level (FANZ, 2019). For example, with the total soil Cd level of 1.1 mg Cd/kg, and an agronomic phosphorus application of 30 kg P/ha/yr, the choice of phosphate fertiliser can be any of the nitric acid, phosphoric acid or sulphuric acid derived products, or DAPR/RPR. Production selection also includes a product declared to be equal to these other products, defined as Cd levels less than 100 mg Cd/kg P (nitric acid derived) or 220 mg Cd/kg P (phosphoric acid derived) or 280 mg Cd/kg P (sulphuric acid derived).

The CMS focuses on reducing Cd loading in soils by managing phosphate fertilisers based on total soil Cd levels. Multiple factors influence Cd bioavailability (see section 2.3), therefore, total soil Cd concentration cannot directly indicate the amount of soil Cd that is available for uptake by plants. For example, low Cd concentrations (< 0.05 mg Cd/kg fresh wt.) were observed in potato tubers grown in NZ soil containing a relatively high total soil Cd concentration (1.48 mg Cd/kg, Tier 3) (Al Mamun et al., 2017). Many studies have demonstrated that plant-available Cd fraction in soils is a reasonable indicator impacting Cd uptake by plants (see section 2.2). In addition to managing phosphate fertilisers, other actions have been considered to minimise the bioavailability of Cd instead, such as changing the soil organic matter content or pH through the addition of various organic or inorganic amendments.

2.4.2 Use of soil amendments

Organic amendments

The application of organic amendments (OAs) as *in situ* immobilisers has been widely employed to ameliorate cadmium (Cd) contaminated soils in agricultural systems (Hamid et al., 2020). The overarching role of OAs used in the field does not aim to decrease total soil Cd concentration, but reduce its bioavailability by the immobilisation of Cd in soils. Because of their unique characteristics, especially the presence of functional groups (see section 2.3.3), OAs have been shown to reduce soil Cd availability to plants due to adsorption, complexation and precipitation processes (Mohamed et al., 2010). In addition, OAs like composts also provide essential plant nutrients. This is beneficial for plant growth and, thereby, decreases Cd concentration in plants by increasing their biomass, causing a “dilution by growth” effect (Al Mamun et al., 2017). Owing to the dual function of OAs, extensive studies have explored the impact of various OAs (e.g. biosolids, compost, biochar and lignite) on Cd concentrations in both soils and plants (Table 2.8). The application of OAs, including biochar and green manure contributed to the decrease of extractable Cd concentration (e.g. Mohamed et al., 2010; Park et al., 2011). However, certain types of OAs with high Cd contents may accelerate soil Cd accumulation. For example, poultry manure caused Cd concentrations in 28% of observed food plants were above the permissible limits, because this additive contained Cd with 0.10–0.30 mg Cd/kg and further accumulated in soils (Muhammad et al., 2020). Thus, it is necessary to understand the effect of OAs on Cd concentration, and ensure that the OAs have low Cd contents, before being widely adopted.

Table 2.8 Selected references on the immobilisation of cadmium by organic amendments application.

Organic amendments	Samples	Observation and mechanisms	Reference
Peat, coffee grounds, biosolids, composts	Ten organic soil amendments, NZ	Composts have the highest capacity of binding Cd due to the high CEC, but may enhance Cd mobility by dissolved organic matter complexes.	Welikala et al. (2018)
Composts	Spiked fluvial soil with low Cd, Egypt	Compost can decrease Cd phyto-availability to sorghum (dry soil), but increase barnyard grass Cd concentration (wet soil).	Shaheen et al. (2017)
Charcoal, lignite, sawdust, biosolids, compost, bentonite, zeolite powder	Two different market garden soils, NZ	Composts (2.5% dry w/w) reduced Cd uptake by more than 20% in lettuce, spinach and onions in both soils because of the addition of OM functional groups and Zn concentrations; the lower rate of lignite (1%) was more effective in reducing Cd uptake by vegetables, which induced less decrease in soil pH, compared to the 2.5% lignite treatment.	Al Mamun et al. (2016)
Biochar	Metal-spiked and naturally metal-contaminated soils, Australia	Biochar (1%) decreased NH_4NO_3 extractable Cd, Cd and Pb concentrations in soils, and improved plant biomass. This caused the significant reduction of metal accumulation in Indian mustard.	Park et al. (2011)
Rice straw, green manure, pig manure	Soil with 4.55 Cd mg/kg, China	The concentrations of soluble/exchangeable Cd declined significantly, while the organic-bound Cd concentrations increased by 20.0%, 43.6%, and 77.4% in soils with pig manure (5.2 t/ha), green manure (5.2 t/ha) and rice straw (2.2 t/ha), respectively.	Mohamed et al. (2010)
Animal-waste compost	Fluvisoil with the rotation of vegetables crops, Japan	Cadmium concentrations in spinach was reduced by 34%, 38% and 37% in the amended soils with cattle (7.75 t/ha), swine (6.50 t/ha) and poultry compost (6.10 t/ha), respectively, compared to the chemical fertilizer treatment due to the high carbon, Mn/Fe, and functional groups in these composts.	Sato et al. (2010)

Biosolids have been known as the semi-solid residual material derived from industrial and municipal wastewater. It can provide plant nutrients (e.g. N, P and K), but commonly contain potentially toxic elements (PTEs, e.g. As, Cd, Cu, Pb, Sb and Zn), organic compounds as well as pathogenic micro-organisms (e.g. bacteria, viruses and protozoa), which may pose risks to soil and plant health (Garau et al., 2019). To limit the inherent disadvantages linked to the PTEs, Bolan et al. (2003a) utilised alkaline materials to stabilise PTEs in biosolids, named alkaline-stabilised biosolids, and demonstrated that this adapted biosolids (0–100 g OC/ kg soil) reduced NH₄OAc extractable Cd fraction, as well as Cd uptake by Indian mustard in glasshouse experiment. Another strategy was the co-composting of biosolids with livestock manure or organic wastes (Tandy et al., 2009). In a glasshouse trial, the application of biosolids compost to a Cecil silty loam topsoil significantly decreased Cd concentrations in the corn plants (*Zea mays* L.) (Shuman et al., 2002). Generally, biosolids may be an effective sorbent for Cd with increasing soil pH (Al Mamun et al., 2016; Welikala, et al., 2018).

In addition to these modified biosolids, composts have been broadly used as highly effective and practical materials for the reclamation of heavy metal contaminated soils. Composts are produced from organic wastes by the composting process, which contain abundant organic functional groups, microorganisms, and inorganic components such as Fe and Mn (Huang et al., 2016). Al Mamun et al. (2017) explored the impact of various composts derived from differential source materials on the transfer of Cd from soil to potato in pot trial. They found that tuber Cd concentrations in potatoes were reduced by 71%, 58–66%, 46–63%, 52–53%, and 29–49%, through the application of 5% (w/w) shredded corn stover, pig manure compost, mushroom compost, sawdust-animal waste compost, and municipal compost, respectively, compared to the control treatment. These composts had high concentration of organic carbon (20–47%) and CEC values, which significantly increased the Cd-binding sites in the amended soils.

Biochar (i.e. carbonaceous material) as an environmentally friendly candidate for toxic elements immobilisation in contaminated soils has also been highlighted (Manzano et al., 2020). Biochar produced by slow pyrolysis of biomass at relatively high temperatures may show properties as porous structure and high surface area, alongside the presence of various functional groups such as amino, hydroxyl, carboxyl and carbonyl (Abou Jaoude et al., 2020). These features can, therefore, influence heavy metal mobility by favouring the formation of complexes, increasing adsorption of

cations or promoting metal precipitation depending on soil pH (Fang et al., 2016; Qiao et al., 2018). For example, O'Connor et al. (2018) reviewed 29 studies referring to the use of biochar at polluted field trials in 8 countries, and reported that biochar can potentially be applied to reduce Cd bioavailability, particularly for rice crops grown in Cd contaminated soils in humid subtropical China. Moreover, biochar could also improve plant growth by adding plant-available nutrients. The application of 1% w/w of chicken manure-derived biochar significantly improved plant dry biomass by 353 and 572% for shoot and root of Indian mustard, respectively, because of the increased availability of nutrients, such as P and K (Park et al., 2011), suggesting that biochar application can help decrease the use of mineral fertiliser. This study also found that biochar when applied at a high rate, equivalent to about 15 t/ha (0–15 cm soil depth), reduced Cd accumulation by Indian mustard (*Brassica juncea*).

In addition, the use of lignite has also been considered as an effective strategy to remediate metal polluted soils because of its carboxylic and hydroxyl-phenolic groups (Doskočil & Pekař, 2012). Simmler et al. (2013) designed a pot experiment using NZ pasture soils, and reported that the independent application of lignite (1 wt %) decreased soil $\text{Ca}(\text{NO}_3)_2$ -extractable Cd concentrations, as well as Cd concentration in ryegrass by 30%, compared to the control pot, due to the increase of bound Cd to sulphur and carboxylic groups in lignite. In particular, they suggested that the application of 1 wt % (dry matter) lignite has the best effectiveness in pastures, which is equivalent to applying about 7.5 t/ha (0–7.5 cm soil depth). These findings are similar to results reported by Pusz (2007), who found that when the use of brow coal increased from 0 to 105 t/ha, the grass Cd concentration (I swath) decreased from 2.69 to 0.95 mg Cd/kg for the soil from I zone of Copper-Smelter Legnica (0–30 cm soil depth).

The above-mentioned studies have shown that OAs have the ability to reduce soil Cd availability and plant Cd concentration, when applied at high rates (i.e. 1–5 % of soil weight). However, their effectiveness in reducing soil and plant Cd levels depends on a variety of factors, such as their quality and properties (Huang et al., 2016) as well as field-specific features (e.g. time period, climate, mixing soil depth and dosage rate) (O'Connor et al., 2018). Some methods have been suggested to improve the ability of OAs to reduce soil Cd concentration that is available for plant uptake. For example, the application of OAs in combination with inorganic soil amendments has been recommended (Huang et al., 2016). In addition, ur Rehman et al. (2017) observed the

lowest Cd concentration in straw with the application of limestone plus biochar, compared to other amendments.

Inorganic amendments

Different *in situ* inorganic amendments have been manifested in the immobilisation of Cd in soils. These additives include liming materials (e.g. limestone- CaCO_3 , slaked lime- Ca(OH)_2 , dolomite- $\text{CaMg(CO}_3)_2$, quicklime- CaO , oyster shells and eggshells), phosphate compounds (e.g. hydroxyapatite- $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ and mono-ammonium phosphate- $\text{NH}_4\text{H}_2\text{PO}_4$) as well as gypsum- CaSO_4 , which can reduce Cd mobility in soils by adsorption, complexation and precipitation (Hamid et al., 2019). Different inorganic amendments have been evaluated on their effects on the bioavailable Cd concentration in soils and its uptake by plants with different application rates (Table 2.9). The single application of liming materials, can reduce Cd bioavailability, resulting in the reduce of Cd concentration in vegetables (e.g. Maier et al., 2002; Zaniewicz-Bajkowska et al., 2007; Pandit et al., 2012) and crops (e.g. Lim et al., 2013; Wang et al., 2017; Qayyum et al., 2017). Moreover, liming materials in combination with other soil amendments have also been explored, such as limestone plus peat (Chen et al., 2016), slaked lime plus organic matter (Kumarpandit et al., 2017) as well as oyster shells plus ureolytic bacteria (Peng et al., 2020).

