Redevelopment of the cadmium balance model

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Contents

1. Executive Summary

CadBal is a cadmium (Cd) balance model that estimates Cd accumulation or depletion in agricultural soils over time. The estimation of total soil Cd is based on the initial soil Cd concentration for a land management unit (LMU), along with a series of estimates of Cd inputs and losses. The CadBal model was originally developed for the Fertiliser Association of New Zealand (FANZ) in 1996 and updated in 2005. In 2018, FANZ recognised the need to incorporate new Cd research to improve how the CadBal model estimates Cd accumulation in soil. This report documents the redevelopment of the CadBal model to include Cd research published since 2005 and new research undertaken as part of the update.

The structure of the CadBal model remains essentially the same as the previous model, with updates to some existing Cd inputs, addition of some new Cd inputs and changes to how Cd losses are modelled.

- Soil bulk density data and sediment load data for different land use activities for estimating Cd loss by soil erosion have both been updated.
- The model now provides default Cd concentrations for different phosphorus (P) fertiliser products.
- Lime, farm dairy effluent (FDE) and FDE pond solids are all new Cd input options.
- Leaching and crop offtake of Cd now use a mechanistic approach that accounts for changes in soil Cd concentrations over time. This makes the CadBal model consistent with methods used in international models to estimate these Cd losses from soils.
- Cadmium leaching now uses the drainage leaving the topsoil, multiplied by an estimate of the soil solution Cd concentration predicted from soil pH, soil organic matter (OM) content and total soil Cd concentration.
- Crop offtake of Cd is now able to be calculated for a wider range of crop species than the previous model, grouped into either grazed and annual crops or short rotation crops. Crop offtake is calculated using the total soil Cd concentration, a plant uptake factor, the crop dry matter yield and the proportion of crop biomass removed.

A single factor sensitivity analysis compared the relative effect different input parameters in the CadBal model had on predicted soil Cd concentrations. The analysis highlighted that regardless of the agricultural system, it is important there is accurate data on Cd concentrations in P fertilisers, as this is the parameter which has the greatest effect on the rate of soil Cd accumulation. It is also important to have accurate data on the parameters that affect Cd leaching (pH, OM, total Cd, and the drainage flux). For systems where crops are harvested, accurate estimates of the crop yield and the proportion of the crop removed are important. Data on Cd input parameters from lime, FDE, atmospheric accession and erosion appear less important.

To assess how well the CadBal model predicts soil Cd concentrations, we compared CadBal-predicted values to measured values from the Winchmore long-term P fertiliser trial. Measured values were based on data from 1974 to 2016 due to the availability of measured Cd concentrations in single superphosphate fertiliser from that period. It was found that soil Cd concentrations predicted using the CadBal model were within 10% of the measured soil Cd concentrations for the two fertiliser treatments.

2. Background

There is concern regarding the accumulation of cadmium (Cd) in New Zealand agricultural soils because of its potential toxicity to humans and other living organisms. In 2011 a National Cd Working Group released a National Cd Management Strategy (MAF 2011) to address these concerns, based on an assessment of the risk Cd poses to agricultural systems. The strategy, which was revised in 2019, outlines a risk-based approach for managing Cd in agricultural soils based on a Tiered Fertiliser Management System (TFMS). This framework is intended to allow landowners to self-manage Cd accumulation in soils over time. It contains five tiers and four trigger soil Cd concentrations, where increasingly stringent fertiliser management practices are stipulated as total soil Cd concentrations increase. One of the recommendations in the revised Cd management strategy was to support implementation of a Cd balance model into the TFMS. This will provide insight into the rate of Cd accumulation in soils and help ensure that Cd concentrations in agricultural production systems pose minimal risks to health, trade, land use flexibility and the environment over the next 100 years.

At present, the only Cd balance model available for use in New Zealand is CadBal, a model that estimates accumulation or depletion of Cd in agricultural soils over time. The model estimates total soil Cd based on the initial soil Cd concentration for a land management unit (LMU), the scale the model is intended to be applied, and a series of estimates of Cd inputs and losses. The CadBal model was developed for the Fertiliser Association of New Zealand (FANZ) more than 20 years ago (Roberts and Longhurst 1996) and updated 13 years ago (Roberts and Longhurst 2005).

