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Environmental and edaphic factors affecting soil cadmium uptake by spinach, potatoes, onion and wheat

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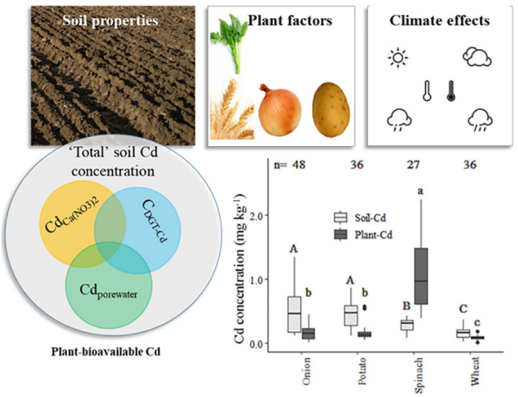
HIGHLIGHTS

- Cadmium accumulation in soils increases risk of toxic concentrations in plants.
- Soil Cd bioavailability was tested and compared to concentrations in crop plants.
- 0.05 M $Ca(NO_3)_2$, DGT and porewater tests were better predictors than total Cd.
- Soil and environmental factors were important for determining Cd accumulation.
- Understanding regional differences in Cd uptake is important for managing risk from soil Cd.

GRAPHICAL ABSTRACT



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ABSTRACT

The relative ease with which cadmium (Cd) in agricultural soils can transfer to crop plants can pose a potential health risk to consumers. However, efforts to predict and mitigate these risks are often confounded by the various factors that influence metal accumulation in the edible plant parts. The aim of this work was to identify key drivers that determine Cd concentrations in spinach leaves, potato tubers, onion bulbs and wheat grain grown in commercial horticultural operations across New Zealand (NZ). Paired soil and plant samples (n = 147) were collected from farms across different NZ growing regions. Cadmium concentrations in the edible parts were measured and four different tests were used to examine the potential bioavailability of soil Cd: pseudo-total and porewater concentrations, 0.05 M $Ca(NO_3)_2$-extraction and diffusive gradients in thin-films (DGT). Information on a range of soil and climatic variables was also collected. The methods' ability to represent Cd concentrations in the plant parts was assessed through single and multiple regression analysis that considered the different variables and the farm locations. Soil Cd concentrations determined by the different tests were positively related to plant concentrations and there were clear regional differences between these relationships. The $Ca(NO_3)_2$ extraction predicted over 76% of the variability in Cd concentrations in onion bulbs and spinach leaves, while DGT and porewater Cd provided the best estimates for potato tubers and wheat grains, respectively, once regional differences were considered, along with certain environmental and soil variables. The results show that certain soil and environmental factors can be a key influence for determining Cd accumulation in the edible

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parts of some plants and that regional differences are important for modulating the extent to which this occurs. These effects should be considered when trying to mitigate the potential risks arising from Cd in agricultural soils.

1. Introduction

Cadmium (Cd) is a non-essential, potentially toxic metallic element that is a naturally occurring impurity in many phosphate fertilizers. The continued use of these fertilizers has led to the accumulation of Cd in many agricultural soils to concentrations above natural background levels (Chaney, 2010). These soils are the main source of the Cd to the edible parts of most food crops (McLaughlin et al., 2011); however, only a small proportion of soil Cd is available for uptake by plants and is mainly composed of the readily soluble fractions in the soil (Menzies et al., 2007). Phosphate fertilizers are essential for maintaining productivity in many agricultural operations, therefore the ability to quantify the soil Cd that can be taken up by a plant between planting and harvest (forthwith, 'bioavailable Cd', for simplicity) is an important prerequisite for predicting the associated potential risk for Cd transfer into food crops. A technique that can accurately estimate bioavailable Cd should account for the variability between the factors that determine the amount of soil Cd taken up by a plant. It follows that such a technique could also be used to interrogate variables that determine the extent to which Cd accumulates in crops. Further estimation of the risks to consumers of those plants should also consider factors that influence the translocation of the metal to the plant's edible parts.

The solubility of soil Cd is affected by a wide range of many soil chemical properties, of which pH and organic carbon are most often important (Degryse et al., 2009a); however, total Cd concentrations (Gray et al., 1999a), complexing inorganic ligands (*e.g.* Cl^-) (Rasa et al., 2006; Dahlin et al., 2016) and metal oxides (Michálková et al., 2014) also contribute. The accumulation of Cd in plants can be further affected by plant nutrients and the plant in question. Applications of P and N fertilizers have been shown to increase the solubility of soil Cd and its uptake by plants (Gray et al., 2002; Wångstrand et al., 2007; Gao et al., 2010). Maier et al. (2002) showed that adding Ca (as calcium nitrate) increased Cd uptake by potatoes, which they attributed to increased displacement of Cd from soil sorption sites. Both synergistic and antagonistic effects of Zn on Cd concentration in plants have been well documented (Nan et al., 2002; Wu et al., 2002; Hart et al., 2005; Sarwar et al., 2015; Qaswar et al., 2017). Cd concentrations in plant tissue also depend on the species, varieties and cultivars considered (Gray et al., 2001; Gray and McLaren, 2005; Khan et al., 2010; McLaughlin et al., 2011; Ashrafzadeh et al., 2017).

A wide-range of methodologies for assessing bioavailable Cd have been proposed, including: water extraction (Gray and McLaren, 2006), weak and neutral salt extractions (Gray et al., 1999a; Gray et al., 2001; Guiwei et al., 2010) and chelating agents (Jiang et al., 2003; Song et al., 2015). Menzies et al. (2007) synthesized the findings from 104 different studies on extraction-based bioavailability measurements and came to the general conclusion that the neutral salt extractants appear to provide the best predictive capability for plant Cd uptake, while total concentrations and chelant-based extractants performed poorly. Others have suggested that the diffusive gradients in thin-films (DGT) technique is a good predictor of Cd uptake (Nolan et al., 2005; Agbenin and Welp, 2012; Song et al., 2015). Most of these tests are influenced by some of the aforementioned soil properties that determine Cd solubility in soils (*e.g.* pH, organic carbon and cation exchange capacity) (Gray and McLaren, 2006; Pérez and Anderson, 2009; Reiser et al., 2014).