Most soils are naturally acidic in NZ, and become further acidified because of the long-term impact of legume-based pastures on soil pH (Morton, 2020). Liming has been routinely added to pasture soils to neutralise the impacts of acidification (Sime & Hill, 2001). In general, liming is needed to adjust soil pH when it is below 5.4 on hill soils in NZ (Gray & Morton, 2019). Morton (2020) also has suggested that liming is vital to maintain the optimum soil pH with 5.8–6.1 for mineral soils and 5.0 for organic soils in the 0–7.5 cm soil depth in mown pasture system. This ubiquitous liming practice can benefit pasture systems by improving soil fertility, increasing clover nodulation, mitigating soil molybdenum (Mo) deficiency as well as remediating soil toxicities (e.g. aluminum (Al) and toxic metals) in NZ (Sime & Hill, 2001; Morton, 2020). Additionally, lime materials have been demonstrated to reduce the Cd solubility in NZ soils (Bolan et al., 2003b; Al Mamun et al., 2017).

Table 2.9. Selected references on the immobilisation of cadmium by differential lime application.

Inorganic amendments	Application Rate	Observation	Reference
CaO	2.0 t/ha	Reduced Cd concentration in soil and vegetables	Zaniewicz-Bajkowska et al. (2007)
CaMg(CO ₃) ₂	0.5–3.8 t/ha	Reduced the seed Cd concentrations in soybeans	Miura et al. (2016)
CaCO ₃	0–20 t/ha	Reduced Cd accumulation in potato tubers	Maier et al. (2002)
Ca(OH) ₂	0–8.8 t/ha	Reduced Cd uptake of radish	Hong et al. (2007)
Eggshells	5% (w/w)	Reduced Cd mobility in slightly alkaline soil	Ashrafi et al. (2015)
Eggshells and Oyster shells	1% and 5% (w/w)	Decreased exchangeable Cd fraction in soil, and Cd uptake by maize shoots	Lim et al. (2013)
Thermal-treated oyster shells	4% (w/w)	Reduced NH ₄ NO ₃ -extractable Cd and Cd uptake by maize shoots	Wang et al. (2017)
Hydroxyapatite (apatite II TM , fish bones)		Removed Cd in slightly acid to neutral waters	Oliva et al. (2011)
Mono-ammonium phosphate (MAP) gypsum and elemental sulfur	0.2%, 0.4% and 0.8% (w/w)	MAP and gypsum both reduced Cd uptake in wheat, but elemental sulfur increased Cd uptake in plants	Qayyum et al. (2017)
Flue gas desulphurization gypsum (FGD) and hydroxyapatite (FGD-HAP)	1% (w/w)	Both reduced bioavailable Cd concentration in spiked soil	Yan et al. (2020)

Various reasons have been given for the decrease of Cd bioavailability to plants by liming. The primary reason is linked to the pH-induced increase in negative charge on soil colloids, and the resultant decrease in Cd phyto-availability (Sime & Hill, 2001; Bolan et al., 2003b). Limestone increases soil pH due to the release of hydroxyl ion after hydrolysis of CaCO_3 (Hong et al., 2007). Such increase of soil pH can increase the net negative charge because of the dissociation of H^+ from acidic functional groups in organics and clay minerals (Curtin et al., 1996), which can induce the increase of Cd adsorption (see section 2.3.3). An earlier study observed that the maximum addition of limestone rate of 10% (w/w) increased soil pH by 1.52 and 0.56 pH units in the Pukekohe and Levin Soil, respectively (Valentinuzzi et al., 2015). Such amount of lime applied (i.e. 150 t/ha, 0–15 cm soil depth) to achieve a target soil pH value was excessively high, indicating the high cost of lime. However, another study observed that the application rate of 0.6% and 1.3% (w/w) limestone increased soil pH by 1.0 and 1.2 pH units, respectively, compared to the control treatment, which decreased the uptake of Cd by potato (Al Mamum et al., 2017). Similarly, Soybeans (*Glycine max* (L.) Merr.) grown in the dolomite added soils at the rate of 1.8 t/ha for the target pH of 6.2, had lower Cd concentrations (0.48 mg Cd/ kg DW) in seeds, as compared to those grown in the absence of dolomite soil (0.92 mg Cd/ kg DW) (Miura et al., 2016).

Liming also adds Ca^{2+} to soils, which can compete with Cd^{2+} for ion transport specific channels (see section 2.3.3). This competition for exchange sites at the root surface probably inhibits Cd uptake by roots (Wang et al., 2017). For example, liming (limestone) at 1 g/kg and 2 g/kg rate resulted in the decrease of mean Cd concentration of spinach root by about 12.9% and 27.2%, respectively, compare to the un-limed treatment (Pandit et al. 2012). However, there is widely divergent view of the effects of lime-induced Ca^{2+} on Cd stabilisation in soils. Bolan et al. (2003b) reported that Ca^{2+} added through liming can increase the Cd^{2+} concentration in soil solution because of the competition for adsorption sites. They assessed the impacts of $\text{Ca}(\text{OH})_2$ and potassium hydroxide (KOH) on Cd adsorption in NZ soils, namely Egmont and Tokomaru Soil. The aim of KOH used in this study was to examine the influences of pH and Ca^{2+} concentration on the adsorption of Cd^{2+} . They emphasized that both alkaline materials increased the adsorption of Cd^{2+} , but KOH treatment had higher Cd^{2+} adsorption than the $\text{Ca}(\text{OH})_2$ treatment in both soils, due to the competition between Ca^{2+} and Cd^{2+} for adsorption. What is noteworthy is that they pointed out that CaCO_3 as the most common lime material caused less competition from Ca^{2+} for Cd^{2+} adsorption

because of its lower dissolution. Therefore, the effectiveness of liming materials in Cd immobilisation depends on the change of pH and Ca^{2+} concentration in soil solution.

As expected, phosphate compounds and gypsum also can immobilise Cd in soils, resulting in the decrease of Cd uptake by plants (Table 2.9). The possible mechanisms for the Cd immobilisation by phosphate compounds are related to the Cd adsorption by P compounds, rhizosphere modification through acidification, and the precipitation of Cd with P as Cd phosphates, such as $\text{Cd}_5(\text{PO}_4)_3\text{OH}(\text{s})$ (Oliva et al., 2011; Seshadri et al., 2016). However, the addition of phosphate compounds should be done with care, especially as rock phosphate is the main source of Cd input into agricultural soils in NZ and Australia (see section 2.1.1). The effectiveness of phosphate compounds depends on the phosphate fertilisers types and rates, soil properties, and agricultural practices (Seshadri et al., 2016).

2.4.3 Soil tillage practices

Influence of tillage practices on soil properties and cadmium concentration

Tillage refers to different agricultural activities to manipulate, modify, or ameliorate soil conditions using tools, such as a moldboard plow, chisel plow, disk plow and rotary cultivator (Carter & McKyes, 2005). Traditionally, farmers used conventional tillage practices to loosen soils and control weeds for the improvement of crop productivity. Conventional tillage has been defined as the tillage practices reversing and stirring a deep layer of soil with a moldboard plow or harrows, resulting in the upper soil buried to an average soil depth of about 20 cm (Morris et al., 2010). Due to some limitations with conventional tillage, such as soil erosion or degradation, alongside high agronomic cost, innovations in tillage practices lead to the development of conservation tillage.

The conservation tillage (e.g. reduced tillage, minimum tillage and shallow tillage) is “any tillage sequence, the object of which is to minimise or reduce loss of soil and water; operationally, a tillage or tillage and planting combination that leaves 30% or greater cover of crop residue on the surface” (Carter, 2005). The main characteristics of selected tillage practices are shown in Table 2.10. The choices of these tillage practices depend on the soil type, crop rotation and agronomic cost, as well as weather conditions. For example, high clay or sand content, or poor permeability, or cool soils may need intensive and deep tillage, while less compacted soils may require less intensive tillage (Carter & McKyes, 2005).

Table 2.10 The main characteristics of common tillage systems (Carter & McKeyes, 2005; Carter, 2005).

Tillage types	Definition
Conventional tillage	Combined primary ^a and secondary ^b tillage operations normally performed in preparing a seedbed for a given crop and area.
Deep tillage	Primary tillage that plows soil by moldboard plow, deep disk plow, or heavy chisel to a greater soil depth (>10–20 cm soil depth).
Inversion tillage	Primary tillage that 'inverts' soil by moldboard plow to a deeper soil depth (> 15–25 cm soil depth).
Minimum tillage	The minimum operation of primary and secondary tillage to meet crop production requirements under given soil and climatic conditions.
Reduced tillage	Reduction in total number of primary and secondary tillage operations usually used in conventional tillage, to prepare a soil for crop establishment.
Shallow tillage	Primary tillage confined to shallow soil depth (< 15 cm soil depth) with the absence of soil inversion tillage.
No tillage	Soil undisturbed with no primary or secondary tillage. Crop seeded/planted directly into the soil.

^aPrimary tillage is the initial major soil manipulation usually employed to loosen soil and bury or incorporate crop residue.

^bSecondary tillage is any sequence of tillage operations that follow primary tillage generally used to prepare the soil for seeding/planting operations.

Over recent decades, conservation tillage has received extensive attention on its economic and environmental benefits to facilitate its wider adoption. Many studies have demonstrated the benefits of conservation tillage on increasing soil quality (Aziz et al., 2013), reducing soil erosion (Klik & Rosner, 2020), increasing enzyme or earthworm activities (House & Parmelee, 1985; Hamido & Kpombleko-A, 2009; Briones & Schmidt, 2017), reducing nitrogen losses (Zhang et al., 2020), increasing topsoil organic carbon content (Rahmati et al., 2020), and reducing fuel and labour costs (Cooper et al., 2020). However, these advantages that relate to the reduction of tillage intensity are not universal. For example, a five-year on-farm research proved that conservation tillage (direct drill and shallow non-inversion) did not significantly improve soil fertility and reduce nutrient leaching losses into field catchment in the lowland intensive arable area, UK (Cooper et al., 2020). In addition, the absence of deep plough may result in the increase in compaction of the topsoil, which can restrict plant root development and rainfall infiltration (Cooper et al., 2020).

