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ASSESSING CADMIUM UPTAKE IN NEW ZEALAND AGRICULTURAL SYSTEMS

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Abstracts

Soil cadmium (Cd) concentration is the primary indicator through which fertiliser-derived Cd is currently managed under the New Zealand Cadmium Management Strategy (MAF 2011). However, there is a lack of New Zealand-specific data on the soil Cd concentrations that may actually pose a risk for New Zealand agricultural systems and how these risks might be managed. This paper presents an overview of the results from a two-year study on cadmium uptake into food crops (wheat, potato, onion and leafy greens), effects on soil rhizobia-clover symbiosis and uptake into lambs grazed on crops with a range of Cd concentrations. Specifically, this includes the results of field surveys of these crops in their primary commercial growing regions across New Zealand and field trials to assess the influence of lime and compost addition on plant Cd; studies to assess the toxicity of Cd to clover in the presence and absence of rhizobia, and the influence Cd on plant nitrogen content, and investigation of the accumulation in the livers of lambs grazed on ryegrass, lucerne, plantain and chicory. The implications for managing the risk associated with fertiliser-derived Cd are discussed.

Introduction

Soil cadmium (Cd) concentration is the primary indicator through which fertiliser-derived Cd is currently managed under the New Zealand Cadmium Management Strategy (MAF 2011). Specifically, the Tiered Fertiliser Management System (TFMS) aims to minimise Cd accumulation in soil by imposing increasingly stringent fertiliser management practices as Cd concentrations increase[1.] The strategy further outlines general farm management practices that can be implemented to reduce plant uptake of Cd.

However, there is a lack of New Zealand-specific data on the soil Cd concentrations that may actually pose a risk for New Zealand agricultural systems and how these risks might be managed. A number of research priorities have been identified to address these issues (MAF 2011). This project addresses some of these issues and extends previous research on the influence of cultivar on plant uptake of Cd and preliminary investigation of effects on rhizobia (Cavanagh et al. 2016), with a particular focus on:

- achieving a greater understanding of the factors that influence plant uptake of Cd to better assess the current risk of exceeding food standards, and to assess the efficacy of potential mitigation options through the addition of lime and compost

[1] A full description of the Tiered Fertiliser Management System is available from: http://www.fertiliser.org.nz/Site/resource_center/Tech_Papers.aspx

- undertaking further investigation of the role of Cd in toxicity to white clover and rhizobia, and specifically the legume–clover symbiosis and outcomes for N_2 fixation (i.e. the impact on pasture nutritional quality)
- assessing the uptake of Cd in livestock grazed on pasture species with varying Cd concentrations.

Methods

Food crops

An extensive survey of one or two cultivars of wheat, onions, potatoes and spinach in the main growing regions of New Zealand was undertaken to assess current Cd concentrations in these crops and associated soils. In addition, eight lettuce cultivars were sampled from three locations. The focus of the current project was to provide a better understanding of the influence of soil properties on Cd uptake in agricultural crops. As such soil and plant sampling is largely focussed on one cultivar of leafy greens (lettuce, spinach), potatoes, onions and wheat sampled from the main growing areas of each crop across New Zealand (Figure 1).