Since the last update, there has been a significant amount of Cd research in New Zealand that could potentially improve how the CadBal model estimates Cd accumulation in agricultural soils. This new research, along with information on how Cd accumulation in soil is modelled in other jurisdictions was reviewed and summarised recently by Gray and Cavanagh (2018). That review recommended a range of updates and additions to the CadBal model and actions required to implement those changes that should both improve the estimation of Cd accumulation in soil and bring the CadBal model in line with how international Cd balance models operate. The review indicated that while the overall model structure and outputs of the CadBal model would remain unchanged, it recommended additions to Cd inputs and some important changes to the approach used to calculate Cd losses via leaching and plant offtake.

This report documents the redevelopment of the CadBal model based on the recommendations of Gray and Cavanagh (2018). The changes made to CadBal are based on existing published Cd research, along with new research undertaken as part of the update. The report addresses the following objectives:

1. Provide a summary of the updated structure of the CadBal model and the input parameters required by a user to operate CadBal.
2. Describe how input parameters have changed from the previous version of the CadBal model.
3. Undertake a single factor sensitivity analysis of the updated CadBal model.
4. Report on the testing of the updated CadBal model against field data.

3. Summary of the updated CadBal model

CadBal is a mass-balance model that estimates Cd accumulation or depletion in agricultural soils over time. It is based on the initial total soil Cd concentration for a LMU, along with a series of Cd inputs and losses. This section of the report summarises the structure of the CadBal model, including changes to some of the Cd input and loss parameters.

3.1 Structure of the CadBal model

The updated CadBal model is essentially the same as the previous model (equation 1).

$$[Cd]_{total\ soil}^{n+1} = [Cd]_{total\ soil}^{n} + ((Cd_{input}\ ha^{-1} - Cd_{loss}\ ha^{-1})^{n}/soil\ weight\ ha^{-1}) \quad (1)$$

Where:

$[Cd]_{total\ soil}^{n}$ = total soil Cd concentration (mg Cd kg^{-1} soil) at year n

3.1.1 Cadmium input parameters

Cadmium inputs for the model include a wider range of sources including atmospheric accession, P fertiliser, lime, and farm dairy effluent (FDE) (equation 2).

$$Cd_{input}\ ha^{-1} = AA + R \times [Cd]_{fertiliser} + L \times [Cd]_{lime} + PS \times [Cd]_{pond\ solids} + FDE \times [Cd]_{FDE} \quad (2)$$

Where:

AA = atmospheric accession (mg Cd ha^{-1} yr^{-1})

R = rate of P fertiliser application (kg ha^{-1} yr^{-1})

$[Cd]_{fertiliser}$ = concentration of Cd in P fertiliser (mg Cd kg^{-1} P)

L = rate of lime application (kg ha^{-1} yr^{-1})

$[Cd]_{lime}$ = concentration of Cd in lime (mg Cd kg^{-1} lime)

PS = rate of FDE pond solids application (kg ha^{-1} yr^{-1})

$[Cd]_{pond\ solids}$ = concentration of Cd in FDE pond solids (mg Cd kg^{-1} pond solids)

FDE = rate of FDE application (mm ha^{-1} yr^{-1})

$[Cd]_{FDE}$ = concentration of Cd in FDE (µg Cd L^{-1} FDE)

3.1.2 **Cadmium loss parameters**

Cadmium losses are calculated from three sources including crop offtake (CO), leaching loss (LL) and soil erosion loss (EL) (equation 3).

$$Cd_{loss}\ ha^{-1} = CO + LL + EL \quad (3)$$

Where:

$$CO\ (mg\ Cd\ ha^{-1}\ yr^{-1}) = [Cd]_{total\ soil}^{n} \times (PUF \times Y \times BR) \quad (4)$$

Where:

$$PUF = plant\ uptake\ factor = [Cd]_{plant}/[Cd]_{total\ soil}^{n} \quad (5)$$

Where:

$[Cd]_{plant}$ = plant Cd concentration (mg kg^{-1})

$[Cd]_{total\ soil}^{n}$ = total soil Cd concentration (mg Cd kg^{-1} soil) at year n

Y = crop yield (kg ha^{-1} dry matter)

BR = biomass removal = proportion of the total crop yield removed at harvest (%)

$$LL\ (mg\ Cd\ ha^{-1}\ yr^{-1}) = (Log[Cd]_{soil\ soln} \times DF)/1000 \quad (6)$$

Where:

$$Log[Cd]_{soil\ soln}\ (\mu g\ L^{-1}) = 6.243 - 0.987\ pH - 0.513\ logOM + 0.818\ log[Cd]_{totalsoil}^{n} \quad (7)$$

Where:

pH = soil pH measured in water

Log OM = organic matter (%)

Log $[Cd]_{total\ soil}^{n}$ = total soil Cd concentration (mg Cd kg^{-1} soil) at year n

DF = drainage flux (mm ha^{-1} yr^{-1})

$$EL\ (mg\ Cd\ ha^{-1}\ yr^{-1}) = (SY/soil\ weight\ ha^{-1}) \times [Cd]_{total\ soil}^{n} \quad (8)$$

Where:

SY = sediment yield (kg ha^{-1} yr^{-1})

$$\text{Soil weight ha}^{-1} = BD \times D \times 10000 \quad (9)$$

Where:

BD = bulk density (kg m^{-3})

D = soil modelling depth (m)

The outputs from the updated CadBal model are the same as the previous model:

1. Soil Cd accumulation over time (annual iterations) in mg Cd kg^{-1}.
2. Time in years (limited to 1000 years) to reach a user defined soil Cd trigger value (mg Cd kg^{-1} soil).
3. Calculation of the maximum Cd concentration in fertiliser (mg Cd kg^{-1} P) in order not to exceed a pre-defined soil Cd target in a specified number of years.

3.2 User guide summary

This is a summary of the input parameters required by the user to operate the updated CadBal model. The information and data supporting the different input parameters are reported in detail in section 4 of the report.

3.2.1 Agricultural system

To calculate crop offtake of Cd in the CadBal model, the user is required to firstly select the agricultural system of their LMU, grouped as either i) grazed or annual crop or ii) short rotation crop.

For a grazed or annual crop where a single crop is grown for one or more years, including crops grazed by livestock, the user can select a crop type from a lookup table for which a default PUF will be assigned. The user will then be asked if the crop is grazed or not grazed. For grazed crops, a default value of 1% biomass removal will be assigned for that crop. For crops that are not grazed e.g. a cut and carry system or an annual food crop, the user is required to select the proportion (2 to 100%) of the crop biomass that is harvested from their LMU. The user needs to select the P fertiliser application rate and fertiliser product applied to the crop from a dropdown list, input the anticipated dry matter or fresh weight yield for the crop, and the application rate and Cd concentration of lime and/or FDE if applied to their LMU.

For short rotation crops, the user can select from up to a maximum of six crops grown in a rotation period of either one, two or three years. The crop types are available from a lookup table for which a default PUF will be assigned. The assumption for short rotation crops is that 100% of the edible yield is removed. For each crop, the user needs to select the P fertiliser application rate and the P fertiliser product applied to the crop from a dropdown list, input the anticipated dry matter or fresh weight yield (based on the edible portion) for each crop, and the application rate and Cd concentration of lime, if applied to their LMU.

3.2.2 Rate of P fertiliser

The user is required to enter the rate P fertiliser is applied to their LMU in units of kg P ha^{-1} yr^{-1}. This can be the amount of P fertiliser from a single product or from the application of more than one product in a year. For example, if P fertiliser is applied to different crops which have different P requirements.