The accumulation and distribution of Cd in agricultural soils can be altered by tillage practices (Oliver et al., 1993; Chen et al., 2009; Minari et al., 2017). A modified model demonstrated that total soil Cd concentrations of the tillage layer (0–20 cm soil depth) increased approximately 82% from

the initial concentration 0.22 to 0.40 mg Cd/kg over 100-years because of continuous cultivation (Chen et al., 2009). Oliver et al. (1993) found that there were higher Cd concentrations in wheat under zero tillage, and suggested that the restriction of root growth (high soil strength) could increase the Cd uptake by plants from the surface soil horizons where the highest soil Cd concentrations were located. However, Cd concentrations in durum grain were lower in the reduced tillage due to the reduced release of Cd from residue fraction, compared to the conventional tillage (Gao et al., 2010). The inconsistent influences of tillage practices on crop Cd concentrations have not been well understood, but should be linked to a wide range of factors such as soil type, plant species, fertiliser type, application duration, weather condition as well as the tillage techniques. Therefore, field investigations in local agricultural environment are essential to understand the influences of tillage practices on the distributions of Cd and its uptake by plants.

Full inversion tillage at pasture renewal and its potential influence on cadmium in pasture soils

Pasture performance tends to decline over time caused by a myriad of factors in NZ, including overgrazing, moisture stress, soil treading damage, weeds incursion or pest infestations (see section 1.1). The practicable solution is periodically pasture renewal, by removing the existing pastures and re-sowing forage species, to remain farm profitability (McNally et al., 2017; Hanly et al., 2017). For example, NZ dairy farms are usually renewed every 10 years (Trolove et al., 2019). Tozer et al. (2015) examined the effect of pasture renewal on dairy pasture performance in Waikato and Bay of Plenty from 2009–2014, and found that renewed pastures produced an addition of 1.5, 1.8 and 1.9 t DM/ha in the first, second and third year of monitoring period, respectively, compared to unrenewed pastures. They suggested that most farmers would make a profit through pasture renewal. In NZ, the annual pasture renewal rate has been estimated 3–7% and 8–12% for sheep/beef and dairy pastures, respectively (Thomas et al., 2014). However, farmers may have different aims which can influence the level of pasture renewal, including crop requirement, historical, an event response, development and cost/benefit (Kerr et al., 2015). In addition, they also encounter with many choices during pasture renewal, such as pasture renewal sequences (e.g. grass-crop-grass or grass-grass), forage species and soil tillage (Trolove et al., 2019).

Inversion tillage can be used at the time of renovating inferior pastures as a consequence of the intrusion of weeds or fungal diseases (Reheul et al., 2007). Knowledge of its influences on the

pastoral productivity and environment is crucial to evaluate its efficiency. In NZ, Trolove et al. (2019) assessed the impact of tillage during pasture renewal on nitrate leaching losses in Flaxton Deep Silt Loam (a field trial in Lincoln), and no difference was found between conventional tillage (approximately 20 cm soil depth) and no-till. Similarly, some field-based trials have been established to investigate how soil tillage (e.g. full inversion tillage, shallow tillage and no tillage) at pasture renewal influence SOC sequestration (Calvelo Pereira et al., 2019; McNally et al., 2019), agronomic cost (Calvelo Pereira et al., 2020; Beare et al., 2020), and nitrous oxide emissions (McNally et al., 2019). They suggest that the use of one-off full inversion tillage (FIT, approximately 25–30 cm soil depth) has potential agronomic and environmental benefits. However, limited research on the impacts of tillage at pasture renewal on profile distribution of Cd, and its uptake by plants has been studied.

Full inversion tillage may alter Cd vertical stratification in the soil profile. Total soil Cd concentration shows a distinct stratification within soil profile in the long-term pastures (Zanders et al., 1999; Stafford et al., 2018b), which is similar to the SOC stratification in NZ pasture soils. In Manawatū and Taranaki/Wanganui region, recent studies demonstrated that FIT redistributed the SOC in the soil profile, whereby C-rich topsoil (0–5 cm soil depth) was buried into the subsoil, and the C-depleted subsoil was brought into the surface, resulting in the decrease of SOC in the new topsoil (Calvelo Pereira et al., 2019, 2020), suggesting that FIT modified soil distribution with soil depth. Therefore, it is hypothesised that FIT may also impact on the profile Cd distribution in these pasture soils, causing the decrease of total soil Cd concentrations in the surface layer.

A one-off FIT using a modified mouldboard plow transfers soil from top to deeper below 20 cm soil depth. Such soil transference changes soil properties (e.g. soil pH and soil organic matter), which are determining factors in plant-available Cd concentration. For example, the effect of FIT (below 50 cm soil depth) on ecological restoration in UK was examined by Milligan et al. (2017), who found that FIT significantly increased soil pH but decreased total SOC in the surface layer (0–12 cm soil depth) in an unused agricultural land, compared to the no tillage treatment. In NZ, the first 15 years field results from the Chertsey Establishment Trial established in 2003 by the Foundation for Arable Research in Canterbury, found that soil pH was lower with inversion tillage for dryland plots with the value of 5.6 in the soil depth of 0–7.5 cm, compared to the minimum tillage with the value of 6.0, in Apr. 2018 following lime application in Feb. 2018 (Brooker et al.,

2020). Such changes of soil chemical properties may impact on bioavailable Cd concentrations, then subsequently impact on its uptake by plants. Thus, field investigation on the influences of FIT on soil chemical properties is indispensable to evaluate its resultant effects on plant-available Cd.

Chapter 3: Materials and Methods

On-going research in the North Island of New Zealand (NZ) is studying the impact of FIT-renewal on dry matter production, N leaching, as well as soil C storage (Calvelo Pereira et al., 2019, 2020). As part of this research, archived soil and plant samples taken from two field trials, during the period of 2016–2019, were used for cadmium (Cd) determination. The following sections describe key information on field trials establishment, sample collection and Cd analysis. A more detailed description of both field trials can be found in Calvelo Pereira et al. (2019, 2020).

3.1 Experimental design of field trials

3.1.1 Trial 1: Pallie Soil

Trial 1 site was located on a dairy farm (Massey University's Dairy 4 Farm) on a Pallie Soil, near Palmerston North, Manawatū Region ($40^{\circ} 23' 46.79''$ S; $175^{\circ} 36' 35.77''$ E; Figure 3.1a and b). Prior to the establishment of this field trial, the farm was under a mixed pasture of predominantly perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.), which was grazed by dairy cows. The initial fertility status for this soil in the 0–15 cm soil depth, including soil pH, Olsen P, SO₄, K, Ca, Mg, Na and CEC, have been reported by Calvelo Pereira et al. (2019).

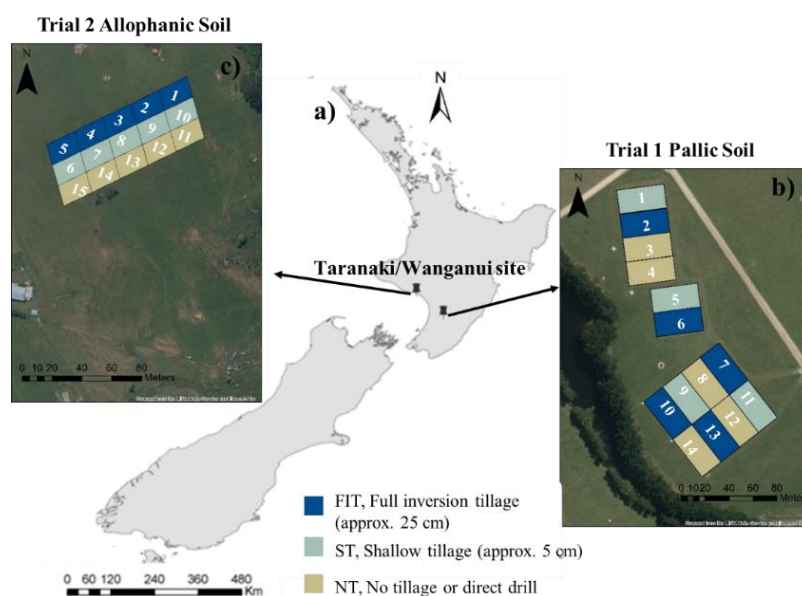


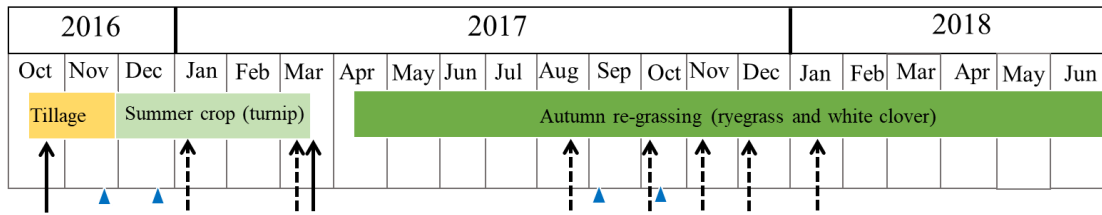
Figure 3.1 Location of two field trial sites in the North Island of New Zealand (a) and the experimental design of plots at the (b) Trial 1 and (c) Trial 2 site. The boxes with different colour represent different tillage treatments following pasture renewal established at both trial sites. The number in the boxes indicate how many plots were designed at each trial site.

Trial 1 experimental design comprised three contrasting tillage treatments applied in spring to establish a summer crop (leafy turnip) followed by re-sowing new pasture by direct drilling into the turnip stubble in autumn. These three tillage methods were: (1) ploughing to a soil depth of approximately 25 cm by a moldboard plow fitted with a disc and skimmer (FIT); (2) shallow rotary hoeing-shallow tillage of approximately 5 cm soil depth (ST); and (3) direct drill or no tillage (NT). There were 5 replicates for each NT and FIT treatment, but 4 replicates for ST treatment (a total of 14 plots; Figure 3.1b), from which all plots (approximately 0.09 ha per plot) were established by means of the completely randomized design.

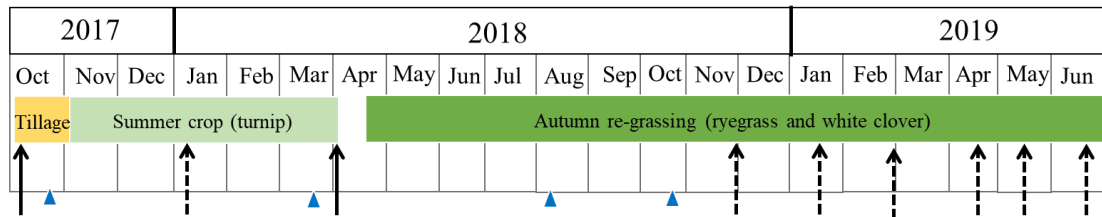
Trial 1 development and monitoring between 2016–2018 are shown in Figure 3.2a. On 11 Oct. 2016, all plots were sprayed with glyphosate to destroy the original sward, and then cultivated following the tillage treatments (i.e. FIT, ST and NT) until the 23 Nov. 2016. The delay of tillage practices from 11 Oct. to 23 Nov. was due to the wet conditions during the late spring (Calvelo Pereira et al., 2019). Basal fertilisers were applied on late Nov. 2016, before sowing a leafy turnip (*Brassica campestris spp rapa*, var Hunter) as a summer crop. During the summer crop growth phase, additional basal N fertiliser (148 kg N/ha) was used, and turnip crop were grazed by dairy cows as part of farm's grazing rotation for all treatments at the end of Jan. 2017 and on 14 Mar. 2017 (Calvelo Pereira et al., 2019). Soil Olsen P and exchangeable K concentrations following FIT were lower than the other treatments, so it received as much as two times higher P (60 kg P/ha) and K (120 kg K/ha) fertiliser. The P fertiliser used in this study was a food grade type named Kynofos 21, thereby, no additional Cd was added to the newly cultivated pasture soils (Calvelo Pereira et al., 2019).