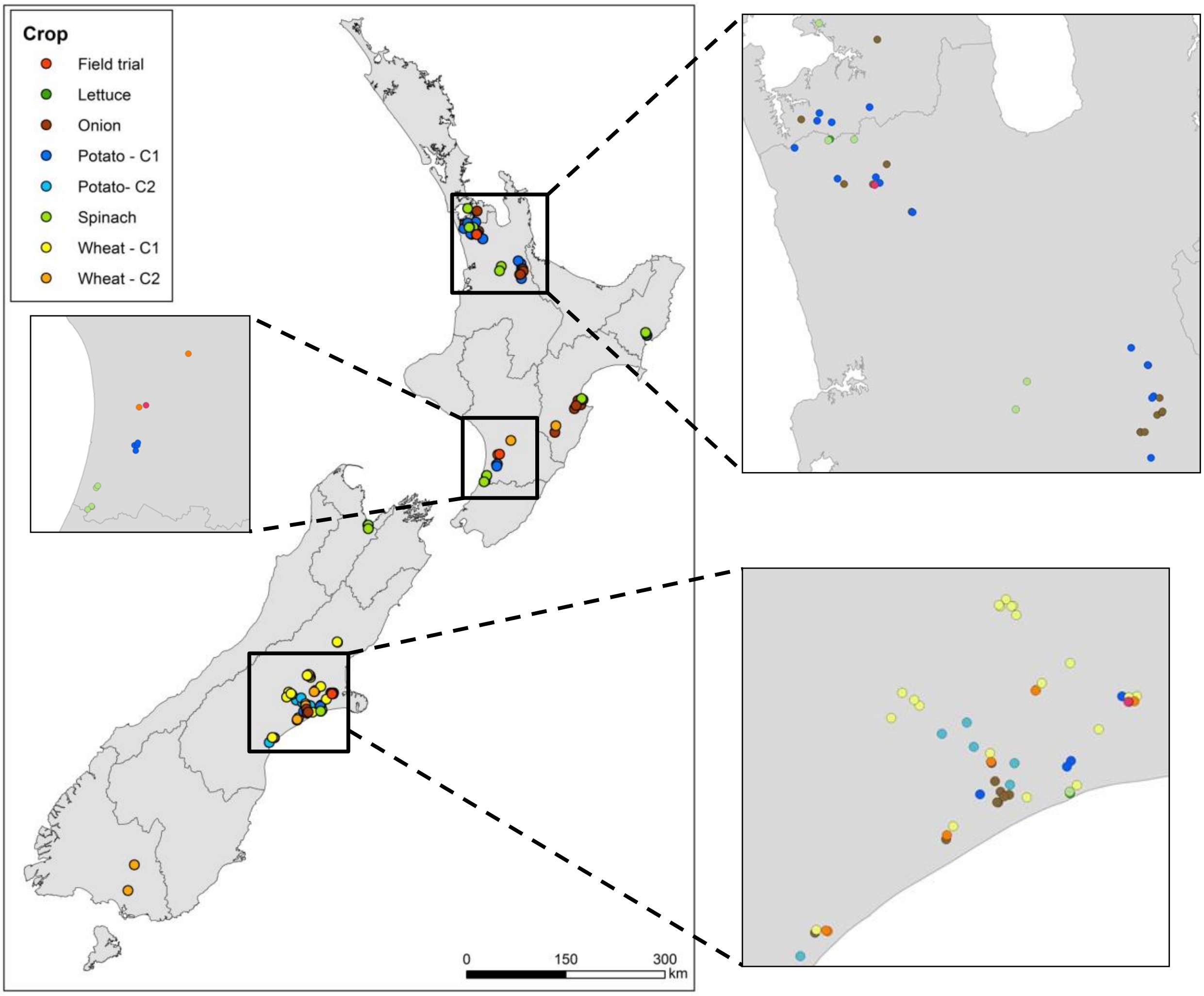

Fig. 1: Sampling location for different crops during the field survey over 2016 and 2017, and during a previous study (one wheat site for C1 and three sites for C2, three potato sites for C1, one for C2, three onion sites, two lettuce sites). C1 and C2 are individual cultivars (Cavanagh et al. 2017).

As a general overview, soil and plant samples were collected from existing industry trials and/or commercial fields. At each site plant and soil samples were taken from each of three or four replicate plots per cultivar/species. A sample was a composite sample of soil or the edible/millable portion from several individual plants within a plot. The plot size differed, depending on the crop being sampled. Multiple soil cores (2.5 × 15 cm for crops) provided a composite sample for each plot. A summary of samples collected for each crop is provided in Table 1.

Table 1: Summary of crops, cultivars and number of sites used in the two studies. Three to four replicate plots were sampled for crop and soil samples at each site.

Crop	Soil study - Cultivar
Wheat (*Triticum aestivum*)	C1 – bread wheat, Site *n* = 26
	C2 – biscuit wheat, Site *n*=9
Onions (*Allium cepa*)	C1, Site *n* = 28
Potatoes (*Solanum tuberosum*)	C1, Site *n* =28
	C2, Site *n* =7
Spinach (*Spinacia oleracea*	Baby leaf, Site *n* =10
	Bunching, Site *n* =11
Lettuce (*Lactuca sativa*)	3 sites each for comparison of 4 different lettuce types, 8 cultivars tested in total.