3.2.3 Cadmium in P fertiliser products

The user is required to select the name/s of the P fertiliser product they applied from a lookup table in the CadBal model. This is because different P fertiliser products have different assumed maximum Cd concentrations. The products are grouped into either direct application phosphate rock, sulphuric acid derived, phosphoric derived or nitric acid derived products as categorised in the TFMS (FANZ 2019). There is also the option for the user to enter their own 'other' Cd concentration for their P fertiliser product in units of mg Cd kg^{-1} P.

3.2.4 Rate of lime application

The user has the option to enter the rate lime is applied to their LMU in units of kg lime ha^{-1} yr^{-1}.

3.2.5 Cadmium in lime

The user will be required to select either a default lime concentration in the CadBal model (0.15 mg kg^{-1}) or enter their own 'other' lime Cd concentration in units of mg Cd kg^{-1}.

3.2.6 Rate of FDE application

The user has the option to enter the rate FDE is applied to their LMU in units of mm FDE ha^{-1} yr^{-1}.

3.2.7 Cadmium in FDE

The user will be required to select a default FDE concentration in the CadBal model (0.55 µg L^{-1}) or enter their own 'other' FDE Cd concentration in units of µg Cd L^{-1}.

3.2.8 Rate of FDE pond solids application

The user has the option to enter the rate FDE pond solids are applied to their LMU in units of kg pond solids ha^{-1} yr^{-1}.

3.2.9 **Cadmium in FDE pond solids**

The user will be required to select a default FDE pond solids concentration in the CadBal model (0.09 mg kg^{-1}) or enter their own ‘other’ FDE pond solids Cd concentration in units of mg Cd kg^{-1}.

3.2.10 **Soil order**

The user is required to select the soil order for their LMU from a lookup table stored in the CadBal model. If the user does not know the soil order of their LMU, it may be obtained from Smap (https://smap.landcareresearch.co.nz) or from their regional council.

3.2.11 **Soil bulk density**

When the user selects the soil order for their LMU, a default bulk density value is assigned from a lookup table stored in the CadBal model. There is also the option for the user to enter their own ‘other’ bulk density value in units of kg m^{-3}.

3.2.12 **Soil depth**

The user is required to select the soil depth Cd concentrations will be modelled for their LMU. A default soil depth of 0 – 0.150 m has been assigned because in the context of the TFMS, a ‘critical and definitive’ measure of soil Cd is based on concentrations calculated at this depth. There is also flexibility for the user to select two other soil depths (0 – 0.075 m and 0 – 0.100 m) where soil Cd data is commonly available or select their own soil depth.

3.2.13 **Initial soil cadmium concentration**

The user is required to enter the current total soil Cd concentration for their LMU measured at the 0 – 0.150 m depth in units of mg Cd kg^{-1} soil. However, as described above, they can also enter a soil Cd concentration measured at 0.075 m and 0.100 m soil depths or a soil Cd concentration measured from their own soil depth. Soil Cd concentrations should be obtained using the sampling and analysis protocols outlined in the TFMS (FANZ 2019).

3.2.14 **Erosion loss**

The user is required to enter the sediment load in units of kg ha^{-1} yr^{-1} for the landuse activity that best represents their LMU based on default values in a lookup table in the CadBal model. Landuse is categorised into sheep, dairy, winter crop, mixed (sheep/beef), deer and market garden/arable cropping. The user can also enter their own 'other' sediment load in units of kg ha^{-1} yr^{-1}.

3.2.15 **Atmospheric accession**

The user is required to enter a Cd input from atmospheric accession for their LMU from a lookup table stored in the CadBal model. Atmospheric accession has been categorised by region. If the region is not available, the user can select the New Zealand average or enter their own 'other' atmospheric accession value in units of mg Cd ha^{-1} yr^{-1}.

3.2.16 **Cadmium leaching**

To calculate Cd leaching loss, the user is required to enter input parameters for soil pH (measured in water), soil organic matter (OM) content (%), and the total soil Cd concentration (mg kg^{-1}). The user is also required to enter a measurement of annual drainage (mm) for their LMU, preferably obtained from OVERSEER® or a soil water balance setup for the LMU. If drainage data is not available from either of these sources, a user can select the slope of the landuse activity that best represents their LMU i.e. flat < 3° or hill > 3°, enter the annual rainfall (mm) and annual irrigation (mm) applied to their LMU, and a predicted drainage value will be calculated for the LMU that will be used to calculate Cd leaching in the CadBal model.