On 16 Mar. 2017, all plots were sprayed again using glyphosate to prepare the seed bed for the new pasture establishment. And then (on 10 Apr. 2017), a mix of perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) as autumn re-grassing was sown by direct drilling into the *Brassica* stubble. Four months later (Aug. 2017), all plots were grazed by dairy cows as part of this farm's grazing rotation. Basal fertilisers were used during the new pasture phase in Sep. and Oct. 2018, respectively (Figure 3.2a).

(a) Trial 1 Pallic Soil



(b) Trial 2 Allophanic Soil



—→ Soil sampling - - - -> Herbage sampling ▲ Fertiliser application

Figure 3.2 Calendar summarising the process of spring pasture renewal and main events for (a) the Trial 1 site between 2016–2018 and (b) the Trial 2 site between 2017–2019.

3.1.2 Trial 2: Allophanic Soil

Trial 2 site was located in a commercial sheep and beef farm on an Allophanic Soil, near Maxell in Taranaki/Wanganui Region (39° 47' 46.50" S; 174° 54' 1.62" E; Figure 3.1a and c). Before the start of spring pasture renewal trial, this farm was grazed by sheep and beef under a mixed pasture of predominantly perennial ryegrass and white clover. The layout of this trial was blocked to accommodate slope. The same tillage treatments (i.e. FIT, ST and NT) were assigned along the slope gradient, and each treatment was replicated 5 times (a total of 15 plots; approx. 0.03 ha for each plot; Figure 3.1c). Following similar activities as described for Trial 1 (see section 3.1.1), the establishment and development of this trial from 2017 to 2019 are shown in Figure 3.2b. All plots were sprayed in early Oct. 2017, and then cultivated following the same tillage practices mentioned above to sow leafy turnip. After about 5 months of crop growth, in early Apr. 2018, all plots were grazed as part of this farm’s grazing rotation (Figure 3.2b). On 17 Apr. 2018, a mix of perennial ryegrass and white clover was sown by direct drill. During the pasture phase, grass growth was monitored using a rising plate meter, and the new pasture was grazed by sheep and beef following the farm’s grazing rotation. Apart from the application of basal fertilisers during the summer crop growth, lime was applied (3209 kg/ha) on 19 Mar. 2018 (Figure 3.2b).

3.2 Sample collection and analysis

3.2.1 Soil sampling and analysis

Collection and preparation of soil samples

In order to examine the influence of spring FIT-renewal on soil organic matter and Cd concentration at both trials, soil cores were collected twice from each plot for all tillage treatments (i.e. FIT, ST and NT): (1) prior to the establishment of tillage treatments (baseline or pre-tillage: Trial 1 on 19 Oct. 2016 and Trial 2 on 4 Oct. 2017; Figure 3.2); and (2) following grazing of the leafy turnip (post-tillage: Trial 1 on 17 Mar. 2017 and Trial 2 on 3 Apr. 2018; Figure 3.2).

Soil cores were collected to a soil depth of 40 cm at each plot (3 soil cores per plot) using a 43.5 mm diameter percussion corer. Each soil sample core was separated into 0–5, 5–10, 10–15, 15–20, 20–25, 25–30 and 30–40 cm soil depths. All soil samples (pre- and post-tillage) were air-dried, and then ground (< 2 mm) and stored for further analysis. Prior to the current study, subsamples were used to analyse soil C, N as well as soil bulk density, which were used to study the short-term changes in C and N storage caused by spring FIT-renewal (Calvelo Pereira et al., 2019, 2020). These archived samples were used in this study for the analysis of total soil Cd and extractable Cd concentration, as well as soil pH.

Representative composite samples were obtained from the archived soil samples for each individual depth (0–5, 5–10, 10–15, 15–20, 20–25, 25–30 and 30–40 cm soil depths) at both stages (pre- and post-tillage). Briefly, each pre-tillage soil sample was a composite of 3 cores, which was made up of one soil core selected randomly from each of the three treatment plots per block for each soil depth. Each post-tillage soil sample was a composite of 3 cores from each individual treatment plot for each soil depth. Generally, 4 replicates of composite samples of each treatment at Manawatū site and 5 replicate samples at Taranaki/Wanganui site were prepared for the analysis of total soil Cd concentration (0–40 cm soil depth) and extractable Cd concentration and soil pH (0–15 cm soil depth).

Analysis of soils: total soil cadmium, extractable cadmium and soil pH

Total soil Cd concentration was determined for the composite samples for each soil depth previously mentioned. A wet digestion method was used for the total soil Cd analysis. Soil samples

were digested by adding 10 mL of 75% HNO₃ for every 1 g of sample in glass tubes, and diluted up to 25 mL with deionised water. These glass tubes were placed in a fume hood to predigest overnight, before being digested for 2 hours at 120°C. In order to digest completely, the temperature was gradually increased from 75°C to 120°C by increasing 15°C at 15 minutes interval. In addition, glass funnels were inserted into the digestion tubes during the whole digestion process. When the digestion was completed, the funnels were removed and the temperature was increased to 145°C for approximately 1 hour to evaporate the extra nitric acid in the glass tubes until approximately 1 mL of solution remained. During the heating process, aluminium foil was used to wrap the tubes in order to trap the heat. The remaining samples were left to cool down, and deionised water were then added up to 25 mL. Samples were mixed using a vortex mixer for the homogenization of samples and then filtered using Whatman 42 filter paper. Samples were analysed using GFAAS (Perkin Elmer 900z, Germany), but some samples were diluted with 2% nitric acid before analysis. Two blanks (10 mL of 75% HNO₃) were included within every batch of 60 samples for quality control.

Extractable Cd was determined for composite samples at the 0–5, 5–10, and 10–15 cm soil depths, which represent the majority of the plant root zone. The 0.05 M Ca(NO₃)₂ extractant was chosen to measure extractable Cd concentration (McLaren et al., 2005). About 5 g of sub-samples was weighed into 50 mL centrifuge tubes, and then 30 mL 0.05 M Ca(NO₃)₂ were added. Following this, all samples were placed in an end-over-end shaker for 2 hours, before being centrifuged at 1,068 G force for 10 minutes. And then, samples were filtered through Whatman 42 filter paper and stored at < 4 °C, before being analysed using GFAAS (Perkin Elmer 900z, Germany).

Soil pH was determined for the same depths selected for extractable Cd analysis. The soil pH value was measured in a 1:2.5 soil/water suspension with a glass electrode pH meter. A soil weight of 5 g was weighed into a pH beaker, and then 12.5 mL of deionised water was added. Samples were stirred thoroughly using a glass rod, before being left them to sit overnight. Samples were then re-stirred, and analysed using a pH meter (Acumen 910, Fisher Scientific Ltd, Pittsburgh, PA, USA).

3.2.2 Plant sampling and cadmium determination

For both summer turnip crop and new pasture, plants were collected from both Trial 1 and Trial 2 sites (Figure 3.2). Turnip yield was monitored by using quadrats (0.6 × 1.2 m; one quadrat per plot) at selected dates. Fresh turnip crops for each quadrat were cut and weighted, and finally converted

to dry matter (DM) using subsamples that were washed to remove soil, before being oven-dried at 70 °C for about two days. During the pasture phase, herbage yield was monitored using riding plate-meter at selected dates (Figure 3.2). These yield results are reported by Calvelo Pereira et al. (2020) to compare the agronomic benefits of all tillage treatments (i.e. FIT, ST and NT). Samples were oven-dried (65°C) and ground to < 1 mm, and then underwent Cd determination (for methods see <https://www.hill-laboratories.com>).

3.3 Data and statistical analysis

The mean total soil Cd and extractable Cd concentrations were compared for each soil depth among tillage treatments (i.e. FIT, ST and NT) with a one-way ANOVA test using SPSS 16.0 software package at the 0.05 level of significance. Correlations between plant Cd concentration and measured soil/plant variables, including total soil Cd concentration, extractable Cd, soil pH, soil total C and N concentration, and plant yield, were analysed using Spearman correlation coefficients.

Chapter 4: Results

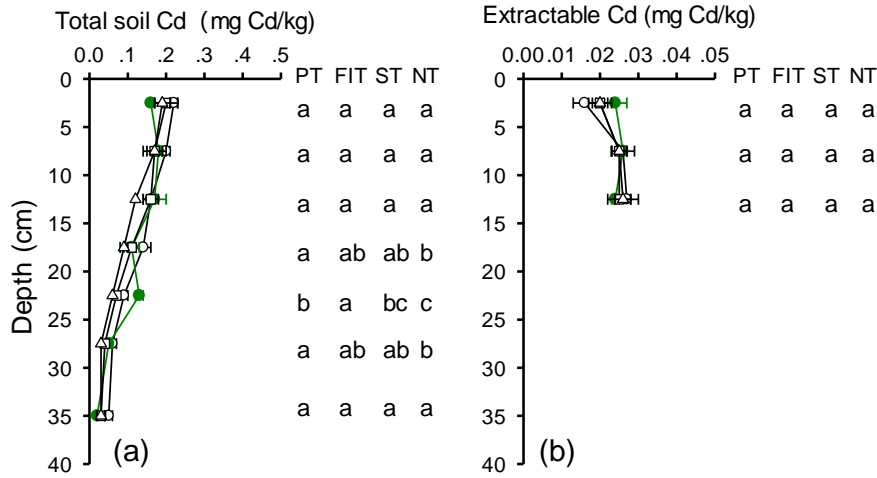
4.1 Changes in soil cadmium approximately half year after pasture renewal

4.1.1 Total soil cadmium and extractable cadmium concentration and stratification

Trial 1: Pallic Soil

At the Trial 1 site, prior to the pasture renewal establishment (pre-tillage (PT) sampling in Oct. 2016), the vertical distribution of total soil Cd concentrations showed a decreasing trend with soil depth in the 0–40 cm soil depth (Figure 4.1a). The 0–5 cm soil depth on average as total soil Cd concentration (0.21 mg Cd/kg) was more than about 4 times higher than that of the 30–40 cm soil depth (0.05 mg Cd/kg). Approximately 4 months after tillage cultivation was conducted at this trial site (post-tillage sampling in Mar. 2017), all tillage treatments (i.e. full inversion tillage-FIT, shallow tillage-ST and no tillage-NT) did not significantly decrease ($P > 0.05$) total soil Cd concentration in the 0–5 cm soil depth (Figure 4.1a). However, the FIT treatment had the lowest total soil Cd concentration of 0.16 mg Cd/kg on average in this soil depth, which was about 24%, 20% and 16% lower than that of the PT, ST (average: 0.20 mg Cd/kg) and NT (average: 0.19 mg Cd/kg) treatment, respectively (Figure 4.1a). In contrast, the FIT treatment had the highest total soil Cd concentration in the 20–25 cm soil depth (average: 0.13 mg Cd/kg), being significantly different ($P < 0.05$) from the other two tillage treatments and the PT values (Figure 4.1a). Overall, the FIT treatment resulted in a higher total soil Cd concentration in the newly-formed subsoil, compared to the ST and NT treatments, which reflects a greater degree of topsoil burial compared to the other two tillage treatments.

