Stafford, A., Jeyakumar, J., Anderson, C., Hedley, M., 2017. Influence of fluctuating soil moisture on cadmium phytoavailability and accumulation in plantain. In: Science and policy: nutrient management challenges for the next generation. (Eds L.D. Currie and M.J. Hedley). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 30. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 8 pages.

INFLUENCE OF FLUCTUATING SOIL MOISTURE ON CADMIUM PHYTOAVAILABILITY AND ACCUMULATION IN PLANTAIN

Aaron Stafford[1], Jeya Jeyakumar[2], Chris Anderson[2] and Mike Hedley[2]

[1]Ballance Agri-Nutrients, Private Bag 12503, Tauranga 3143, New Zealand
[2]Institute of Agriculture & Environment, Massey University Manawatu,
Private Bag 11 222, Palmerston North 4442, New Zealand
Email: Aaron.Stafford@ballance.co.nz

Abstract
A pot trial was undertaken on contrasting Allophanic and Gley soils (total cadmium [Cd] 0.79 and 0.61 mg kg^{-1}, respectively) to explore the effect of fluctuations in soil moisture on soil Cd phytoavailability and Cd accumulation in plantain. Increases in 0.05 *M* $CaCl_2$ soil extractable Cd concentration aligned with increases in soil moisture following periods of soil drainage/drying. However, there was no difference ($P > 0.05$) in soil extractable Cd or plantain Cd concentrations under either continuously-drained or 3-day flooded/11 day drained irrigation regimes, indicating that short-term saturation and the onset of reducing conditions has little influence on soil Cd phytoavailability. Despite the greater total Cd concentration of the Allophanic soil, soil extractable Cd concentrations were much greater in the Gley soil, likely due to its much lower soil pH and organic matter content. Overall, the difference in soil extractable Cd concentrations between soil types was much greater than the fluctuations brought about by changes in soil moisture. These results are discussed in the context of managing Cd accumulation in Cd-sensitive crops.

Introduction
Cadmium in a non-essential element that is readily taken up by plants, with plant tissue Cd concentrations increasing with increasing soil Cd phytoavailability (Adriano, 1986; Smolders and Mertens, 2012). Increased Cd accumulation in agricultural plant species is undesirable since this increases dietary exposure to grazing livestock, and ultimately, humans.

Many factors are known to influence phytoavailability of Cd and other metals in the soil, most importantly soil pH, which is considered to be the single largest factor influencing metal solubility (Bolan et al., 1999; Christensen and Haung, 1999; Gray et al., 1999; Loganathan et al., 2012; Young, 2012). Change in soil redox potential, driven by variation in soil moisture, is also another factor. Internationally, most research on the influence of soil moisture on Cd phytoavailability has focused on prolonged periods of soil saturation (e.g. cultivation of rice), where development of strongly-reducing soil conditions leads to a decrease in Cd solubility through the formation of insoluble Cd-sulphide complexes (de Livera et al., 2011; Zhang et al., 2012; Zheng et al., 2013).

Such soil moisture extremes are not relevant to New Zealand agricultural soil conditions, and little information exists on Cd phytoavailability under fluctuating soil moisture conditions that are typified by only short periods (i.e. several days) of soil saturation. However, phytoavailability of cobalt (Co) and arsenic (As) is known to increase under weakly- to moderately-reducing soil conditions, linked to the dissolution of iron (Fe) and manganese

(Mn) hydrous oxides that provide important sorption surfaces for these metals (Cornu et al., 2009; Bhatti et al., 2013). As Fe/Mn hydrous oxides are also important sorption surfaces for Cd (Kim and Fergusson, 1992; Backes et al., 1995; Gray et al., 1999; Loganathan et al., 2012), it is possible that fluctuations in soil moisture may also influence Cd phytoavailability in soils. Given the paucity of data, research was designed to evaluate the effects of fluctuating soil moisture and short periods of soil saturation on soil Cd phytoavailability.

Methodology

Two contrasting soils (Kereone fine sandy loam and Topehaehae sandy clay loam; Table 1), were sourced from a Waikato dairy farm in early April 2015 and sieved to 4 mm. This soil was then potted into square 5 litre containers that were adapted (following the methodology of Bhatti et al. (2013)) to facilitate contrasting irrigation strategies. These irrigation strategies (based on the methodology of Bhatti et al. (2013)) were

(i) 'Non-flooded', where soil moisture was maintained at 70% potted field capacity (Fc_P) utilising a 7-day irrigation cycle; and

(ii) 'Flooded', where soil moisture was maintained at 110% Fc_P for 3 days, subsequent to which drainage was permitted allowing aeration of the soil over the ensuing 11 days, before the 14-day irrigation cycle was repeated.