Soil samples were oven-dried (35^{o}C) sieved through 2mm sieve and sent to a commercial laboratory for analysis for Olsen P, pH, cation-exchange capacity (CEC) and to Lincoln University for chloride, total carbon and trace element analysis using microwave-assisted digestion and inductively coupled plasma mass spectrometry (ICP-MS, Cd – at Canterbury University, method detection limit: 0.017 mg/kg) and ICP-optical emission spectroscopy (ICP-OES) for other elements, including Zn, P, Al, and Fe. Plant materials were oven-dried to a constant weight and sent to Lincoln University for Cd analysis via ICP-OES (MDL: Cd 0.005 mg/kg). Analyte recovery was confirmed using certified plant and soil reference materials. In addition, measures of bioavailable Cd were made: Cd in pore water, calcium-nitrate extractable Cd and using diffusive gradients in thin-films (DGT (as described in Cavanagh et al. 2017).

Field trials

Field trials were undertaken to assess the efficacy of lime and compost additions to reduce Cd uptake and to assess the role of pH and carbon (C) in influencing Cd uptake in those soils. Effecting changes in pH and C at a given site enables all other soil properties to be kept essentially the same, allowing an assessment of the efficacy of those measures to reduce Cd uptake under field conditions.

Field trials were established at research farms at Lincoln (wheat and potato) and Manawatū (potato and spinach) and a commercial field in Pukekawa (potatoes). The target treatments are shown in Table 2. The final treatments were dependent on the properties of the soil at the site and the results of pH incubation studies to determine the amount of lime required to give the required pH change. Compost addition rates were made on the basis of typical rates feasibly applied by growers (25 t/ha) and a higher rate (50 t/ha), and were informed by a previous study on compost in agricultural soils (Horrocks et al. 2012).

Table 2. The proposed treatments for the field trials: final treatments depended on the soil properties at the specific location of the trial

Target/ anticipated pH	Sulphur/lime	Compost
5.6	Acid (sulphur)	0
6	0	0
	0	med (25 t/ha)
	0	high (50 t/ha)
6.3	low	0
	low	med
6.7	med	0
	med	med
7	high	0
	high	med

Rhizobia-legume symbiosis

Pottle-based assays using vermiculite and nutrient solution spiked with cadmium chloride to yield Cd concentrations from 0 to 50 mg/L were used to quantify the effects of increasing Cd concentration on the growth of white clover seedlings (shoot dry weight) in the presence and absence of rhizobia and effect on plant N. All methods are adapted from Wakelin et al. (2016) and described in Cavanagh et al. (2017).

Cadmium uptake in lambs

At four commercial farms recently weaned (14−16 weeks), pasture-fed only, Romney composite lambs (Highlanders) were mustered. Lambs were randomly divided into groups of 15 using the ‘odds and evens’ drafting technique to determine whether they were grazed on pasture or forage crop (Table 3). Liver biopsies were taken on 3 or 4 occasions over December 2016 to March 2017, with soil and plant samples also collected. All procedures using animals were approved by the Massey University Animal Ethics Committee (approval number 16/116).

Table 3 Field locations and forage treatments, and number of liver samplings at each location

Location	Forage crop	Number of animals	Number of times sampled
Tangimoana	Ryegrass, lucerne	30	3
Waipukurau	Ryegrass, lucerne	30	4
Taihape – township	Ryegrass, plantain	30	3
Taihape – rural	Ryegrass, plantain, chicory	45	3

Biopsy samples were immediately chilled and frozen for Cd analysis. Liver samples were prepared for analysis following the method adapted from Vihnanek Lazarus et al. (2013). Soil and plant samples were digested using concentrated nitric acid and heating following the method of Zheljazkov and Nielsen (1996). Cadmium in the digests was determined by graphite furnace atomic adsorption spectroscopy (GFAAS; Perkin Elmer Analyst 800) using orthophosphoric acid as a matrix modifier. The detection limit for total Cd analysis was 0.00026 mg/kg DM.