**Trial 1
Pallic Soil**



**Trial 2
Allophanic Soil**

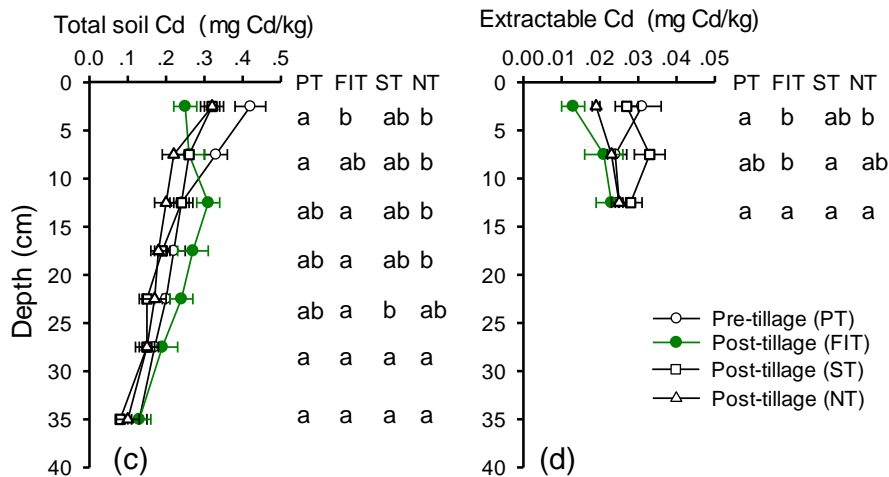


Figure 4.1 Vertical distribution of total soil cadmium and extractable cadmium concentrations (mg Cd/kg) with soil depth, at (a-b) the Trial 1 and (c-d) Trial 2 site. Data were given as means \pm S.E.M. (standard error of the mean). Results (*P*-values) from one-way ANOVA comparing the pre-tillage (PT) and the contrasting pasture renewal tillage methods (i.e. FIT, ST and NT) in each soil depth were present. The significance of differences between each treatment and each soil depth were marked by different lowercase letters indicating statistical significance at $P < 0.05$ per protected the LSD (least significant difference) test.

Extractable Cd concentration was also assessed in the 0–15 cm soil depth, which is the main part of the root-zone in pasture soils (Figure 4.1b). The PT extractable Cd concentration with soil depth was the lowest in the 0–5 cm soil depth (average: 0.016 mg Cd/kg), which was opposite to its initial profile distribution of total soil Cd concentration in this soil depth. After tillage cultivation, there was no significant difference ($P > 0.05$) in extractable Cd between the different tillage

treatments or compared to the PT values in any of the soil depths sampled. However, although the FIT treatment had the lowest average total soil Cd concentration in the 0–5 cm soil depth, it had the highest average extractable Cd level in this soil depth (average: 0.024 mg Cd/kg). Such value of extractable Cd concentration was about 52%, 17% and 17% higher than that of the PT, ST (average: 0.020 mg Cd/kg) and NT (average: 0.020 mg Cd/kg) treatment, respectively (Figure 4.1b). In addition, the other tillage treatments had lower extractable Cd concentrations in the 0–5 cm soil depth, compared to the 5–10 and 10–15 cm soil depths. This is in contrast to their total soil Cd levels which, in general, tended to be the highest in the 0–5 cm soil depth after tillage practices (Figure 4.1a).

Trial 2: Allophanic Soil

At the Trial 2 site, before implementing the tillage practices (PT sampling in Oct. 2017), similar to the Trial 1 site, total soil Cd concentrations also had a decreasing trend with soil depth in the 0–40 cm soil depth (Figure 4.1c). Average total soil Cd concentration reduced from 0.42 mg Cd/kg in the 0–5 cm soil depth to 0.13 mg Cd/kg in the 30–40 cm soil depth. However, pre-tillage total soil Cd stratification was more remarkable above the 25 cm soil depth at the Trial 2 site, compared to the Trial 1 site. For example, at the Trial 2 site, pre-tillage total soil Cd concentrations in the 5–10 and 10–20 cm soil depth were about 80% and 50% of topsoil samples (0–5 cm soil depth), respectively, whereas total soil Cd concentrations in the corresponding soil depth were about 90% and 70% of topsoil samples, respectively, at the Trial 1 site (Figure 4.1a and c). About 6 months after tillage practices were established at the Trial 2 site (post-tillage sampling in Apr. 2018), a decrease of total soil Cd concentration on average was detected for all tillage treatments in the 0–5 cm soil depth (Figure 4.1c). However, the FIT-renewal treatment had the lowest total soil Cd concentration in this soil depth (average: 0.25 mg Cd/kg), which was about 40%, 24% and 24% lower than that of the PT, ST (average: 0.32 mg Cd/kg) and NT (average: 0.32 mg Cd/kg) treatment, respectively (Figure 4.1c). In contrast, the FIT treatment had higher total soil Cd concentrations in the 10–15, 15–20, 20–25, 25–30 and 30–40 cm soil depths sampled. There were no significant differences ($P > 0.05$) in total soil Cd concentrations below the 25 cm soil depths between all tillage treatments or compared to the PT values (Figure 4.1c). Overall, the FIT treatment modified pre-tillage total soil Cd stratification, generating a lower total soil Cd concentration in the 0–5 cm soil

depth, compared to the ST and NT treatments.

As shown in Figure 4.1d, the pre-tillage extractable Cd concentration on average decreased from 0.031 mg Cd/kg in the 0–5 cm soil depth to 0.024 mg Cd/kg in the 5–15 cm soil depth at the Trial 2 site. This was consistent with its total soil Cd distribution with soil depth before tillage, while it was dissimilar from extractable Cd concentration stratification before tillage at the Trial 1 site. After pasture renewal, all tillage treatments reduced the extractable Cd concentrations in the 0–5 cm soil depth, but there was no significant difference ($P > 0.05$) in extractable Cd between tillage treatments in this soil depth (Figure 4.1d). However, the FIT treatment had the lowest extractable Cd concentration in the 0–5 soil depth (average: 0.013 mg Cd/kg), which was about 57%, 50% and 31% lower than that of the PT, ST (average: 0.027 mg Cd/kg) and NT (average: 0.019 mg Cd/kg) treatment, respectively (Figure 4.1d). In addition, tillage treatments had lower extractable Cd concentration in the 0–5 cm soil depth, compared to the 5–10 cm 10–15 cm soil depths, which was in contrast to the PT profile distribution of extractable Cd.

4.1.2 Soil cadmium mass to 40 cm soil depth

Trial 1: Pallic Soil

At the Trial 1 site, the total mass of soil Cd in the 0–40 cm soil depth was not significantly different ($P > 0.05$) for the pre-tillage value and the three tillage treatments, which were on average of 56.77, 54.06, 54.33 and 48.29 mg Cd/m² soil for the PT, FIT, ST and NT value, respectively (Table 4.1). The only soil depth was the 20–25 cm soil depth where a significant difference ($P < 0.001$) in the quantity soil Cd was found. In this soil depth, the FIT treatment had higher total mass of Cd (8.15 mg Cd/m² soil), compared to the other tillage treatments and the pre-tillage values. The quantity of Cd in this soil depth for the FIT treatment was 54% and 99% higher than the ST and NT treatment, respectively (Table 4.1).

Table 4.1 Average total mass of cadmium (mg Cd/m² soil) calculated using the soil dry bulk density in each soil depth and average cumulative cadmium mass for the soil depth of 0–40 cm at the Trial 1 and Trial 2 site. Results (*P*-values) from one-way ANOVA comparing the pre-tillage value (PT) and the post-tillage treatments (i.e. FIT, ST and NT) for each soil depth were included. In each row and each soil depth, means followed by different lowercase letters indicated statistical significance at *P* < 0.05 per protected LSD (least significant difference) test. SEM, standard error of the mean. NS, not significant.

Site Soil type	Soil depth (cm)	Total soil Cd mass (mg Cd/m ² soil)				SEM	<i>P</i> value
		PT	FIT	ST	NT		
Trial 1	0–40	56.77 a	54.06 a	54.33 a	48.29 a	1.86	NS
Pallic Soil	0–5	9.69 a	11.12 a	11.61 a	10.68 a	0.49	NS
	5–10	11.98 a	10.89 a	11.20 a	11.38 a	0.50	NS
	10–15	10.23 a	9.35 a	10.62 a	8.33 a	0.48	NS
	15–20	9.00 a	6.60 ab	7.56 ab	6.18 b	0.48	NS
	20–25	5.90 b	8.15 a	5.28 bc	4.09 c	0.45	0.001
	25–30	3.72 a	4.06 a	3.34 a	2.50 a	0.29	NS
	30–40	6.25 a	3.90 a	4.73 a	5.14 a	0.58	NS
Trial 2	0–40	83.66 a	75.54 a	64.86 a	67.72 a	3.91	NS
Allophanic Soil	0–5	11.96 a	9.57 a	9.39 a	10.54 a	0.50	NS
	5–10	14.77 a	10.27 b	10.41 b	9.71 b	0.68	0.017
	10–15	11.86 a	12.17 a	11.05 a	10.01 a	0.53	NS
	15–20	11.11 a	10.57 a	8.64 a	9.32 a	0.61	NS
	20–25	10.29 a	9.97 a	7.72 a	9.12 a	0.5	NS
	25–30	9.29 a	8.77 a	8.18 a	7.65 a	0.64	NS
	30–40	14.38 a	13.23 a	9.47 a	11.37 a	1.19	NS

Trial 2: Allophanic Soil

At the Trial 2 site, no significant difference (*P* > 0.05) of total mass soil Cd to 40 cm soil depth was found for the pre-tillage value and the three tillage treatments, which were on average of 83.66, 75.54, 64.86 and 67.72 mg Cd/m² soil for the PT, FIT, ST and NT value, respectively (Table 4.1). A significant difference (*P* < 0.05) in total soil Cd mass was only measured in the 5–10 cm soil depth where the PT value in the quantity soil Cd was higher than tillage treatments. The quantity of Cd in this soil depth for the PT values was 44%, 42%, and 53% higher than the FIT, ST and NT treatment, respectively.

4.2 Plant cadmium concentration and uptake after pasture renewal

Trial 1: Pallic Soil

At the Trial 1 site, during the summer turnip crop phase, the tillage treatments did not significantly ($P > 0.05$) affect tissue Cd concentrations in turnip leaves, which were on average of 0.92, 0.79 and 0.95 mg Cd/kg DM for the FIT, ST and NT treatment, respectively (Figure 4.2a). However, Cd uptake by this turnip crop for the FIT treatment (6.24 g Cd/ha DM) was about one and a half times higher than that of the NT treatment (3.71 g Cd/ha DM), which was likely to be due to the FIT treatment resulting in a significantly higher ($P < 0.05$) turnip yield as reported by Calvelo Pereira et al. (2020). They evaluated that the turnip yields were 6.78, 5.65 and 3.90 t DM/ha for the FIT, ST and NT treatment, respectively.