Many of the studies above that have contributed towards the validation of these tests for estimating Cd bioavailability have been undertaken as pot trials in controlled or semi-controlled environments. Arguably, the greatest benefit of this is to minimize the influence of spatially and temporally variable edaphic and environmental conditions, and this approach has provided mechanistic insight into the factors that affect Cd uptake by different species. However, the applicability of these tests for estimating Cd uptake under field conditions has proved to be difficult. Higher spatial and temporal variability in soil moisture and nutrient content and different root densities and rooting depths among plants in the field (Thorup-Kristensen, 1999; Friesl et al., 2006) are difficult to replicate meaningfully in pot trials. Moreover, environmental factors that increase the transpiration rate (*e.g.* temperature and rainfall) can support greater Cd uptake through elevated mass flow to the root (McLaughlin et al., 2011), as demonstrated at a regional scale in Germany for potatoes (Ingwersen and Streck, 2005). Reiser et al. (2014) found that, in addition to soil variables, total solar radiation was a significant, but minor, explanatory variable for the variation of the Cd concentration in pasture (no reason was suggested for this). Certain crop management practices arise due to region-specific environmental conditions, which can subsequently be important determinants in Cd bioavailability to plants, these include: irrigation (Gray et al., 2002), rate and timing of fertilizer applications (Grant and Sheppard, 2008), crop rotation sequence (Oliver et al., 1993) and tillage practices (Gao and Grant, 2012). The challenge for any test of potentially bioavailable Cd is to be able to integrate as many of these effects as possible and in appropriate proportions.

Various field campaigns have shown the difficulty in relating results from soil Cd measurements to plant tissue concentrations directly. Peris et al. (2007) found a negative correlation ($r = -0.67$) between total soil and artichoke Cd concentrations and no significant relationships for EDTA-extractable Cd or total soil Cd for leafy vegetables in eastern Spain. A study into Nigerian urban garden soils showed a non-linear relationship between Cd measured by DGT and lettuce leaf concentrations (Agbenin and Welp, 2012). Black et al. (2011) analysed total and soil solution Cd concentrations, Cd in $Ca(NO_3)_2$, EDTA and DGT extracts, and modelled Cd^{2+} free ion activity, in a wide variety of New Zealand (NZ) soils and showed that ryegrass and wheat shoot Cd concentrations correlated with all of the measurements, but with poor overall precision ($R^2 \leq 0.49$). An extensive survey of Cd concentrations in NZ horticultural soils and crops (onions, spinach, wheat and potatoes) between 2016 and 2017 did not find direct correlations between total Cd concentrations in the soil and the edible tissues of the plants. However, upon inclusion of other variables (*e.g.* pH, cation exchange capacity and soil Zn concentration) in empirical multiple regression models, just over half of the variability in the tissue concentrations were represented for onion and spinach (Cavanagh et al., 2019). Conversely, none of the soil factors measured by Gray et al. (2019a) and Gray et al. (2019b) explained the Cd concentration variability in potato tuber or wheat grain, respectively.

We hypothesise that the accuracy of an empirical model that uses total soil Cd concentration to predict the variability in the edible tissue concentrations of onion, spinach, wheat and potatoes under field conditions suffers from the cumulative uncertainty arising from factors that (i) determine the soluble fraction of Cd and (ii) affect Cd uptake by those plants and its translocation to their respective edible parts. This work aims to test this hypothesis by seeking to eliminate some of the uncertainty from the former through tests for Cd bioavailability and then analysing how those results represent Cd concentrations in the edible parts of those crops alongside a variety of environmental and edaphic variables. This will allow an examination which goes beyond analysing soil Cd solubility and seeks to discover other contributing factors that may inform potential risks arising from Cd accumulation in horticultural products grown under field conditions.

2. Method and materials

This study is a targeted investigation into a large subset of samples from the wider survey of horticultural crops and farms in NZ carried out 2016–2017 (Cavanagh et al., 2019; Gray et al., 2019a; Gray et al., 2019b). The analysis here was limited to single varieties and commercially grown cultivars of spinach (cv. *Jedi*), onion (cv. *Rhinestone*), potato (cv. *Moonlight*) and wheat (cv. *Reliance*) (Table 1) and the soils in which they were grown, and consisted of 147 paired soil and plant samples collected from 48 sites around NZ (*c.f.* the wider survey analysed 396 paired samples from 103 sites). The locations where the samples in this subset were collected from are shown in Fig. S1. The total-extractable Cd concentrations (forthwith, Cd_{Tot}, analysis method provided below) within the subset of samples had low mean and median concentrations (0.29 and 0.37 mg kg^{-1}, respectively), but with a large range (0.02–1.35 mg kg^{-1}; Table 2). The median Cd_{Tot} in the subset of soils in which the four crop species were grown decreased in the order potato (0.47 mg kg^{-1}) > onion (0.465 mg kg^{-1}) >> spinach (0.31 mg kg^{-1}) >> wheat (0.16 mg kg^{-1}) (>> where the difference was significant, $P < 0.05$; Fig. 1, see below for description of statistical analyses). The median plant Cd concentrations within this subset of samples decreased in the following order: spinach leaves (0.96 mg kg^{-1} DW) >> onion bulbs (0.15 mg kg^{-1} DW) > potato tubers (0.13 mg kg^{-1} DW) >> wheat grains (0.09 mg kg^{-1} DW) (>> where the difference was significant, $P < 0.05$; Fig. 1, analysis method provided below).

These samples were used specifically to investigate the relationship between the bioavailable soil Cd, environmental factors and the Cd concentrations in the edible parts of these crop cultivars. Full details of soil and plant sample collection have been given by Cavanagh et al. (2019) for onion and spinach, by Gray et al. (2019a) for potatoes and by Gray et al. (2019b) for wheat. A brief description is provided in the Supplementary Information for convenience.