Provisional soil guideline values

Provisional soil guideline values were established using two approaches. The first approach is based on the Freundlich equation (1), which can be expanded to include other soil properties (2). Equations of this format are widely used to describe plant uptake, and to derive critical limits for soils, such as concentrations at which food standards are met (de Vries et al. 2007), with coefficients determined through regression analyses.

These relationships are developed on the basis of plant concentrations expressed as dry weight. Thus, the relevant food standards were converted to dry weight (hereafter referred to as MLFS) assuming constant dry matter contents of onions (10%), spinach (9%), non-iceberg (5%) and iceberg (3%) lettuce, potatoes (20%), and wheat grain (90%) based on data in Cavanagh et al. (2017), and used in equation 2 to back calculate soil Cd for specified values of the individual soil properties.

$$\text{Plant Cd} = 10^{a}[\text{soil Cd}]^{b} \text{ or} \tag{1}$$

$$\text{Log10(Plant Cd)} = a + b.\text{log10(soil Cd)} + c.\text{(pH)} + d.\text{log10(C)} + \ldots \tag{2}$$

The second approach is using the plant uptake factor (PUF), which is a commonly used, simple measure of plant uptake of inorganic contaminants and is given by:

$$PUF = \frac{Cd_{plant}\ (mg/kg\ (DW))}{Cd_{soil}\ (mg/kg\ )} \tag{3}$$

As a first approximation, equation (3) can be rearranged to indicate the soil concentration at which a specific plant concentration is reached at a given site, *assuming conditions, including soil properties (and therefore PUF)*, do not change. Using the relevant food standard for a given crop as the target plant concentration ($Cd_{plant\ limit}$), a conservative estimate of the soil concentration at which the food standard can be reached ($nCd_{food\ standard}$). As the food standard is expressed as fresh weight, this requires conversion to a Cd concentration based on dry weight, as discussed above. Thus, $nCd_{food\ standard}$ for a specific crop at a specific site is given by equation 4:

$$nCd_{food\ standard}\ (mg/kg\ ) = \frac{Cd_{plant\ limit}\ (mg/kg\ (DW))}{PUF} \tag{4}$$

These values are not intended as threshold limits, but rather provide insight into soil properties influencing plant uptake and the Cd concentrations at which management to mitigate the risk of exceeding food standards should be considered. Any application of these values will be considered as part of the further development of the Cadmium Management Strategy.

Results

Cadmium uptake in food crops

Wheat grain Cd concentrations ranged between 0.004 and 0.205 mg/kg fresh weight (FW), with an overall mean concentration of 0.067 mg/kg FW, which is lower than the Food Standards Australia New Zealand (FSANZ) maximum limit for Cd in wheat of 0.1 mg/kg FW. Eleven samples (9%) exceeded the FSANZ limit. Cd concentrations were on average higher for the bread wheat cultivar than for the biscuit wheat cultivar. There were few significant relationships between soil properties or site management factors and wheat grain Cd concentrations, with observed relationships sometimes being contradictory between cultivars.

Onion Cd concentration ranged from 0.015 mg/kg FW to 0.053 mg/kg FW, with an overall mean concentration of 0.016 mg/kg FW. These concentrations generally complied with the European Union (EU) standard for onions of 0.05 mg/kg FW (no equivalent FSANZ standard exists). Soil pH and total soil Cd were identified as key soil properties influencing accumulation of Cd in onions, explaining 38% of the variation. Inclusion of region in the regression relationships explained a greater proportion of variation (50%).

No relationships between soil properties and Cd concentrations in potato tubers were identified. With the exception of one site in Pukekohe (P9), potato Cd concentrations were remarkably uniformly low (<0.04 mg/kg, mean 0.02 mg/kg FW), and much lower than the FSANZ food standard of 0.1 mg/kg FW. In contrast, tuber Cd concentrations at site P9 were at the food standard. Soil properties at this site were similar to those at other sites, and the only point of note was that the crop sampled was the first crop grown after conversion from long-term pasture.