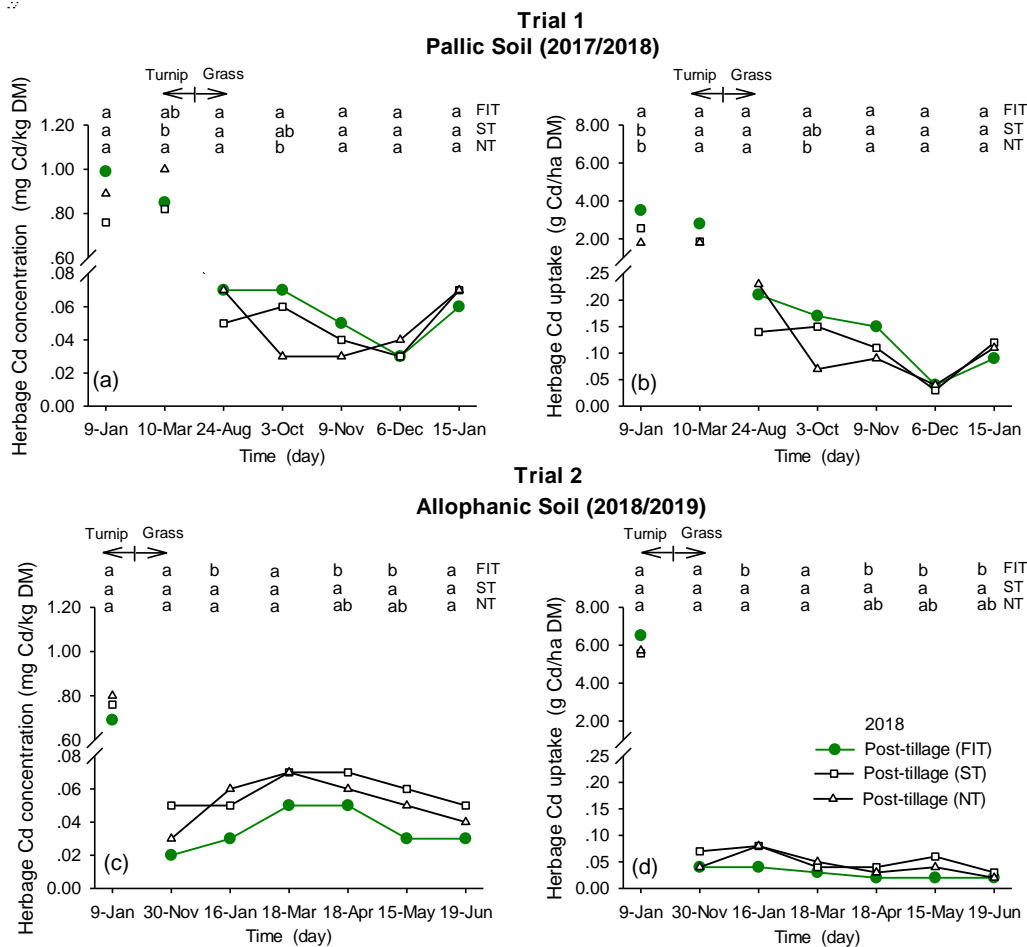


Figure 4.2 Average cadmium concentration (mg Cd/kg DM) and accumulation (g Cd/ha DM) in the summer turnip crop and new pasture periods, at (a-b) the Trial 1 and (c-d) Trial 2 site. Results (P -values) from one-way ANOVA comparing the post-tillage treatments (i.e. FIT, ST and NT) per sampling date were given. The significance of differences between each tillage treatment and each sampling date were marked by different lowercase letters representing statistical significance at $P < 0.05$ per protected the LSD (least significant difference) test.

During the re-grassing pasture phase, the new pasture Cd concentrations were generally low, being < 0.08 mg Cd/kg DM, which was only about 10% of values measured for the turnips crop

(Figure 4.2a). There was a significant difference between tillage treatments, only at one sampling time (i.e. Oct. 2017), when the FIT treatment had higher ($P < 0.05$) grass Cd concentrations (average: 0.07 mg Cd/kg DM), compared to the NT treatment values (average: 0.03 mg Cd/kg DM). In terms of Cd uptake in the new pasture system, no differences ($P > 0.05$) were detected between tillage treatments over the monitoring period of 6 months, with an average of 0.66, 0.55 and 0.55 g Cd/ha for the FIT, ST and NT treatment, respectively (Figure 4.2b). The FIT, ST and NT treatments also did not significantly affect the new pasture biomass production, with estimates for the 6 months period being about 11.24, 11.33 and 11.6 t DM/ha, respectively, on average (Calvelo Pereira et al., 2020).

Trial 2: Allophanic Soil

At the Trial 2 site, although the tillage treatments did not significantly ($P > 0.05$) impact on turnip crop Cd concentrations, the FIT treatment had lower turnip Cd concentration on average (0.69 mg Cd/kg DM), compared to the ST (0.76 mg Cd/kg DM) and NT (0.80 mg Cd/kg DM) treatments (Figure 4.2c). However, an average of the accumulated Cd in the summer turnip crop under the FIT treatment (6.61 g Cd/ha DM) was about 18% and 17% higher than that of the ST (5.59 g Cd/ha DM) and NT (5.66 g Cd/ha DM) treatment, respectively. It was likely to be related to the FIT treatment causing a significantly higher ($P < 0.05$) summer turnip crop yields as reported by Calvelo Pereira et al. (2020). They found that the average turnip yields were about 9.58, 7.35 and 7.07 t DM/ha for the FIT, ST and NT treatment, respectively.

As shown in Figure 4.2c, grass Cd concentrations in the new pasture at the Trial 2 site, were < 0.06 mg Cd/kg DM for all tillage treatments. In general, the FIT treatment also had lower Cd concentration in new grass over the monitoring period of 7 months, with an average of 0.04 mg Cd/kg DM, in comparison with the ST (0.06 mg Cd/kg DM) and NT (0.05 mg Cd/kg DM) treatments. In terms of Cd accumulation in this new pasture, the FIT treatment had lower values on average (0.18 mg Cd/kg DM) than that of the ST (0.32 mg Cd/kg DM) and NT (0.27 mg Cd/kg DM) treatments, during the experimental period (Figure 4.2d). Similar to the Trial 1 site, all tillage treatments did not significantly affect the new pasture biomass production for the selected 7 months period, which were on an average of 5.64, 5.97 and 5.64 t DM/ha for the FIT, ST and NT treatment, respectively (Calvelo Pereira et al., 2020).

4.3 Changes in soil organic carbon, nitrogen and pH values

Trial 1: Pallic Soil

At the Trial 1 site, approximately 4 months after pasture renewal including FIT, there was a redistribution of soil C and N contents in the 0–15 cm soil depth (Figure 4.3a and b; Calvelo Pereira et al., 2019, 2020). Average soil organic C and N concentration under the FIT treatment decreased approximately 58% (29.31 g/kg) and 62% (3.07 g/kg), respectively, in the 0–5 cm soil depth, compared to the PT value (50.73 and 5.01 g/kg for soil C and N, respectively, on average). However, the ST and NT treatments had similar vertical distribution with the PT values (Figure 4.3a and b). In addition, at the end of summer forage crop phase, changes on soil pH values under the post-tillage treatments in the 0–15 cm soil depth, were not significantly different ($P > 0.05$), compared to the PT values (Figure 4.3c). For example, average soil pH was about 5.83, 5.57, 5.78 and 5.59 for the PT, FIT, ST and NT value, respectively, in the 0–5 cm soil depth.

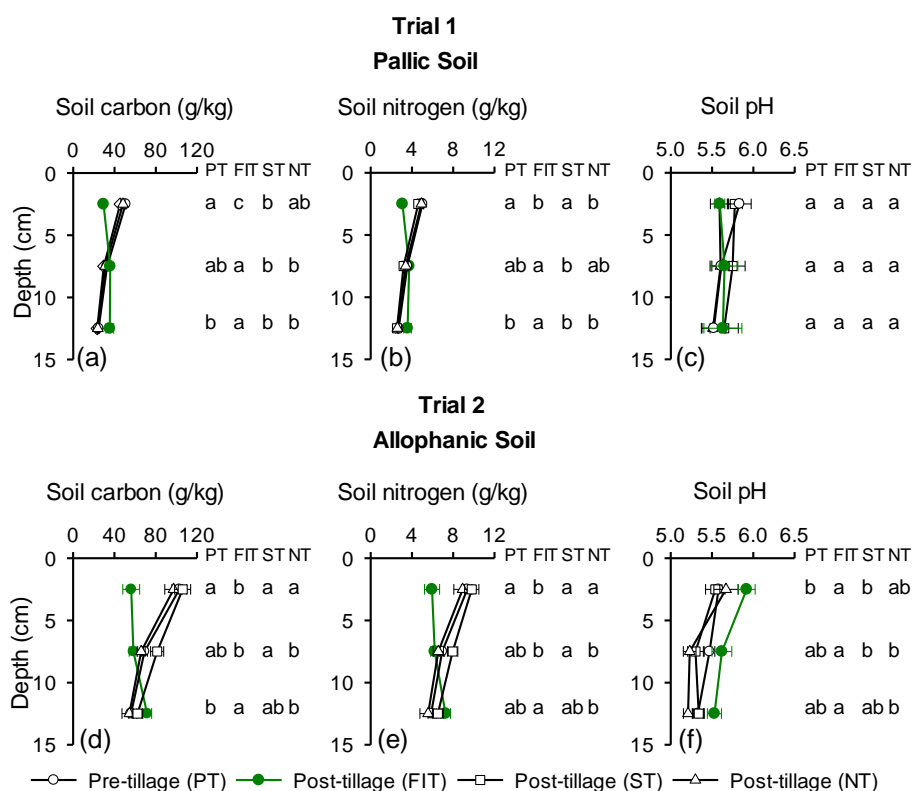


Figure 4.3 Vertical distribution of selected soil properties in the 0–15 cm soil depth, at (a-c) the Trial 1 and (d-f) Trial 2 site. Data were given as means \pm S.E.M. (standard error of the mean). Results (P -values) from one-way ANOVA comparing the pre-tillage value (PT) and the post-tillage treatments (i.e. FIT, ST and NT) in each soil depth were given. The significance of differences between each treatment and each soil depth were marked by different lowercase letters indicating statistical significance at $P < 0.05$ per protected the LSD (least significant difference) test.