For each soil type x irrigation treatment, pots were either sown in plantain (Plantago lanceolata, cultivar 'Ceres Tonic') or left as an unplanted control. Plantain was chosen as the Cd-phytoavailability indicator species since previous research (Stafford et al., 2016) had shown it to be a 'Cd-accumulator'. Five replicates of each treatment were used (i.e. 40 pots in total).

Table 1. New Zealand Soil Classification and characteristics of the two soils used in this study.

Soil type	New Zealand Soil Classification	tCd	tP	tMn	tFe	tC	pH	CEC	P retention
		(mg kg^{-1} DW)			(%)			(meq/100 g)	(%)
Kereone fine sandy loam	Typic Orthic Allophanic	0.79	1577	1840	2.1	5.7	6.3	26	69
Topehaehae sandy clay loam	Typic Recent Gley	0.61	1132	710	2.4	3.2	5.6	17	34

Following sowing of the plantain seeds (20 April 2015) all pots were laid out in 4 rows of 10 pots in completely randomised design. Divergence in irrigation strategy occurred on 10 May 2015 (day 0), once seedlings had germinated and had been thinned to one healthy plant per pot. The trial was completed on 13 September 2015 (day 126). The trial was carried out under a clear Perspex-roofed shelter at ambient air temperature (ranging from 0.1 to 21.7 °C) in Tauranga, Bay of Plenty. Pots were rotated on a weekly basis to ensure there was no environmental bias for any replicate.

A single soil core (100 mm depth, 18 mm diameter) was extracted from each pot immediately prior to the initiation of each 14-day irrigation cycle ('pre-irrigation'), and then again 3 days later ('+3 days') aligning with the end of the saturated phase of the flooded treatments. In total, this fortnightly soil sampling cycle was repeated 9 times (i.e. 18 sampling occasions). Soil removed at each sampling was backfilled with surplus soil from each soil type that had been sieved and kept in storage. Soil sampling sites were rotated clockwise around each pot, with the location of backfilled soil sampling sites marked with a toothpick.

Plantain was harvested from all pots when 'grazing-maturity' was reached within the treatments exhibiting the greatest growth rates (day 126). Plant tissue samples were harvested 20 mm above the soil surface, weighed, washed and oven-dried (60°C for 3 days) for dry matter content (% DM), dry matter yield (g DM pot^{-1}) and tissue Cd (mg kg^{-1} DM) assessment.

Subsamples (6 g wet weight) from each soil core were extracted in 30 mL 0.05 *M* $CaCl_2$ with 24 hours end-over-end shaking, before centrifuging (11,953 g for 10 minutes) and filtering (Whatman No. 42). Plant tissue samples were crushed and homogenised before 0.1 g subsamples were digested in 10 mL of concentrated nitric acid. Cadmium in the soil extracts and plant tissue digests was assessed using a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS; Perkin-Elmer AAnalyst 600). The pH of 0.05 *M* $CaCl_2$ soil extracts was assessed for all samples at sampling days 0, 28, 84 and 112.

Results and discussion

Soil extractable Cd concentrations

Separated into groups representing pre-irrigation and +3 day sample timings, mean soil extractable Cd concentration was significantly ($P < 0.001$) influenced by soil type, although plant and irrigation regime had no significant ($P > 0.05$) effect (Table 2). Overall, soil extractable Cd concentration was approximately 4-times greater in the Topehaehae soil (85 µg kg^{-1}) than the Kereone soil (20 µg kg^{-1}), despite the Kereone soil having the greater total Cd concentration. Mean soil extractable Cd concentrations were consistently greater for the +3 day samples relative to the pre-irrigation samples, however these differences were small relative to the effect of soil type, and only reached significance ($P < 0.05$) for treatments within the Kereone soil.

Table 2. Mean soil extractable Cd concentration (µg kg^{-1}) across the 18 paired sampling dates; **i)** Mean of pre-irrigation samplings, **ii)** Mean of +3 day samplings. Means with the same letter indicate differences are not significant from one another ($P < 0.05$).