2.1. Soil and plant analyses

The soils were analysed for soil pH (soil/water ratio of 1:2.5), cation exchange capacity (CEC) and base saturation (in pH 7, 1 M NH_4OAc) (Blakemore and Price, 1987), and bioavailable soil P (Olsen-P) (Olsen, 1954) by a commercial laboratory (Hill Laboratories Ltd., Hamilton, New Zealand). Total C and N were determined using an Elementar Vario-Max CN Elementar analyser (Elementar®, Germany). The pseudo-total soil elemental concentrations (P, K, Ca, Mg, Na, Fe, Al, Mn and S) as well as key trace elements, Cd (Cd_{Tot}) and Zn (Zn_{Tot}), were analysed using concentrated acid digests (Simmler et al., 2013). Briefly, soil (0.5 g) was digested in 3 mL trace element grade concentrated nitric acid (HNO_3, >65%, Fisher Scientific, UK) and 3 mL hydrogen peroxide (H_2O_2, 30%, Merck KGaA) using a microwave digest system (MARSXPRESS, CEM Corp). The digest was diluted to 25 mL with high purity water (DI water; 18.2 MΩ-cm; Heal Force® SMART Series, SPW Ultra-pure Water system, Model PWUV) and filtered using Whatman 52 filter paper before analysis. Soil texture and water-extractable chloride were measured on a composite sample representative of each site (see Supporting Information). The texture was analysed using the pipette method (Claydon, 1989), while chloride was determined in a DI water extract (soil/water ratio of 1:5) (Rayment and Lyons, 2011). All results are expressed on an oven-dry (105 °C) soil basis.

The plant material (0.2 g) was digested with 4 mL HNO_3 (50:50, *v*/v) and 2 mL H_2O_2 using a microwave digestion (MARSXPRESS, CEM Corp.) (Cindrić et al., 2015). The digests were subsequently diluted with DI water to a final volume of 10 mL for analysis of Cd and Zn concentrations. The plant concentrations are reported here on a dry weight basis.

Table 1
Total number of paired soil-crop plant samples analysed as part of the targeted survey.

Crops	Total no. sites	Total no. paired soil and plant samples
Onion	16	48
Potato	12	36
Spinach	9	27
Wheat	11	36
Total	48	150

Table 2
Descriptive statistics of the element content & physicochemical characteristics of the soils analysed in this study.

Parameter	Minimum	Mean	Median	Maximum
pH	4.88	6.01	5.97	7.23
Sand (%)	1	19	16	45
Silt (%)	19	49	49	71
Clay (%)	14	32	27	76
Bulk density (g cm^{-1})	0.45	0.92	0.94	1.23
Olsen-P (mg kg^{-1})	11	72	51	351
Total P (g kg^{-1})	0.53	1.84	1.60	5.08
Total C (%)	1.12	3.75	2.87	19.79
Total N (%)	0.09	0.33	0.27	1.25
K (mg kg^{-1})	728	3829	3570	11,628
Ca (mg kg^{-1})	2020	6937	6544	45,279
Mg (mg kg^{-1})	510	4703	4299	40,435
Na (mg kg^{-1})	161	376	300	1255
CEC ($cmol_c kg^{-1}$)	10	21	19	48
Total Zn (mg kg^{-1})	29.63	89.90	89.15	154.16
Zn_{pw} (μg L^{-1})	44.26	282.65	254.70	781.70
$C_{DGT\text{-}Zn}$ (μg L^{-1})	0.68	3.12	1.85	26.66
Extractable Cl (mg kg^{-1})	6.71	30.11	22.16	160.29
Soil Fe (mg kg^{-1})	5891	23,730	21,279	66,971
Soil Al (mg kg^{-1})	16,333	50,997	36,192	144,385
Soil Mn (mg kg^{-1})	145	790	523	2829
Soil S (mg kg^{-1})	180	549	471	1971
Cd_{Tot} (mg kg^{-1})	0.02	0.37	0.29	1.35
$Cd_{Ca(NO3)2}$ (μg kg^{-1})	0.05	8.18	3.76	60.21
$C_{DGT\text{-}Cd}$ (μg L^{-1})	0.04	0.83	0.76	2.10
Cd_{pw} (μg L^{-1})	0.06	18.37	21.01	76.32
Total rainfall (mm)	56	416	421	816
Temperature (°C)	8.94	14.51	14.41	21.85
Radiation (KMJ M^{-2} d^{-1})	0.80	3.05	3.51	4.28

2.2. Soil cadmium bioavailability testing

The calcium nitrate extractable soil Cd fraction (forthwith, $Cd_{Ca(NO3)2}$) was determined following the method described by Gray et al.

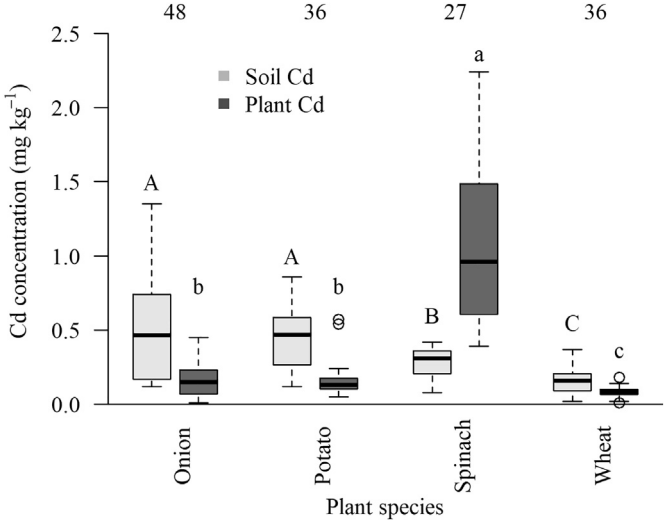

Fig. 1. Boxplot showing Cd concentrations in four cropping soils and plants (dry biomass, DW). Median values between different categories are significantly different where labelled with different letters, with upper and lower cases used for soil and plant concentrations, respectively ($P > 0.05$).

(1999c). Briefly, 5 g of soil was equilibrated with 30 mL of 0.05 M Ca $(NO_3)_2$ (Sigma-Aldrich) for 2 h in an end-over-end shaker. The suspension was then centrifuged for 10 min at 3300 rpm, after which the supernatant was filtered using a Whatman 52 filter paper. The filtrate was stored at −20 °C until analysis.