Differences in Cd concentrations between different lettuce types (e.g. cos, frill lettuce, iceberg) were not consistent across sites. Lettuce concentrations were very low (<0.04 mg/kg FW). Regional differences in lettuce Cd were observed, which were not related to soil Cd concentrations – i.e, higher concentrations were found in regions with lower soil Cd. In contrast to lettuce, Cd concentrations in both baby leaf and bunching spinach from across New Zealand were close to, or above, the FSANZ food standard of 0.1 mg/kg FW. Cd concentrations were higher in bunching spinach. Soil carbon and soil Cd were identified as key factors influencing Cd uptake in bunching spinach, explaining 42% of the variation in spinach Cd. In contrast, Zn, total P and exchangeable Ca, but not soil Cd, were identified as key factors influencing uptake in baby spinach, explaining 57% of variation.

Data from bioavailability testing also confirmed that a range of soil properties influence Cd uptake by the different crops, and no one test adequately predicted Cd concentrations in plants. However, $Ca(NO_3)_2$-extractable Cd and diffusive gradients in thin-films (DGT) generally represented plant available Cd better than the total soil Cd. Bioavailability data were also used to refine a mechanistic computer model describing plant uptake of Cd to be specific for New Zealand, including the effect of the addition of amendments on plant uptake.

Field survey data, including bioavailability data, clearly highlight regional differences in plant uptake of Cd. While there are recognised differences in soil types between regions, detailed soil investigations on a subset of samples did not identify the specific soil properties that are giving rise to the observed differences. However, an increase in pyrophosphate-extractable aluminium correlated with increases in plant Cd concentration, while oxalate-extractable (i.e. aluminium and iron oxides) related to reduced plant Cd concentrations. Allophane was also identified as a factor leading to reduced plant uptake of Cd.

Field trials

Field trials demonstrated a small but significant effect from the addition of compost at 25 tonnes per hectare in reducing Cd uptake in wheat grain (Canterbury) and potatoes (Manawatū – field trial only). Contrary to expectations, there was an observed increase in wheat grain concentration with increasing pH, which may be attributable to the high rates of lime application (up to 9 tonnes per hectare to effect the desired pH change) and competitive desorption due to high concentration of Ca. Rain significantly delayed the application of amendments, planting and harvesting of the field trials, and resulted in the abandonment of the spinach field trial.

Cadmium in pastoral systems

Cadmium has been demonstrated to have negative effects on the growth of rhizobia isolated from New Zealand pastures under laboratory conditions, with the current commercial strain, TA1 being most sensitive (Wakelin et al 2016). Conversely, the toxicity of Cd to clover appears to be mediated by *Rhizobium leguminosarum* TA1: a minimum tolerable concentration of Cd for white clover in the absence of rhizobia was determined to be 0.040 mg/kg $Ca(NO_3)_2$-extractable Cd, and 3.34 mg/kg in the presence of rhizobia. These concentrations are markedly higher than current environmental concentrations of $Ca(NO_3)_2$-extractable Cd of up to 0.00068 mg/kg (Reiser et al. 2014). No effect on nitrogen content in clover was observed in clover/rhizobia exposed to extractable Cd concentrations up to 5 mg/kg.

Increased liver Cd concentrations were observed in lambs grazed on crops with higher Cd (plantain and chicory), with the highest liver concentration occurring in lambs grazed on chicory (see Anderson et al. this proceedings for more detail).

Discussion

The primary purpose for undertaking this research was to inform future management of cadmium to manage risks associated with soil Cd and is discussed below.

Implications for crop management

The absence of identifiable relationships between soil properties and Cd in wheat grain, and the proximity of grain Cd concentrations to the food standards, suggests that the use of low-Cd-accumulating cultivars is likely to be the most effective way to manage Cd in wheat grain. Field trials (not discussed here) indicated addition of compost may also help to reduce Cd in grain, although the extent of this reduction is potentially small. Management of Cd in potatoes is also likely to be most effective by using low-Cd-accumulating cultivars, given the absence of identified relationships with soil properties. In contrast to wheat, given that tuber concentrations are generally much lower than the FSANZ food standard, a less restricting approach ensuring that high-Cd-accumulating do not become widely grown could provide an appropriate management approach. We found that variation in Cd uptake by different cultivars varied across sites, highlighting the importance of assessing cultivars at a number of sites.

Maintaining soil pH at around 6 appears to be sufficient to ensure Cd concentrations in onions comply with food standards. Further assessment is required to determine if this advice is more generally applicable to a wider range of onion cultivars.