Sampling timing	Treatment								*P* value
	KPN	KUN	KPF	KUF	TPN	TUN	TPF	TUF	
i) Pre-irrigation mean	19.3(a)	19.4(a)	17.9(a)	16.1(a)	83.0(b)	87.6(b)	85.4(b)	81.4(b)	***
ii) +3 day mean	22.6(a)	22.7(a)	22.1(a)	20.7(a)	86.0(b)	91.0(b)	92.5(b)	90.4(b)	***
P value (pre-irrigation vs +3 day)	*	*	**	**	*n.s.*	*n.s.*	*n.s.*	*n.s.*	

Treatment codes: K = Kereone, T = Topehaehae; P = Planted, U = Unplanted; N = Non-flooded, F = Flooded
*P≤0.05 **P≤0.01 ***P≤0.001 n.s. = not significant.

Changes in mean soil extractable Cd concentration throughout the duration of the trial are demonstrated in Figure 1, showing the flooded and non-flooded treatments for each of the Kereone planted (Figure 1.a) and unplanted (Figure 1.b) pots. The general trend for greater soil extractable Cd concentrations at +3 day samplings relative to the pre-irrigation samplings in both flooded and non-flooded treatments (as indicated in Table 2) is illustrated in these graphs. These trends were very similar for the Topehaehae soil type (data not shown).

During the initial 4-6 weeks of the trial, the increase in soil extractable Cd concentrations that occurred between each pre-irrigation and +3 day sampling was not reversed (or completely reversed) over the subsequent drained phase, resulting in a gradual increase in soil extractable Cd concentrations over days 0-42 (Figure 1). With relatively dry soil conditions at the time of soil collection (gravimetric moisture content (θm) for both soils of ~0.42 g g-1, compared to θm at 'potted field capacity' of 0.64 and 0.73 g g-1 for the Topehaehae and Kereone soils, respectively) it is possible that the trend for increasing soil extractable Cd concentrations over the first 4-6 weeks of the trial was a consequence of an abrupt increase in soil moisture driving re-equilibration of soil extractable Cd, following the initiation of regular irrigation inputs. Alternatively, as soil organic matter is an important sink for Cd in New Zealand agricultural soils (Gray et al., 2000) it is also possible that mineralisation of soil organic matter following sieving/potting may have reduced the soils Cd sorption potential, thereby increasing labile-Cd during the first 4-6 weeks of this study.