Trial 2: Allophanic Soil

At the Trial 2 site, approximately 6 months after tillage, the FIT-renewal treatment redistributed soil C and N stratification in the 0–15 cm soil depth (Figure 4.3d and e; Calvelo Pereira et al., 2019, 2020). Similar to the Trial 1 site, the FIT treatment decreased average soil organic C and N concentrations to 56.24 and 5.94 g/kg, respectively, in the 0–5 cm soil depth, compared to the PT values (97.87 and 8.96 g/kg for soil C and N, respectively, on average). The ST and NT treatments did not significantly change ($P > 0.05$) these selected soil properties in the 0–15 cm soil depth when comparing to the PT values. However, at the end of summer forage crop phase, an increase of soil pH values in the 0–15 cm soil depth, was detected for the FIT treatment at the Trial 2 site, compared to the PT values (Figure 4.3f). For example, average soil pH significantly increased ($P < 0.05$) from 5.58 (PT) to 5.92 (FIT) in the 0–5 cm soil depth, whereas the ST and NT treatments did not significantly change ($P > 0.05$) soil pH in the 0–15 cm soil depth, compared to the PT values (Figure 4.3f).

4.4 Correlation between cadmium and parameters of soil and plants

A correlation matrix was constructed between Cd and other parameters of soil and plants about half year after pasture renewal at both trial sites.

Correlation between soil cadmium and selected soil chemical properties

After tillage at both trial sites, Spearman correlations between the soil Cd (i.e. total soil Cd and extractable Cd for post-tillage treatments) and the selected soil properties (i.e. soil C, N and soil pH for post-tillage treatments) in the 0–5 cm soil depth were measured (Table 4.2). It revealed that total soil Cd concentration correlated positively with soil organic matter concentrations (C: $\rho = 0.790$, $P < 0.001$; N: $\rho = 0.814$, $P < 0.001$). However, no significant relationship was observed between total soil Cd concentration with soil pH ($\rho = 0.126$, $P = 0.539$). Furthermore, association between extractable Cd concentrations and these soil parameters was investigated (Table 4.2). The extractable Cd concentration did not correlate with soil organic matter concentrations (C: $\rho = 0.166$, $P = 0.418$; N: $\rho = 0.169$, $P = 0.409$), but negatively and significantly correlated with soil pH ($\rho = -0.522$, $P = 0.006$). However, our data did not find any significant relationship between total soil Cd and extractable Cd concentrations ($\rho = 0.146$, $P = 0.476$).

Table 4.2 Spearman correlation coefficients (ρ) between soil/plant cadmium concentration and soil/plant factors (n= 26). Soil cadmium concentrations (i.e. TSCd and ExCd) and soil chemical properties (i.e. SOC, SON and soil pH) were mean of each post-tillage plot in the 0–5 cm soil depth (Trial 1: 12 plots, Mar. 2017; Trial 2: 14 plots, Apr. 2018). Plant parameters (i.e. TY, TCdC, TCdU, GY, GCdC, and GCdU) were mean of each post-tillage plot at the selected dates that were close to the date of post-tillage soil sampling (Trial 1: Mar. 2017 for turnip and Aug. 2017 for grass; Trial 2: Jan. 2018 for turnip and Nov. 2018 for grass). ** Correlation is significant at $P < 0.01$ (2-tailed). * Correlation is significant at $P < 0.05$ (2-tailed).

Factors	Units	TSCd	ExCd	SOC	SON	Soil pH	TY	TCdC	TCdU	GY	GCdC	GCdU
TSCd	mg Cd/kg	--										
ExCd	mg Cd/kg	0.146	--									
SOC	g/kg	0.790**	0.166	--								
SON	g/kg	0.814**	0.169	0.988**	--							
Soil pH		0.126	-0.522**	-0.123	-0.123	--						
TY	t DM/ha	0.565**	-0.225	0.482*	0.477*	0.306	--					
TCdC	mg Cd/kg DM	-0.346	0.235	-0.259	-0.270	-0.106	-0.536**	--				
TCdU	g Cd/ha DM	0.526**	-0.169	0.485*	0.475*	0.298	0.961**	-0.343	--			
GY	t DM/ha	-0.553**	-0.099	-0.632**	-0.672*	0.140	-0.674**	0.334	-0.700**	--		
GCdC	mg Cd/kg DM	-0.206	0.366	-0.153	-0.162	-0.340	-0.347	0.473*	-0.249	0.117	--	
GCdU	g Cd/ha DM	-0.481*	0.304	-0.495*	-0.520**	-0.184	-0.648**	0.550**	-0.580**	0.638**	0.815**	--

Soil parameter

TSCd: total soil Cd concentration
ExCd: extractable Cd concentration
SOC: soil organic carbon
SON: soil organic nitrogen

Plant parameter

TY: turnip yields
TCdC: turnip Cd concentration
TCdU: turnip Cd uptake
GY: grass yields
GCdC: grass Cd concentration
GCdU: grass Cd uptake

Correlation between plant cadmium and selected soil/plant factors

After tillage at both trial sites, Spearman correlations between the plant Cd concentration (i.e. Cd concentration in turnip and new grass) and selected soil/plant parameters (i.e. total soil Cd and extractable Cd concentration for post-tillage treatments in the 0–5 cm soil depth, as well as turnip and grass yields) were tested (Table 4.2). The plant Cd concentration did not significantly relate with total soil Cd concentration (turnip: $\rho = -0.346$, $P = 0.083$; grass: $\rho = -0.206$, $P = 0.314$), and extractable Cd concentration (turnip: $\rho = 0.235$, $P = 0.248$; grass: $\rho = 0.366$, $P = 0.66$) in the topsoil (0–5 cm soil depth). The turnip tissue Cd concentration had negative relationship with its total biomass ($\rho = -0.536$, $P = 0.005$); however, the grass tissue Cd concentrations did not significantly relate with its biomass productivity ($\rho = 0.117$, $P = 0.568$). In addition, no clear relationship between plant Cd uptake with extractable Cd concentrations (turnip: $\rho = -0.169$, $P = 0.409$; grass: $\rho = 0.304$, $P = 0.132$) in the 0–5 cm soil depth was found. However, plant Cd uptake had positive relationship with total soil Cd concentrations only in turnips (turnip: $\rho = 0.526$, $P = 0.006$; grass: $\rho = -0.481$, $P = 0.013$). As expected, a significant and positive relationships between both plant Cd uptake with their respective biomass were measured (turnip: $\rho = 0.961$, $P < 0.001$; grass: $\rho = 0.638$, $P < 0.001$).

Chapter 5: Discussion

The field experiment aimed to examine whether pasture renewal, consisting of one-off full inversion tillage (FIT), has potential to modify vertical stratification of soil cadmium (Cd) within soil profile, by directly transferring Cd-rich topsoil into the subsoil at furrow bottom (approximately 20–25 cm soil depth) and lifting up the subsoil with low-Cd into the upper soil depths. Then, it was assessed whether the new topsoil Cd concentrations caused by FIT could impact on the Cd concentrations in both summer forage crop and new pasture grass, compared to other tillage methods (i.e. shallow tillage-ST and no tillage-NT). The influence of FIT on soil Cd with soil depth as well as plant Cd are discussed in the following sections. Other findings of this on-going field trials in the North Island of New Zealand (NZ) have been reported by Amanor (2019) and Calvelo Pereira et al. (2019, 2020).

5.1 Difference in pre-tillage soil cadmium concentration and stratification between two trial sites

Pre-tillage total soil cadmium concentration

Prior to the establishment of pasture renewal at both trial sites, total soil Cd concentrations were within Tier 0 (< 0.6 mg Cd/kg), and lower than the average total soil Cd level in NZ pasture soils (0.43 mg Cd/kg), on a national basis, during 1989–1995 and 2000–2006 (Taylor et al., 2007), but they were higher than the average concentration of total soil Cd in the unfertilised Allophanic Soil (< 0.3 mg Cd/kg) and Pallic Soil (< 0.2 mg Cd/kg) in NZ, respectively (Cavanagh, 2014). It is well known that the historic and long-standing phosphate fertiliser application is the primary factor determining total soil Cd concentrations in NZ agricultural soils, especially the application of Cd-rich phosphate fertiliser containing up to 450–600 mg Cd/kg P, prior to 1997 (Syers et al., 1986; Roberts et al., 1994; Zanders et al., 1999).

The total soil Cd concentrations before tillage in Allophanic Soil at the Trial 2 site were nearly double that in Pallic Soil at the Trial 1 site (Figure 4.1a and c). Other authors also reported that Allophanic Soils have higher total soil Cd concentrations in the 0–7.5 cm soil depth than other Soil Orders in NZ (Roberts et al., 1994). The affinity of P in Allophanic Soil is relatively high, in which the appreciable amount of allophane is a hydrous aluminium silicate clay mineraloid with amorphous/poorly crystalline structure (Parfitt, 1990), consequently this soil requires greater

phosphate fertiliser inputs to target soil P test values. Meanwhile, allophane with the considerable number of negative charges can adsorb cations, like Cd (Bolan et al., 2003a, 2013). Therefore, the higher P-retention of Allophanic Soil, compared to Pallic Soil, would have resulted in a higher historic P fertiliser requirement and, hence, would have contributed to the high Cd inputs.

Pre-tillage vertical stratification of total soil cadmium concentration

At the start of pasture renewal, both soils showed a decreasing trend of total soil Cd with soil depth in the 0–40 cm soil depth (Figure 4.1a and c). Such characteristic of total soil Cd variation with soil depth is in agreement with other studies (Stafford et al., 2018b; Salmanzadeh et al., 2016a) who reported 3–10 times higher total soil Cd concentrations in the 0–7.5 cm soil depth, compared to the 7.5–60 cm soil depth. In NZ agricultural soils, approximately 75% of the fertiliser-derived Cd has accumulated in the top of 0–7.5 cm soil depth (Zanders et al., 1999), as soil Cd originating from phosphate fertilisers is fairly immobile (Gray et al., 2003b). Moreover, the low rate in the downward movement of fertiliser-derived Cd is caused by its adsorption into soil organic matter (Adriano, 2013). Other soil Cd sources from atmospheric deposition and herbage Cd recycling through dung deposition as well as plant decomposition also accumulated in the topsoil (Roberts et al., 1994). However, total soil Cd stratification in Pallic Soil at the Trial 1 site was not as marked as in Allophanic Soil at the Trial 2 site (Figure 4.1a and c), likely because of lower total soil Cd concentrations in Pallic Soil.

Pre-tillage extractable cadmium concentration

Before the establishment of pasture renewal, greater extractable Cd concentration in the 0–5 cm soil depth was measured in Allophanic Soil at the Trial 2 site, compared to Pallic Soil at the Trial 1 site (Figure 4.1b and d). Total soil Cd concentration and soil properties (e.g. soil C and N, soil pH) have been referred to as essential factors influencing plant-available Cd concentrations (e.g. Loganathan et al., 1997; Gray et al., 1999a). Soil with high total soil Cd concentration may also result in high bioavailable Cd in this soil (e.g. Loganathan et al., 1997; Gray et al., 1999b; Yi, 2019). In terms of soil properties, higher soil organic matter contents can bind more soil Cd through cation exchange or specific adsorption (Loganathan et al., 2012), and an increase in soil pH can increase soil Cd adsorption (e.g. Naidu et al., 1994; Gray et al., 1999a; Ardestani & van Gestel, 2016). In

current study, there was lower total soil Cd concentrations, and lower soil organic matter contents but similar soil pH values before tillage, in Pallic Soil, compared to Allophanic Soil (Figure 4.1 and 4.3), thereby, higher total soil Cd concentrations in Allophanic Soil probably contributed to the higher extractable Cd in this soil before tillage.