The DGT-measured Cd fraction followed an adapted version of the method described by Zhang et al. (1998). Here, air-dried soil (*ca.* 20 g) was weighed into a small clean cylindrical container, where the soil extended at least 1 cm in each direction from the probe interface. DI water was added to create a homogeneous slurry with a moisture content equivalent to 100% maximum water-holding capacity, after which the slurry was left to equilibrate for 48 h at room temperature. Standard DGT soil probes were used, which comprised of an agarose cross-linked polyacrylamide (APA) hydrogel layer (thickness of 0.08 cm), polyethersulfone filter membrane (0.45 μm pore diameter; 0.014 cm thickness) and a 0.04 cm-thick APA resin gel with Chelex-100 binding resin (200–400 mesh, Bio-Rad), housed within in a polycarbonate piston probe (DGT Research Ltd.). The probes were deployed ensuring complete contact between the soil slurry and the device sampling window (physical area: 2.54 cm^2). The deployment took place in a humidity (100%) and temperature-regulated (21 ± 1 °C) incubator for 24 h. At the end of the deployment the soil attached to the DGT devices was carefully removed using a gentle jet of DI water and the housings were dismantled. The resin gels were eluted with 1 mL of 1 M HNO_3 for 24 h. Following DGT retrieval, the soil porewater Cd and Zn concentrations (forthwith, Cd_{pw}, and Zn_{pw}, respectively; μg L^{-1}) was measured, as described by Ernstberger et al. (2002). Briefly, the slurry was allowed to equilibrate for up to 4 h, after which it was transferred into a 50 mL centrifuge tube and centrifuged at 2000 rpm for 10 min. The supernatant was then filtered through a polyethersulphone disc filter (0.45 μm). The filtrate was diluted two-fold with 0.1 M $Ca(NO_3)_2$ immediately after filtration and stored at −20 °C until analysis.

The total mass (M) of Cd bound by the resin gel during the deployment was calculated using Eq. (1):

$$M = C_e \times (V_{eluent} + V_{resin})/f_e \quad (1)$$

where, C_e is the concentration of the metal in the eluent, V_e and V_r are the eluent and resin volumes, respectively, and f_e is the metal-specific elution efficiency, (0.84 for Cd according to Garmo et al. (2003)).

The DGT-extractable Cd and Zn concentrations ($C_{DGT\text{-}Cd}$ and $C_{DGT\text{-}Zn}$, μg L^{-1}) were calculated according to Eq. (1) (Zhang et al., 1998).

$$C_{DGT} = M \times \delta_{MDL}/(D \times A_E \times t) \quad (2)$$

where, δ_{MDL} is the total thickness of the material diffusion layer (diffusive hydrogel and filter membrane: 0.094 cm), D is the temperature-specific diffusion coefficient for the two metals in the diffusive gel (cm^2 s^{-1}) over the deployment time (at 21 °C); A_E is the effective exposure area of the DGT device (3.08 cm^2); and t is the deployment time (s). All extracts and eluents were diluted five-fold with 2% HNO_3 before Cd analysis.

2.3. Climate information

Weather data for each sampling site was obtained from the nearest climate station of the NZ National Institute of Water and Atmospheric Research to each site. The data collected comprised of total solar radiation, total annual rainfall and the average daily air temperature (forthwith 'average temperature') for the crop-specific growth periods at the respective sites.

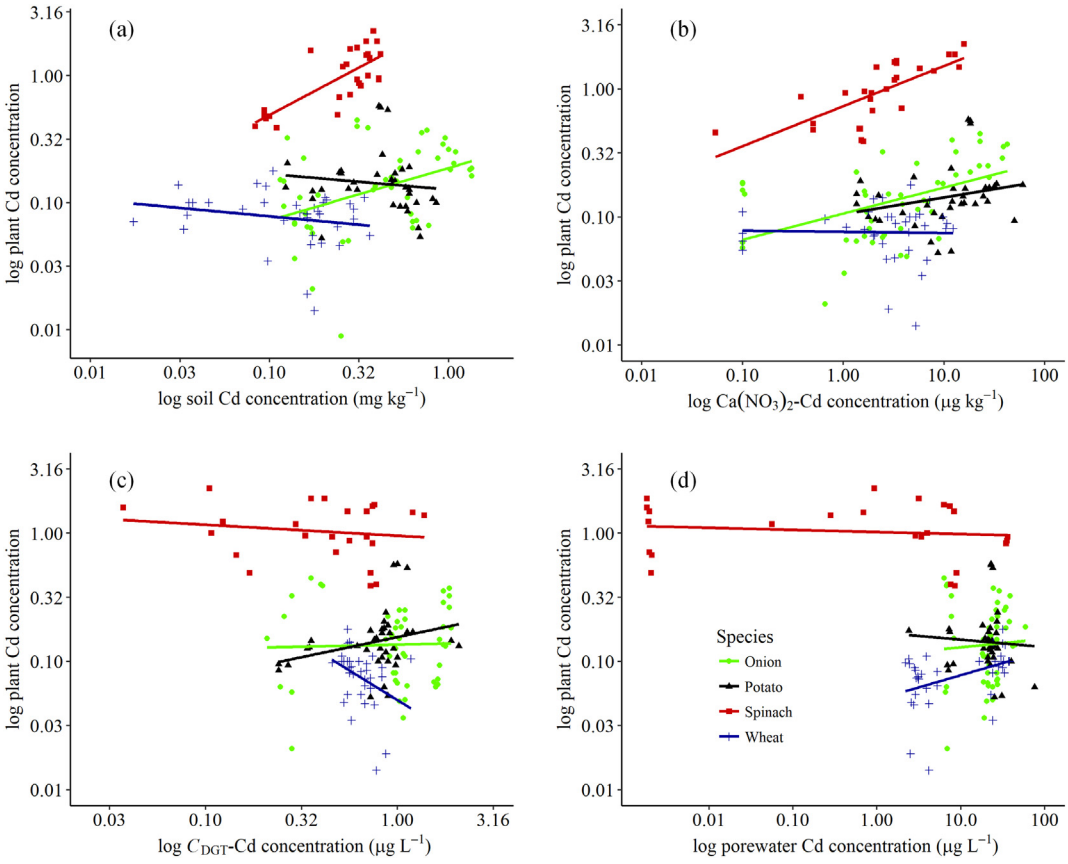

Fig. 2. Relationships between plant Cd (mg kg^{-1} DW) and (a) soil pseudo-total Cd concentration, (b) 0.05 M $Ca(NO_3)_2$-extractable Cd, (c) DGT-extractable Cd and (d) soil Cd concentration in soil porewater. The equations and coefficients of determination for the linear regression lines shown are given in Table 3.