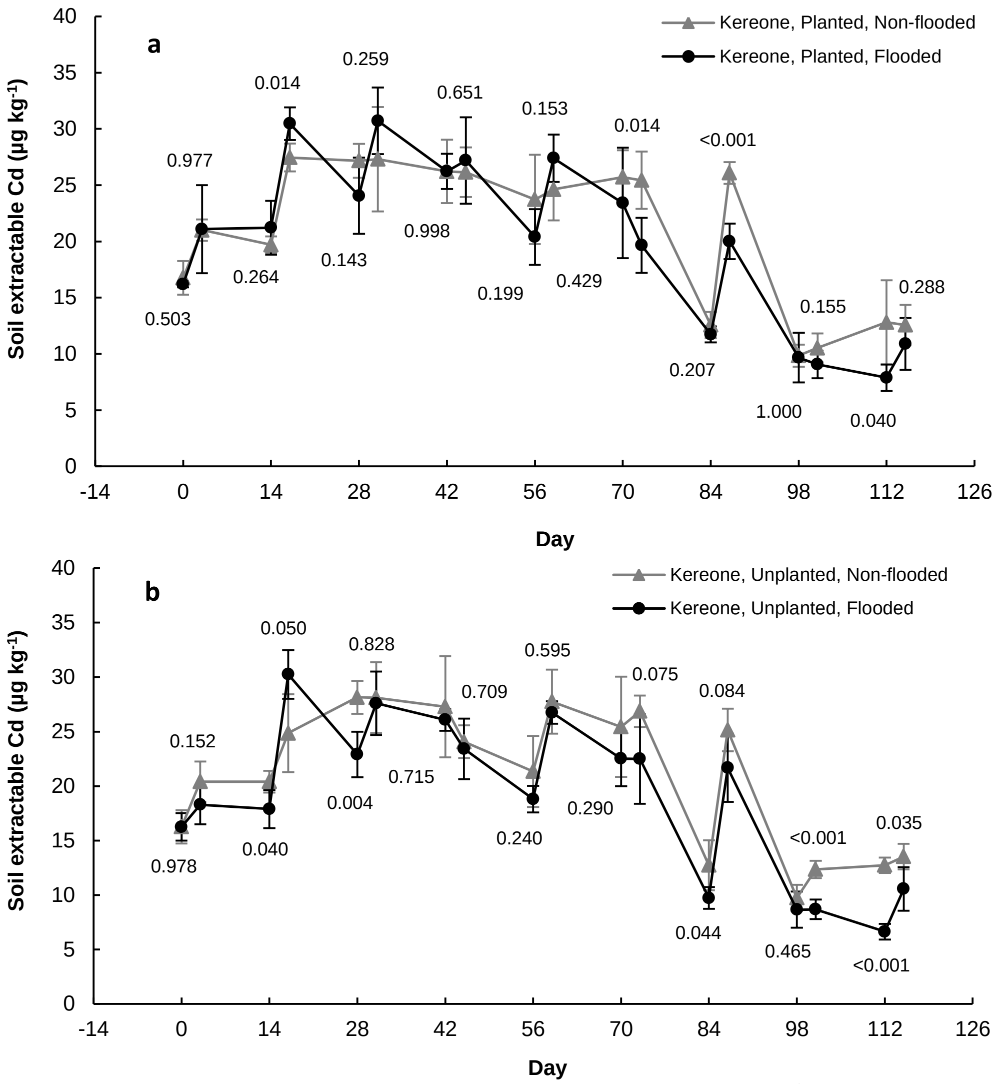

Figure 1. Mean soil extractable Cd concentrations (µg kg^{-1}) at each sampling date under Flooded and Non-flooded irrigation regimes for the **a)** Kereone Planted and **b)** Kereone Unplanted treatment. ANOVA *P* values are provided for comparison of means at each sampling date. Error bars represent the 95% confidence interval.

Table 3. pH of 0.05 *M* $CaCl_2$ extracts assessed periodically throughout the trial. Means with the same letter indicate differences are not significant from one another ($P < 0.05$).

Treatment	Day of sampling				*P* value
	0	28	84	112	
KPN	4.04	4.09 (ab)	4.29	4.44	
KPF	3.94	4.28 (b)	4.38	4.27	
TPN	3.97	4.00 (a)	4.17	4.23	
TPF	3.92	4.10 (ab)	4.13	4.12	
P value	*0.150*	*0.042*	*0.294*	*0.144*	
Sampling mean	3.97 (a)	4.11 (ab)	4.24 (b)	4.27 (b)	*<0.001*

Beyond day 42, there was a gradual but large (approximately 50-60%) decrease in soil extractable Cd concentration. This decline was not an effect of plant uptake, since soil extractable Cd concentrations in non-planted treatments (Figure 1.b) showed the exact same patterns as the planted treatments (Figure 1.a) throughout the duration of the trial. It is uncertain what drove this overall decrease in soil extractable Cd concentration over time, although it coincides with a small but significant increase in the pH of soil extracts assessed periodically over the course of the trial (Table 3).

Plant Cd uptake and accumulation

Consistent with the soil extractable Cd data, plantain tissue Cd concentrations were significantly (P < 0.001) influenced by soil type (Table 4.i). Tissue Cd concentrations of plantain grown in the Topehaehae soil were approximately double those of plants grown in the Kereone soil. There was no significant (P > 0.05) effect of irrigation regime on plantain tissue Cd concentration. Conversely, plant yield was significantly (P < 0.001) influenced by irrigation regime with lower yield in flooded treatments as a consequence of repeated soil saturation phases, however there was no significant (P > 0.05) effect of soil type (Table 4.ii).

Table 4.i) Mean plant tissue Cd concentration (mg kg^{-1} DM), **ii)** Plant yield (g DM pot^{-1}), and **iii)** Plant Cd uptake (µg Cd pot^{-1}). Means with the same letter indicate differences are not significant from one another (P < 0.05).