The comparatively high Cd concentrations in baby, and particularly bunching, spinach (i.e. close to or above FSANZ food standard) suggests that management actions should be implemented to reduce Cd uptake. As soil pH is typically managed to around 7 for spinach crops, lime addition offers limited value in reducing Cd uptake in spinach. Given the dependence of Cd concentrations in bunching spinach on soil carbon, the addition of compost may help to reduce Cd uptake, although the extent to which it is reduced needs to be determined.

It is notable that the EU food standards for both wheat and spinach are double those of the existing FSANZ food standards (0.2 mg/kg FW vs 0.1 mg/kg FW). Cadmium concentrations in these crops are close to the food standards in low Cd soils, and management options are limited. Food standards are established on the basis of being as low as reasonably achievable while ensuring protection of human health. It may therefore be relevant to review the applicability of the FSANZ food standards for wheat and spinach to determine whether this principle is being met.

Soil cadmium management implications

Soil Cd concentrations in the majority of sites assessed in this study fell into Tier 0 of the Tiered Fertiliser Management System (TFMS), for which only 5-yearly monitoring of soil Cd is required. However, for some crops (wheat and spinach) or regions, managing to the trigger values in the TFMS is clearly not sufficient to ensure crops comply with applicable food standards.

Provisional soil guideline values to support plant food standards to be met were developed using identified regression relationships where available (onion, bunching spinach) (Table 4). These relationships explained a low to moderate proportion of the variation in onion (38%) and bunching spinach (42%), indicating factors other than those assessed are also influencing plant uptake. Further, the onion relationship under-predicted observed high onion Cd concentrations, suggesting caution needs to be applied in any wider application of these values to support compliance with food standards.

Table 4 Provisional Cd soil guideline values (pFS-SGV) to support meeting EU maximum limits for onions (0.05 mg/kg FW) and the FSANZ standard for leafy greens (0.1 mg/kg FW, as a function of soil properties (38% and 42% of variation in plant Cd was explained by soil Cd and pH or soil C, respectively)

Onions		Spinach	
soil pH	**pFS-SGV**	**soil C**	**pFS-SGV**
5.5	1.7	2	0.24
6	2	3.5	0.36
6.5	2.2	5	0.48

The plant uptake factor (PUF, $\frac{Cd_{plant}\,(mg/kg\ (DW))}{Cd_{soil}\,(mg/kg\,)}$) was also used to provide a first approximation empirical estimate of the soil concentrations to support compliance with food standards at individual sites. This approach assumes that site conditions, including soil properties and management (and therefore PUF), do not change. These values ranged from 0.4 to 16 mg/kg for individual crops, with clear regional differences (Table 5).

Table 5. Estimated soil Cd concentrations (mean and 95th percentile range) above which food standards, based on observed plant uptake in different regions, may be exceeded.

<table>
<tr><th rowspan="2">Region</th><th colspan="4">nCdFS (mg/kg)</th></tr>
<tr><th>Onion</th><th>Potato</th><th>Lettuce</th><th>Spinach (all regions)</th></tr>
<tr><td>Pukekohe</td><td>1.43
(0.38–2.94)</td><td>2
(0.40–3.54)</td><td>5.6</td><td rowspan="6">0.35 baby leaf
(0.14–0.7)

0.29 bunching spinach
(0.2–0.44)</td></tr>
<tr><td>Waikato</td><td>2.54
(1.05–4.97)</td><td>4.7
(1.19–16.7)</td><td>—</td></tr>
<tr><td>Gisborne</td><td>—</td><td>—</td><td>0.7</td></tr>
<tr><td>Hawke's Bay</td><td>2.32
(0.80–5.66)</td><td>—</td><td>—</td></tr>
<tr><td>Manawatū</td><td>—</td><td>2
(0.70–7.04)</td><td>—</td></tr>
<tr><td>Canterbury</td><td>0.72
(0.35–1.24)</td><td>0.7
(0.31–1.40)</td><td>1.2</td></tr>
</table>

Provisional soil guideline values for livestock were developed from the livestock study using the results for chicory (as a worst-case scenario) and the relationship describing Cd uptake in chicory from Stafford (2017) (Table 6). A critical assumption of the approach used is that feeding behaviour and animal management (e.g. feed intake and slaughter time) is identical to that which occurred in this study. While there is limited wider applicability of these derived values, they do provide an indication of the soil Cd concentrations that might lead to food standards being exceeded in sheep livers for human consumption. Further, as kidneys typically accumulate higher concentrations than liver, soil guideline values to comply with FSANZ or EU maximum limits for offal will be lower.