Table 3
Regression equations and coefficients of determination (R^2) for relationships between different bioavailability tests and Cd concentrations in edible plant parts.

Plant part	Test	Regression equations	R^2
Onion bulb	Total	$\log(Cd_{onion}) = -0.05 + 0.40 \log(Cd_{Tot})$	0.164**
	0.05 M $Ca(NO_3)_2$	$\log(Cd_{onion}) = 1.46 + 1.09 \log(Cd_{Ca(NO3)2})$	0.259**
	DGT	$\log(Cd_{onion}) = -0.01 + 0.02 \log(C_{DGT\text{-}Cd})$	0.001(NS)
	Porewater	$\log(Cd_{onion}) = 1.32 + 0.02 \log(Cd_{pw})$	0.001(NS)
Potato tuber	Total	$\log(Cd_{potato}) = -0.50 + 0.11 \log(Cd_{Tot})$	0.013 (NS)
	0.05 M $Ca(NO_3)_2$	$\log(Cd_{potato}) = 1.40 + 0.48 \log(Cd_{Ca(NO3)2})$	0.062 (NS)
	DGT	$\log(Cd_{potato}) = 0.10 + 0.26 \log(C_{DGT\text{-}Cd})$	0.082 (NS)
	Porewater	$\log(Cd_{potato}) = 1.23–0.17 \log(Cd_{pw})$	0.001 (NS)
Spinach leaves	Total	$\log(Cd_{spinach}) = -0.60 + 0.79 \log(Cd_{Tot})$	0.589***
	0.05 M $Ca(NO_3)_2$	$\log(Cd_{spinach}) = 0.39 + 1.69 \log(Cd_{Ca(NO3)2})$	0.529***
	DGT	$\log(Cd_{spinach}) = -0.40 - 0.27 \log(C_{DGT\text{-}Cd})$	0.023 (NS)
	Porewater	$\log(Cd_{spinach}) = -0.36 - 0.94 \log(Cd_{pw})$	0.015 (NS)
Wheat grain	Total	$\log(Cd_{wheat}) = -1.25 - 0.31 \log(Cd_{Tot})$	0.041(NS)
	0.05 M $Ca(NO_3)_2$	$\log(Cd_{wheat}) = 0.31–0.06 \log(Cd_{Ca(NO3)2})$	0.001(NS)
	DGT	$\log(Cd_{wheat}) = -0.34 - 0.13 \log(C_{DGT\text{-}Cd})$	0.116*
	Porewater	$\log(Cd_{wheat}) = 1.95 + 0.91 \log(Cd_{pw})$	0.172*

NS = not significant.
* $P < 0.05$.
** $P < 0.01$.
*** $P < 0.001$.

2.4. Trace element analyses and quality control

Cadmium in the soil digests, and Cd and Zn in the DGT eluents, were analysed by inductively-coupled plasma mass spectrometry (ICP-MS, Agilent-7500cx). The other elements in the soil digests and all plant digests and other soil extracts ($Ca(NO_3)_2$ and porewater) were analysed using optical emission spectrometry (ICP-OES, Varian 720 ES – USA). Internal and external reference soils (NIST Montana 2711; Interlab internal WEPAL soil 921; Interlab internal WEPAL soil 981), and plants (NIST 1573a, tomato leaves; ASPAC internal clover; ASPAC internal beetroot) were used as standard reference materials to confirm both the extraction efficiency of the digests and the accuracy of metal analysis on both instruments and comparability between them. The recovery ratios of the standard soils varied from 96 to 106% for Cd and 92–93% for Zn, while standard plants ranged between 92 and 96% for Cd and 103–105% for Zn, respectively.

2.5. Statistical analysis

One-way ANOVA or Kruskall-Wallis tests were used to determine differences in soil and plant Cd concentrations between crops species. Correlations between plant Cd or Zn concentrations and single environmental variables were tested using Spearman correlation coefficients. Stepwise multiple linear regression analyses were used to develop multiple regression models (MRM) to represent plant tissue Cd concentrations and investigate the influence of environmental variables, soil Cd and Zn concentrations, soil properties on these. The different NZ Regions where the crops were grown were included as categorical predictors. Variables were log-transformed if identified as non-normally distributed by the Shapiro-Wilk test. The variance inflation factor (VIF) was used as the criterion to reduce multi co-linearity of the variables in the MRM: predictors with VIF > 5 were excluded. Where VIFs were between 2 and 5, the correlations between MRM variables were tested and where those correlations were significant (*i.e.* Olsen-P and $Cd_{Ca(NO3)2}$ in spinach soils: $\rho = 0.569$; $P < 0.01$, not shown) only the bioavailability test variable was retained in the model. The stepwise linear regression analysis was carried out using Minitab 17 (Minitab, LLC) and all other statistical analyses were carried out using the R software (Pinheiro et al., 2012). Variables that were not significant predictors in the model were excluded from the MRMs. Because soil properties varied between plots within sites, the regression analyses were undertaken using individual plot data, where available. The exception to this was the information on the analytes measured in a single composite sample (*i.e.* particle size distribution and extractable Cl) which was comprised of samples taken along a 50 m transect representative of each site (*c.f.* Supporting Information) and these values were assumed to be representative of all plots on that site. As noted earlier, Zn deficiency has been identified as possible cause of increased Cd uptake by plants. Therefore, Zn concentrations measured both in the plant tissues and in the same samples as Cd from the different bioavailability tests (but not different tests) were included as possible predictors in the multiple regression analyses. Significance was assessed at the 5% level throughout, unless stated otherwise.