Measure		Treatment				*P* value
		KPN	KPF	TPN	TPF	
i) Plant tissue Cd (mg kg^{-1} DM)	Mean	0.208(a)	0.384(ab)	0.650(c)	0.604(bc)	***
	Std. Error	0.059	0.077	0.054	0.068	
	n	5	5	5	5	
	Main effects:					
	- *Soil type*	***				
	- *Irrigation regime*	*n.s.*				
ii) Plant yield (g DM pot^{-1})	Mean	5.40(c)	2.70(ab)	4.02(bc)	1.51(a)	***
	Std. Error	0.57	0.29	0.30	0.16	
	Main effects:					
	- *Soil type*	*n.s.*				
	- *Irrigation regime*	***				
iii) Plant Cd uptake (µg Cd pot^{-1})	Mean	1.001(a)	1.020(a)	2.602(b)	0.880(a)	***
	Std. Error	0.224	0.182	0.280	0.056	
	Main effects:					
	- *Soil type*	*.				
	- *Irrigation regime*	*				

Treatment codes: K = Kereone, T = Topehaehae; P = Planted; N = Non-flooded, F = Flooded.
*P≤0.05 **P≤0.01 ***P≤0.001 n.s. = not significant.

Total Cd uptake (µg Cd pot^{-1}) was significantly (P < 0.05) influenced by both soil type and irrigation regime (Table 4.iii). Within the Kereone soil, plantain total Cd uptake between the flooded and non-flooded treatments was not significantly different (P > 0.05), as a consequence of an inverse relationship being apparent between plant yield and tissue Cd concentration. Such inverse relationships (i.e. whereby dilution of plant tissue Cd concentration occurs as a consequence of greater plant yield / growth rate) have been commonly reported in the literature (Mortvedt et al., 1981; Loganathan et al., 1997; Roberts and Longhurst, 2002). While a large difference in yield also occurred between the flooded and non-flooded treatments of the Topehaehae soil, dilution of tissue Cd concentrations did not occur in the higher yielding non-flooded treatment. This suggests that at the much greater soil extractable Cd concentrations of the Topehaehae soil, soil Cd availability and root Cd uptake did not become a limiting factor to tissue Cd accumulation at greater growth rate. Notably, data of Mortvedt et al. (1981) also indicates that an inverse relationship between plant tissue Cd concentration and plant growth rate only occurs at low soil Cd phytoavailability.

Implications for Cd management in agricultural soils

This trial indicates that soil extractable Cd concentration increases with increasing soil moisture after a period of soil drying / drainage. This new knowledge could be an important consideration with regard to developing appropriate soil Cd management strategies to minimise livestock dietary Cd exposure. For example, chicory and plantain have been shown to be 'Cd-accumulator' species (Stafford et al., 2016) that are commonly sown in many livestock grazing systems to provide high quality feed over summer and autumn. It is likely that tissue Cd concentrations in these plantain and chicory crops will be enriched following rainfall events that substantially increase soil moisture during the predominantly dry summer and autumn soil conditions. This effect has been observed in recent field trials investigating Cd accumulation in chicory (currently unpublished).

As there is little practical ability to avoid grazing these crops following periods of increased soil moisture, this places more emphasis on use of appropriate management interventions to minimise potential increases in Cd phytoavailability that will be aligned with periods of increased soil moisture. As soil pH is considered one of the single most important factors influencing Cd sorption-desorption behaviour and solubility (Bolan et al., 1999; Christensen and Haung, 1999; Gray et al., 1999; Loganathan et al., 2012; Young, 2012) managing soil pH at the upper end of the optimum range for these crops would be logical starting point. However, the effect of increasing soil pH on Cd accumulation in plantain and chicory has yet to be quantified in field trials. Burial of Cd-enriched topsoil via deep 'inversion-tillage' (Angers and Eriksen-Hamel, 2008; Lawrence-Smith et al., 2015) may also be a useful strategy to reduce overall soil Cd phytoavailability. In addition, this will also move Cd-enriched topsoil away from the soil surface, where it will be less influenced by fluctuations in soil moisture.

However, the influence of soil moisture on soil extractable Cd concentration must be kept in perspective, since these effects were relatively small compared to the overall difference in soil extractable Cd concentration between the two soil types studied in this research. Our results also reinforce that while soil total Cd concentration may be suitable for managing soil Cd accumulation, where the objective is to minimise plant Cd accumulation, other soil factors that regulate Cd phytoavailability such as pH and organic matter content also need to be taken into account.

References

Adriano, D.C., 1986. Trace elements in the terrestrial environment. Springer-Verlag, New York, USA. 533 p.