Table 6 Provisional Cd soil guideline values to comply with FSANZ or EU maximum limits for liver (1.25 mg/kg FW and 0.5 mg/kg FW, respectively) in liver for lambs grazed on chicory and aged up to 6 months, as a function of soil properties

Soil properties		Provisional livestock-SGV (mg/kg)	
pH	**C (%)**	**FSANZ**	**EU**
6	2	3.0	1.1
5.5	2	2.6	0.7
6	7	3.1	1.3
5.5	7	2.7	0.9

Conclusions

The findings from this study will inform the ongoing management of Cd in New Zealand agricultural soils, including the development of New Zealand-specific risk-based guideline values, as part of the National Cadmium Management Strategy. Provisional soil guideline values to support compliance with food standards (plant crops and livestock products) were developed. Further data is required to develop robust guideline values, but these values nonetheless provide insight into the Cd concentrations at which management to mitigate the risk of exceeding food standards should be considered. This study also provided insight into crop and soil property factors that may also support compliance with food standards. For example, management of Cd in potatoes and wheat appears likely to be most effectively achieved by cultivar management, given the absence of identified relationships with soil properties. In contrast, management of soil pH may be sufficient to ensure compliance with food standards for onion, while the addition of compost may reduce Cd uptake in bunching spinach. Further monitoring and field studies of plant crops, including a range of cultivars, are required to verify the wider applicability of these findings.

Further assessment of Cd uptake by livestock grazed on pastoral or forage species with elevated Cd is also required to more fully establish the risk of non-compliance, and to identify relevant management options. Finally, there appears to be minimal risk of negative impact from soil Cd on the clover–rhizobia symbiosis, and subsequent effects on plant nitrogen content until Cd concentrations are markedly higher than current concentrations in agricultural soils.

Recommendations to aid in managing risk of non-compliance with food standards

Short term

- Incorporate Cd uptake as a plant trait for routine assessment in wheat plant-breeding trials.
- Review the food standards for wheat and spinach to establish whether the principle of being as low as reasonably achievable while ensuring protection of human health is met.
- Review how domestic food standards are applied, and whether unintentional regulatory problems caused by occasional non-compliances of food standards for Cd can be avoided.
- Focus Cd management for wheat on the use of low-Cd-accumulating cultivars, while a less stringent approach of avoiding the use of high-Cd-accumulating cultivars can be adopted for potatoes.
- Consider the need for further research to establish more robust soil guideline values, versus monitoring to assess the wider applicability of the current findings.
- Consider how soil guideline values might be applied to achieve effective management of the risk of non-compliance with food standards.

Medium term

- Undertake further monitoring of Cd in commonly grown onion and potato cultivars, and associated soils, to determine the wider applicability of the findings from this study (i.e. that concentrations in potatoes are typically markedly below the food standard, and that maintaining a soil pH of 6 or above will ensure onion Cd concentrations are below the EU food standard).
- Incorporate Cd uptake as a plant trait for routine assessment in onion and potato plant breeding trials.
- Undertake further research to confirm the finding of increased liver Cd in lambs grazed on forage crops with higher Cd, and develop a better understanding of Cd accumulation in livestock organs in New Zealand systems.

Research recommendations

- Undertake additional analyses (e.g. oxalate-extractable iron) on an extended set of soil samples, combined with further data analysis, including the influence of climate, to establish whether these factors account for the observed regional differences in plant uptake.
- Investigate the influence of crop management activities, in particularly water management activities, to establish the extent to which these also influence Cd uptake.
- Investigate if elevated plant Cd concentrations occur consistently in the first crop grown after conversion from pasture, and the mechanism for this increase.
- Undertake scaled-up assays and field studies on a range of rhizobia symbioses to validate the finding from this study that Cd poses negligible risk to pastoral systems based on clover–rhizobia symbiosis. This could include investigating the mechanism of tolerance and, in particular, whether it has wider application.

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