3. Results and discussion

3.1. Relationships between plant cadmium concentrations, bioavailability tests and soil variables

Variability in the Cd concentrations in spinach leaves was best represented by $Cd_{Ca(NO3)2}$ (R^2: 0.529) and Cd_{Tot} (R^2: 0.589) ($P < 0.001$)(Fig. 2; Table 3). This is the first comparison of the tests considered in this work being used to estimate the bioavailability of Cd to spinach, however others have shown that they correlate significantly with Cd concentrations in a wide variety of other leafy plants, such as lettuce, ryegrass and clover (Cd_{Tot} R^2: 0.59–0.81; $Cd_{Ca(NO3)2}$ R^2: 0.42–0.79)(Gray et al., 1999b; Black et al., 2011). The $Cd_{Ca(NO3)2}$ concentrations also provided the best representation of Cd concentration in onion bulbs, although the correlation was weaker than for spinach (R^2: 0.259; $P < 0.01$). The $Cd_{Ca(NO3)2}$ correlated well with soil pH ($\rho = -0.71$; $P < 0.01$; Table 4), which agrees with previous studies that have shown pH as a critical determinant of soluble Cd concentrations in NZ soils and elsewhere (Gray et al., 1999a; Hooda, 2010; Reiser et al., 2014). The significant positive correlations between $Cd_{Ca(NO3)2}$ and soil total Fe, Al and Mn concentrations (Table 4) agrees with results from Gray et al. (1999a) and suggests that the test can solubilize some of the Cd associated with Fe-, Al- and Mn-oxide soil minerals to a greater extent than $C_{DGT\text{-}Cd}$ and Cd_{pw} (see also below).

The $C_{DGT\text{-}Cd}$ concentrations were higher than those found in other agricultural soils in the United States and China, not subject to industrial contamination (Pérez and Anderson, 2009; Williams et al., 2012) (0.02–0.63 μg L^{-1}) which is most likely due to the generally lower Cd_{Tot} (0.084–0.356 mg kg^{-1}) in those studies, while Cd_{pw} concentrations were similar to those measured elsewhere (0.002–125.0 μg L^{-1}) (Black et al., 2011; Williams et al., 2012; Song et al., 2015). Only $C_{DGT\text{-}Cd}$ and Cd_{pw} correlated with wheat grain Cd concentrations, but the relationship with the former was negative and relatively weak (R^2 0.116;

Table 4
Spearman correlations (ρ) between Cd bioavailability tests and soil chemical variables.

Parameter	$Cd_{Ca(NO3)2}$ (μg kg^{-1})	$C_{DGT\text{-}Cd}$ (μg L^{-1})	Cd_{pw} (μg L^{-1})
pH	−0.71**	−0.08	−0.11
Sand (%)	−0.24**	0.12	−0.03
Silt (%)	−0.32**	−0.10	0.02
Clay (%)	0.28**	−0.09	0.01
Olsen-P (mg kg^{-1})	0.15	0.10	−0.10
Total P (g kg^{-1})	0.22**	0.22**	0.26**
Total C (%)	0.24**	0.15	0.33**
Total N (%)	0.22**	0.15	0.36**
C/N ratio	0.06	0.00	−0.20*
K (mg kg^{-1})	−0.14	−0.41**	−0.26**
Ca (mg kg^{-1})	−0.47**	−0.10	0.01
Mg (mg kg^{-1})	−0.15	−0.32**	−0.21*
Na (mg kg^{-1})	−0.06	0.34**	0.15
CEC ($cmol_c$ kg^{-1})	0.16	0.07	0.01
Total Zn (mg kg^{-1})	0.23**	−0.05	0.10
Extractable Cl (mg kg^{-1})	0.19*	0.21**	0.20*
Soil Fe (mg kg^{-1})	0.21*	−0.37**	−0.40**
Soil Al (mg kg^{-1})	0.39**	−0.03	−0.11
Soil Mn (mg kg^{-1})	0.18*	0.06	−0.05
Soil S (mg kg^{-1})	0.35**	0.19*	0.28**
Cd_{Tot} (mg kg^{-1})	0.24**	0.36**	0.29**
$C_{DGT\text{-}Cd}$ (μg L^{-1})	0.18*		
Cd_{pw} (μg L^{-1})	0.28**	0.37**	

Significant relationships are indicated by * ($P < 0.05$) and ** ($P < 0.01$).

$P < 0.05$) and only slightly stronger and positive for the latter (R^2 0.172; $P < 0.05$; Table 3). The poor correlation between $C_{DGT\text{-}Cd}$ and plant concentrations is contrary to previous reports that have shown DGT to estimate well the Cd uptake by spinach (Oporto et al. (2009) at low available Cd concentrations), wheat and potato (Nolan et al., 2005; Pérez and Anderson, 2009). Black et al. (2011) found that the DGT-derived Effective Concentration (C_E) was able to predict Cd uptake better than $Ca(NO_3)_2$, where it predicted 49% of the variability in Cd concentration in wheat shoots, compared to 34% by the latter. The results presented here used $C_{DGT\text{-}Cd}$ instead of C_E; however, these two measurements generally vary proportionally to each other (Degryse et al., 2009b) and, therefore, the difference in the relationship to plant tissue concentrations between the two is likely to be insignificant. The index R_{DGT} ($C_{DGT\text{-}Cd}/Cd_{pw}$) shows the relationship between DGT-measured and porewater concentrations, where low values ($R_{DGT} < 0.1$) are indicative of mostly diffusive supply of solute from the soil to the probe interface, with little buffering from labile solid phase reservoirs (Davison et al., 2007). 73% of the samples analysed here had R_{DGT} values below this threshold, which suggests that the DGT-labile solid phase fraction of Cd in these soils was generally lower than seen in other studies (Senila et al., 2012; Dočekalová et al., 2015). McLaughlin et al. (2011) have highlighted the importance Cd transport to leaves from the soil *via* plant transpiration, where advective transport of the metal to the root is likely to be important. Lehto et al. (2006) showed that this transport mechanism is likely to be most important for determining how much solute can be taken up when (re)supply from solid phases (buffering) is low. Spinach has been shown to take up Cd^{2+} at a greater rate than can be resupplied by diffusion alone (Degryse et al., 2012). Hence, the relationship between $C_{DGT\text{-}Cd}$ and spinach Cd concentrations is probably weak because DGT cannot account for the advective transport of Cd from the soil to spinach roots in these soils. The DGT-measured and porewater Cd concentrations ($C_{DGT\text{-}Cd}$ and Cd_{pw}) correlated weakly with soil Fe (ρ values of −0.37 and −0.40, respectively; $P < 0.01$) (Table 4), which may be driven by iron (oxyhydr)oxide minerals reducing the availability of the metal to be measured by these methods through sorption and occlusion (McLaren and Cameron, 1996), the fact that the relationship is relatively weak is probably due to the importance of the types of minerals involved, rather than the amount Fe present (Smith, 1999) and the influence of other factors, such as pH.