Angers, D.A., Eriksen-Hamel, N.S., 2008. Full-inversion tillage and organic carbon distribution in soil profiles: A meta-analysis. Soil Science Society of America journal 72, 1370-1374.

Backes, C.A., McLaren, R.G., Rate, A.W., Swift, R.S., 1995. Kinetics of cadmium and cobalt desorption from iron and manganese oxides. Soil Science Society of America 59, 778-785.

Bhatti, S.M., Anderson, C.W.N., Stewart, R.B., Robinson, B.H., 2013. Risk assessment of vegetables irrigated with arsenic-contaminated water. Environmental Science. Processes & Impacts 15, 1866-1875.

Bolan, N.S., Naidu, R., Syers, J.K., Tillman, R.W., 1999. Surface charge and solute interactions in soils. Advances in Agronomy 67, 88-141.

Christensen, T.H., Haung, P.M., 1999. Solid phase cadmium and the reactions of aqueous cadmium with soil surfaces. In: McLaughlin, M.J., Singh, B.R. (Eds.), Cadmium in soils and plants. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 65-96.

Cornu, S., Cattle, J.A., Samouelian, A., Laveuf, C., Guilherme, L.R.G., Alberic, P., 2009. Impact of redox cycles on manganese, iron, cobalt, and lead in nodules. Soil Science Society of America journal 73, 1231-1241.

de Livera, J., McLaughlin, M.J., Hettiarachchi, G.M., Kirby, J.K., Beak, D.G., 2011. Cadmium solubility in paddy soils: Effects of soil oxidation, metal sulfides and competitive ions. Science of the Total Environment 409, 1489-1497.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., Condron, L.M., 1999. Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. European Journal of Soil Science 50, 127-137.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., Condron, L.M., 2000. Fractionation of soil cadmium from some New Zealand soils. Communications in Soil Science and Plant Analysis 31, 1261-1273.

Kim, N.D., Fergusson, J.E., 1992. Adsorption of cadmium by an aquent New Zealand soil and its components. Australian Journal of Soil Research 30, 159-167.

Lawrence-Smith, E., Curtin, D., Beare, M., Kelliher, F., 2015. Potential applications of full inversion tillage to increase soil carbon storage during pasture renewal in New Zealand. A Plant & Food Research report prepared for: NZAGRC. Milestone No. 61925. Contract No. 31874. Job code: P/442029/08. PFR SPTS No. 12101. 54 p.

Loganathan, P., Hedley, M.J., Gregg, P.E.H., Currie, L.D., 1997. Effect of phosphate fertiliser type on the accumulation and plant availability of cadmium in grassland soils. Nutrient Cycling in Agroecosystems 47, 169-178.

Loganathan, P., Vigneswaran, S., Kandasamy, J., Naidu, R., 2012. Cadmium Sorption and Desorption in Soils: A Review. Critical Reviews in Environmental Science and Technology 42, 489-533.

Mortvedt, J.J., Mays, D.A., Osborn, G., 1981. Uptake by wheat of cadmium and other heavy metal contaminants in phosphate fertilizers. Journal of Environmental Quality 10, 193-197.

Roberts, A.H.C., Longhurst, R.D., 2002. Cadmium cycling in sheep-grazed hill-country pastures. New Zealand Journal of Agricultural Research 45, 103-112.

Smolders, E., Mertens, J., 2012. Cadmium. In: Alloway, B.J. (Ed.), Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Springer, Dordrecht, The Netherlands, pp. 283-311.

Stafford, A.D., Anderson, C.W.N., Hedley, M.J., McDowell, R.W., 2016. Cadmium accumulation by forage species used in New Zealand livestock grazing systems. Geoderma Regional 7, 11-18.

Young, S.D., 2012. Chemistry of heavy metals and metalloids in soils. In: Alloway, B.J. (Ed.), Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Springer, Dordrecht, The Netherlands, pp. 51-95.

Zhang, C., Ge, Y., Yao, H., Chen, X., Hu, M., 2012. Iron oxidation-reduction and its impacts on cadmium bioavailability in paddy soils: a review. Frontiers of Environmental Science & Engineering 6, 509-517.

Zheng, S., Zheng, X., Chen, C., 2013. Transformation of metal speciation in purple soil as affected by waterlogging. International Journal of Environmental Science & Technology 10, 351-358.