Pre-tillage vertical stratification of extractable cadmium concentration

Dissimilar from the total soil Cd stratification before tillage, extractable Cd stratification in the 0–15 cm soil depth showed contrasting patterns between the Trial 1 and Trial 2 site (Figure 4.1b and d). Loganathan et al. (1997) have reported lower extractable Cd concentration in the topsoil for a Pallic Soil, Manawatū Region, which was probably linked to the higher Cd adsorption in the upper soil as a result of higher soil organic matter concentrations and soil pH values, compared to the subsoil. This corresponded with our finding at the Trial 1 site (Pallic Soil) where the increase of extractable Cd concentration with soil depth was observed before tillage (Figure 4.1b), as a consequence of higher soil organic matter concentrations as well as soil pH in the surface layer, compared to the subsoil samples (Figure 4.3). However, at the Trial 2 site (Allophanic Soil), before tillage, Allophanic Soil showed a higher extractable Cd concentration in the 0–5 cm soil depth compared to the lower soil depths. While this trial site had a higher soil organic matter concentration, it also had higher total soil Cd concentrations, which may have been a more important determinant of plant-available Cd concentration for this soil (Gray et al., 1999c).

5.2 Pasture renewal using full inversion tillage to reduce topsoil cadmium concentration

In NZ permanent pasture, the initial topsoil has a greater total soil Cd concentration than the subsoil (Stafford et al., 2018b), therefore, after FIT there should be an immediate reduction in total soil Cd concentration in the new topsoil caused by the transference of low Cd subsoil to the new surface. Here, approximately half year after tillage, the reduction of total topsoil Cd concentration caused by FIT was observed at both trial sites, particularly at the Trial 2 site, where after FIT there was a rapid and significant decrease ($P < 0.05$) in total soil Cd concentration in the 0–5 cm soil depth (Figure 4.1c). However, the result for the other field site (i.e. Trial 1) was less evident, with the difference in total soil Cd concentration in the 0–5 soil depth after FIT not being large enough to be significantly different (Figure 4.1a). The effectiveness of FIT to reduce total topsoil Cd

concentration is dependent on total soil Cd concentration and its degree of stratification before tillage. The total soil Cd concentration was lower and also less stratified at the Trial 1 site, so there was less ability for the FIT to reduce topsoil Cd concentration. However, it will be on soils that have a high degree of stratification that also tend to have higher topsoil Cd concentration, where FIT will be of most benefit and be most effective.

It is generally accepted that plant-available Cd fraction in soils is a reasonable indicator impacting on Cd uptake by plants (Loganathan et al., 1996). Given this, we also explored the influence of the FIT following pasture renewal on extractable Cd concentration and stratification in the 0–15 soil depth. Our data showed vertical distribution of extractable Cd was unaffected by FIT approach at the Trial 1 site (Figure 4.1b), whereas FIT significantly decreased ($P > 0.05$) extractable Cd in the 0–5 cm soil depth at the Trial 2 site (Figure 4.1d). The remarkable reason is likely because the initial extractable Cd concentration stratification was also contrasting between two trial sites. The FIT treatment brought subsoil with higher extractable Cd to the surface layer at the Trial 1 site, but brought subsoil with lower extractable Cd to the surface layer at the Trial 2 site (Figure 4.1b and d).

Taken together, the use of FIT at pasture renewal can be a possible method to mitigate the elevated soil Cd concentrations in soils, where the aim is to reduce total topsoil Cd and extractable Cd concentration, like at the Trial 2 site. In NZ, there is a need to reduce of soil Cd in agriculture soils (Sneath, 2015). This is especially the case for some regions, such as Waikato, Taranaki and Bay of Plenty regions, where the agricultural soil Cd levels were on average higher than the national average value of approximately 0.45 mg Cd/kg (Abraham et al., 2016). Also, within those regions there will be farms with moderately high topsoil total Cd levels (i.e. > 1 mg Cd/kg), where the use of FIT would be particularly useful for reducing these soil Cd concentrations. However, before using FIT, it would be useful to characterise the degree of soil Cd stratification in the at least 0–30 cm soil depth to better assess the potential ability of this tillage practice to be effective at reducing topsoil Cd levels.

5.3 Influence of pasture renewal including full inversion tillage on plant cadmium

Plant Cd concentration and uptake are influenced by specific soil and plant factors. For example, high plant-available Cd can result in high Cd uptake by plants, while high plant growth

rate can dilute plant Cd concentration (Loganathan et al., 1996). Changes in extractable Cd concentration and herbage yield after FIT resulted in contrasting effects on plant Cd concentration and uptake between the two trial sites (Figure 4.2). During the summer forage crop phase, the FIT treatment did not affect Cd concentration in leafy turnip at the Trial 1 site (Figure 4.2a), because there was similar topsoil Cd concentration (Figure 4.1a and b), in spite of higher turnip dry matter accumulation under the FIT treatment, compared to the ST and NT treatments (Calvelo Pereira et al., 2020). In contrast, the FIT treatment decreased Cd concentration in this forage crop at the Trial 2 site (Figure 4.2c), which is likely to be due to lower total soil Cd and extractable Cd concentration in the 0–5 soil depth as well as higher turnip yields after FIT, compared to other two tillage treatments (Figure 4.1c and d; Calvelo Pereira et al., 2020).

During the new pasture phase, similar results for the influence of FIT on Cd in new grass were found. Pasture renewal including FIT showed no difference in grass (ryegrass/white clover) Cd concentration at the Trial 1 site, whereas it resulted in lower pasture Cd concentration at the Trial 2 site, compared to the ST and NT treatments (Figure 4.2a and c). However, unlike the summer forage crop, the FIT treatment did not increase the new pasture dry matter accumulation during the selected dates (Calvelo Pereira et al., 2020). While it is likely that extractable Cd concentration can influence plant Cd concentration, neither trial site showed a significant positive relationship between extractable Cd concentration and Cd concentration for either leafy turnip or new grass (Table 4.2). Our data also demonstrated that plant species had a greater influence on plant Cd concentration than extractable Cd concentration. For example, there was about a 10 times higher Cd concentration in leafy turnip compared to ryegrass/white clover pasture (Figure 4.2). Other authors also reported that forage brassica crops had higher tissue Cd concentrations, compared to perennial ryegrass and white clover (Stafford et al., 2016; Ubeynarayana et al., 2021).

5.4 Implication of changes in soil properties after full inversion tillage to soil and plant cadmium

The long-term influence of FIT-renewal on soil Cd concentration and plant Cd uptake will rely on the newly-inverted soil properties profiles (e.g. soil organic matter and soil pH) caused by FIT as well as other land management practices (e.g. liming) after FIT. The fate of Cd in soils is mostly related to soil properties, by increasing soil organic matter and soil pH, the soil's capacity to adsorb

Cd on soil surface negative charges is normally increased, and subsequently can decrease extractable Cd concentration (Naidu et al., 1997; Loganathan et al., 2012). In this study, pasture renewal including FIT lifted the pre-tillage subsoil with low C and N concentrations, at the end of turnip crop phase (Figure 4.3; Calvelo Pereira et al., 2020). Relatively fast accumulation of soil organic matter from pasture growth can be achieved in the new topsoil generated after FIT (Calvelo Pereira et al., 2019), potentially increasing the binding and immobilisation of Cd. Moreover, other practices after the use of FIT may impact on the performance of FIT to change soil Cd and plant Cd concentrations. In this study, FIT induced lower topsoil pH at the Trial 1 site (Figure 4.3c), whereas the increase of soil pH after FIT in the 0–15 soil depth, at the Trial 2 site was found (Figure 4.3f). At both trial sites, there was a similar soil pH value and stratification before tillage (Figure 4.3c and f). The application of lime (3209 kg/ha) in Mar. 2018, approximately 1 month before post-tillage sampling, may largely resulted in this increase of soil pH after FIT at the Trial 2 site.

It is unclear the influence of the change with decreased pH value in the new topsoil after FIT on extractable Cd and plant Cd concentrations at the Trial 1 site. However, extractable Cd concentration correlated negatively with soil pH after tillage (Table 4.2). Given the results from the Trial 2 site, liming plus FIT can increase soil pH greater, compared to lime with ST or lime with NT, when the same amount of lime was applied (Figure 4.3f). This may be due to the lower organic matter levels in the FIT topsoil, having a lower pH buffering capacity, due to lower soil organic matter levels. This indicates that the application of liming after FIT may increase the efficiency of FIT to reduce extractable Cd concentration, and then decrease Cd concentration in plants, as soil pH is an influential soil factor controlling soil Cd bioavailability (Loganathan et al., 2003; Al Mamun et al., 2016).

Chapter 6: Summary and Conclusion

The use of FIT at pasture renewal modified the vertical distribution of total soil Cd and extractable Cd concentration. The extent of these changes was influenced by pre-tillage soil Cd concentrations and degree of vertical stratification. At the Trial 1 site, the pre-tillage average topsoil Cd concentration was low, and the vertical distribution of Cd with soil depth was not significantly affected by tillage treatments. In contrast, the Trial 2 site had a higher average total topsoil Cd concentration and the FIT treatment significantly decreased total soil Cd and extractable Cd concentrations in the newly-created topsoil. Consequently, FIT resulted in lower Cd uptake by a summer crop (turnip) and following pasture (ryegrass/white clover), compared to the ST and NT treatments. These results suggest that using FIT at pasture renewal, where total soil Cd levels are moderate or high, can successfully mitigate topsoil Cd concentrations through bringing the low Cd subsoil into the new surface layer, and then reduce Cd uptake by forage plants. Because forages like leafy turnips have a greater ability to accumulate Cd, compared to perennial ryegrass/white clover pastures, the use of FIT prior to establishing such forages may be especially relevant for mitigating livestock ingestion of Cd, particularly on farms with high topsoil Cd levels.

In addition to the direct effect that FIT has on soil Cd, it can also influence other soil properties that impact on Cd bioavailability. For example, increasing soil pH can reduce Cd bioavailability, and if the new topsoil following the use of FIT has a lower pH buffering capacity, then will be a larger increase in soil pH for a given quantity of lime applied, compared to the original topsoil with higher organic matter levels. Therefore, in the short-term, less lime may be required to achieve the same reduction in Cd bioavailability. In the longer term, following the use of FIT, as soil organic matter re-establishes in the new topsoil with lower total soil Cd levels, this may also help to further reduce Cd bioavailability due to the influence of soil organic matter on reducing Cd bioavailability. Further work research is required to investigate the long-term influence of changes in topsoil organic matter, following the use of FIT, on plant availability of soil Cd. It will also be useful to assess the benefits of FIT for farms with high soil Cd levels (i.e. > 1 mg Cd/kg), as these farm where the use of FIT is particularly useful at reducing plant uptake of Cd.

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