There were significant but weak positive correlations between all of the soil Cd bioavailability tests and Cd_{Tot} ($0.24 < \rho < 0.36$; $P < 0.01$) (Table 4). Total soil Cd concentrations also correlated with various soil variables (in order of decreasing ρ): P > S > Mn > Al > CEC ($0.86 > \rho > 0.49$; $P < 0.001$, not shown). The relationship between Cd_{Tot} and soil P and S is likely to reflect the historic use of superphosphate fertilizer on those soils (Taylor, 1997), while Mn, Al and CEC are indicative of the soils' capacity to retain Cd, where Mn and Al minerals can provide reactive surfaces that bind Cd from the fertilizers (Backes et al., 1995). Soils with short-range order Al minerals (*e.g. allophane*), also bind phosphate (Parfitt et al., 2005) and, hence, require higher rates of P fertilizer application to sustain productivity, which in turn would also increase the amount of Cd applied to the soil. Other studies have shown through multiple regression analysis how combinations of soil variables can be used to model $Cd_{Ca(NO3)}$ (Gray et al., 1999a; Gray and McLaren, 2006) and $C_{DGT\text{-}Cd}$ (Pérez and Anderson, 2009). Multiple regression analysis that considered various combinations of the variables given in Table 2 was carried to estimate the $Cd_{Ca(NO3)2}$, $C_{DGT\text{-}Cd}$ and Cd_{pw} concentrations measured here. The predictions by these models did not improve upon the results of single regression analysis shown above (results not shown).

3.2. Regional differences in cadmium uptake and other contributory soil variables

The plant uptake factor (PUF = Cd_{plant}/Cd_{Tot}) compares plant (Cd_{plant}, mg kg^{-1} DW) and soil Cd concentrations between the paired samples and can be used to provide a general indicator of differences between the plants' affinity to take up and translocate Cd across the various regions. The PUF results showed that Canterbury generally had the highest Cd PUF across all crops and significant differences between regions were found for onion, potatoes and wheat (Fig. S2). Inclusion of the NZ Region where the samples were grown as a categorical variable in the MRM improved relationships between the Cd bioavailability tests and plant Cd concentrations for all species (Table 5). When the Regions were included as categorical variables, $Cd_{Ca(NO3)2}$ was able to predict a larger proportion of the variability in Cd concentrations in onion bulbs and spinach leaves (R^2_{adj}: 0.596 and 0.790, respectively; Table 5). When considered together with the previously noted strong negative correlation between soil pH and $Cd_{Ca(NO3)2}$ (Table 4), it further indicates that managing soil pH can be an effective tool for reducing Cd uptake by onion and spinach across NZ. However, it should be noted that the addition of Ca^{2+} ions with lime may result in increased Cd solubility and

Table 5
Multiple regression models describing Cd concentrations in onion, potato, spinach and wheat, with the different growing regions in New Zealand included as categorical variables. All model variables were significant ($P < 0.001$).

Plant	Region	Region constant, R_{c_plant}	Regression equation	R^2_{adj} ($P < 0.001$)
Onion	Auckland	−0.46	$\log(Cd_{onion}) = R_{c\_onion} + 0.12 \log(Cd_{Ca(NO3)2})$	0.596 n = 48
	Canterbury	−0.88		
	Hawkes Bay	−1.32		
	Waikato	−0.72		
Potato	Auckland	−0.02	$\log(Cd_{potato}) = R_{c\_potato} + 0.04 \log(C_{DGT\text{-}Cd}) + 2.84 \log(\text{air temperature}) - 1.19 \log(\text{Total P})$	0.767 n = 36
	Canterbury	−0.86		
	Ma-Wan	−0.37		
	Waikato	−0.28		
Spinach	Auckland	−0.21	$\log(Cd_{spinach}) = R_{c\_spinach} + 0.37 \log(Cd_{Ca(NO3)2})$	0.790 n = 27
	Canterbury	−0.43		
	Gisborne	−0.08		
	Ma-Wan	−0.01		
	Tasman	−0.07		
	Waikato	−0.13		
Wheat	Canterbury	0.58	$\log(Cd_{wheat}) = R_{c\_wheat} + 0.08 \log(Cd_{pw})$ - ...0.51 $\log(\text{Olsen-P}) - 0.80 \log(Zn_{wheat})$	0.579 n = 36
	Hawkes Bay	0.63		

Ma-Wan: Manawatu-Wanganui

plant-availability (Bolan et al., 2003; Shaheen and Rinklebe, 2015). None of the methods tested here could successfully represent Cd concentrations in potato tuber by themselves; however, this was achieved by a MRM that included $C_{DGT\text{-}Cd}$, average air temperature and soil total P concentration (R^2_{adj}: 0.767; Table 5), while Cd_{pw}, Olsen-P, wheat grain Zn concentration provided the best model to describe Cd accumulation in wheat grains (R^2_{adj} 0.579; Table 5). The overall representation of plant tissue concentrations by the bioavailability tests ($Cd_{Ca(NO3)2}$, $C_{DGT\text{-}Cd}$ and C_{pw}) was better than those when total Cd concentrations were included in a MRM: there the variability in Cd concentrations in onions was best represented when including the same Regions (as categorical variables), Cd_{Tot} and soil pH (R^2_{adj} 0.50; n = 88), while the best model to describe Cd in spinach included using Cd_{Tot}, extractable Mg and Zn_{Tot} (R^2_{adj} 0.55; n = 64) (Cavanagh et al., 2019). No significant relationships were found between soil properties and Cd concentrations in potato (Gray et al., 2019a) or wheat (Gray et al., 2019b).

The influence of growing region on Cd uptake by the different species, as indicated by the Region constant, R_{c_plant}, was greatest for Cd concentrations in onion and potato (Table 5). The effect of regional differences was also reported by Pérez and Anderson (2009), who successfully employed specific MRMs that used $C_{DGT\text{-}Cd}$ and soil properties to explain Cd uptake by potato and wheat at different field sites with varied climates, soil types and agricultural management practices. Regional influence may result from environmental factors contributing to the differences in climate and soil variables, as well as farm management responses to those differences (*e.g.* irrigation scheduling, crop rotation and tillage) (Oliver et al., 1993; Cooper et al., 2011), whose full influence on Cd availability for plant uptake is unlikely to be captured by these soil tests or other variables that were included in the analysis. For the onion and spinach samples analysed here, only these unspecified regional differences were significant in helping to model the relationship between $Cd_{Ca(NO3)2}$ and tissue Cd concentrations. The negative relationship between total P concentration and potato tuber Cd concentration may be an indirect reflection of the strong binding of P and Cd by Al- and Fe-oxide minerals that are abundant in the soils of the Auckland and Waikato Regions (as reflected by their high region constants, R_{c_potato}, in Table 5).

Temperature was the only climatic variable that was found to significantly affect crop Cd uptake and it was important for determining Cd accumulation in potato tubers (Table 5). Previous studies have shown a positive relationship between temperature and Cd uptake rates through its effect on transpiration rates (Hooda and Alloway, 1993; Tudoreanu and Phillips, 2004). In this study, high transpiration rates may have facilitated Cd accumulation in the stem and leaves of the potato plant, and subsequent translocation of the metal through the phloem into the tuber (Reid et al., 2003; Chen et al., 2014). The mean extractable Cl concentration in the potato soils was 2.7 times higher than in the spinach soil ($P < 0.001$), and the link between Cl and Cd accumulation in tubers has been identified previously at higher Cl concentrations (mean value of 230 mg kg^{-1}) in South Australia (McLaughlin et al., 1994; McLaughlin et al., 1997). Although that connection is not as clear here, Degryse et al. (2012) showed that buffering of Cd^{2+} ion concentrations by cadmium chloride-complexes at the root interface can reduce the diffusion limitation to plant uptake, and therefore diminish the contribution that advective mass flow would make to the overall Cd uptake. This may explain why Cl is a significant explanatory variable in the MRM, along with regional differences, for relating $C_{DGT\text{-}Cd}$ to Cd accumulation in the tuber. This is further supported by the significant correlation between $C_{DGT\text{-}Cd}$ and Cl in the soils analysed (ρ 0.21, $P < 0.01$; Table 4).

The Cd concentration in wheat grains was related positively to Cd_{pw} and negatively to Olsen-P and grain Zn concentration (Table 5). Competition between Zn and Cd for transport across the root cell membrane and subsequent translocation within the plant has been suggested as a possible control for Cd accumulation in wheat (Hart et al., 2002). Olsen-P in the wheat soils correlated with (bioavailable) Zn measured by DGT and 0.05 M $Ca(NO_3)_2$ (ρ = 0.427 and 0.633, respectively; $P < 0.001$; not shown), which indicates that plant availability of Zn in those soils is sufficient to limit the accumulation of Cd into the wheat grains, even when the higher fertility could allow increased biomass production. The net effect of this would be an overall dilution of Cd concentrations in the grain. The effects of P availability on grain Cd concentrations are inconsistent between studies: they have been shown to increase with (low Cd) P fertilizer applications (Grant et al., 2002; Grant et al., 2013), while others linked an increase in biomass to a decrease in grain Cd concentrations (albeit with a much higher Cd_{Tot} of 3.13 mg kg^{-1})(Rehman et al., 2015). The results from this work agree best with Jiao et al. (2004) who demonstrated that combined application of Zn and P to soil achieved a net reduction in wheat grain Cd concentrations. Weak or non-linear relationships between Cd_{pw} and grain Cd concentrations ($P < 0.01$) have been identified previously (Nolan et al., 2005; Pérez and Anderson, 2009; Black et al., 2011), although they did not suggest reasons for these. It could indicate that Cd uptake by wheat is not limited by diffusion (Lehto et al., 2006), which would also be linked to the regulation of Cd^{2+} entry into roots by Zn^{2+} ions, despite the possible effects of increased biomass; solute fluxes to DGT are not affected by such competitive effects at the concentrations seen here, so $C_{DGT\text{-}Cd}$ is less likely to mimic such an effect (Degryse et al., 2009b).

4. Conclusion

The use of different soil Cd bioavailability tests enabled the identification of factors that can contribute to the accumulation of Cd in the edible parts of spinach, onions, potatoes and wheat that could not be identified previously through the use of total Cd concentrations. Moreover, they have helped to predict a larger amount of the variability in the tissue Cd concentrations. Over 77% of the variability in the spinach leaf and potato tuber Cd concentrations was predicted by $Cd_{Ca(NO3)2}$ and $C_{DGT\text{-}Cd}$, respectively, once differences between growing regions, as well as other environmental factors were considered (total P and air temperature for potato). The ability of the two tests to achieve this may reflect the extent to which Cd uptake by the two plants is limited by diffusion in their respective soils, and indirectly suggest that differences in transpiration rates can be more important for Cd uptake by spinach than for potatoes. The best evidence for antagonistic effects by other soil nutrients was seen for wheat grain Cd uptake, where the results confirm previous findings that Zn uptake by the plant could be significant. These results not only underline the greater mechanistic insight that can be gained from using different bioavailability tests, but also their value for estimating possible risks to consumers of these crops with greater precision. Our results also suggest that, on a per unit mass of plant material consumed basis, the highest potential risk to consumers from Cd may be from plants grown on low pH soils, where the Cd solubility is highest, this is especially likely to be important to spinach grown in the Manawatu-Wanganui and Tasman Regions and onions grown in the Auckland Region. On the other hand, wheat grown on soils with low Zn and P bioavailability may have higher Cd grain concentrations, than can be expected from total soil Cd concentrations alone.

While specific drivers for differences between the different growing regions for the plants were not able to be identified, these results further highlight the need to consider other site-specific variables to better understand other factors that may be important, these could include other variables that influence transpiration (*e.g.* relative humidity, wind and soil moisture), as well as differences in biomass production. A better understanding of these factors will further contribute to more effective management practices for reducing the potential risks arising from the transfer of soil Cd to common food crops.

Declaration of competing interest

We confirm that none of the authors are aware of any conflicts of interest regarding this work.

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Appendix A. Supplementary data

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