3.2.17 **Model output**

The outputs from the updated CadBal model are soil Cd accumulation over time (annual iterations up to 1000 yr) in mg Cd kg^{-1}. The user can also calculate the time in years (limited to 1000 yr) to reach three user defined soil Cd triggers (1.0, 1.4 and 1.8 mg Cd kg^{-1}) that align with triggers 2, 3 and 4 in the TFMS or select their own soil Cd target. The user can also calculate the maximum Cd concentration in fertiliser (mg Cd kg^{-1} P) in order not to exceed a pre-defined soil Cd target in a specified number of years.

4. Data and supporting information used to update CadBal

This section summarises the data and supporting information used to update the CadBal model. This is based on published Cd research and research undertaken as part the redevelopment of the CadBal model.

4.1 Soil Order and bulk density

In the previous version of the CadBal model, soil order was only available for eight of the soil groups reported in the New Zealand Genetic Soil Classification (Taylor and Pohlen 1962). In the updated model, these have been replaced with 13 soil orders (excluding the Anthropic and Raw soil orders) reported in the New Zealand Soil Classification (Hewitt 2010). The user will be able to select a soil order for their LMU from a lookup table stored in the CadBal model (Table 1). If the user does not know the soil order of their LMU, it may be obtained from Smap (https://smap.landcareresearch.co.nz/) or from their local regional council.

Table 1. Soil order (Hewitt 2010) and mean soil bulk density (kg m^{-3}) using data extracted from the National Soil Database (Wilde and Ross 1996).

Soil Order	Bulk density (kg m^{-3})
Allophanic	764
Brown	1004
Gley	859
Granular	1010
Melanic	984
Organic	428
Oxidic	961
Pallic	1236
Podzol	875
Pumice	866
Recent	1110
Semi-arid	1373
Ultic	1064

Similarly, the restriction to eight soil groups in the previous model meant that soil bulk density data was only available for eight soil groups. In the updated model, this has been replaced with default soil bulk density data summarised for 13 soil orders extracted from the National Soil Database (Wilde and Ross 1996) (Table 1). When the user selects the soil order for their LMU, a default bulk density value is assigned from Table 1. The option is also available for the user to input their own soil bulk density value in units of kg m^{-3}.

4.2 Soil depth

In the previous version of the CadBal model, the user could select 0 – 0.075 m, 0 – 0.200 m, or enter their own soil depth. In the updated model, a default soil depth of 0 – 0.150 m has been assigned, as a 'critical and definitive' measure of soil Cd in the TFMS based on the soil Cd concentration measured at the 0 – 0.150 m soil depth (FANZ 2019).

The user has the flexibility to select two other soil depths (i.e. 0 – 0.075 m and 0 – 0.100 m) for which soil Cd data is commonly available. The 0 – 0.075 m soil depth is included because this is the depth sampled in pastoral systems as part of routine soil fertility monitoring. The 0 – 0.100 m soil depth is provided because this is the depth sampled by regional councils at State of Environment soil quality monitoring sites (Hill and Sparling 2009). The option is also there for the user to select their own soil depth. Although not providing a definitive measure of soil Cd in line with the TFMS, Cd reported at these depths allow a landowner to 'have a look at' where Cd concentrations are trending using the soil Cd data they may have available.

4.3 Initial total soil Cd concentration

It is essential that measured soil Cd concentrations are available for users as an input parameter into the CadBal model. Given the CadBal model will be predominantly used by land managers and the fertiliser industry within the framework of the TFMS, measured soil Cd data for their LMU at the 0 – 0.150 m depth should be available. Soil Cd data should be obtained using the sampling and analysis protocols outlined in the TFMS (FANZ 2019). Total soil Cd concentrations used should be in units of mg Cd kg^{-1} soil.

4.4 Crop offtake

A key recommendation from the 2018 CadBal model review was to change how crop offtake of Cd is calculated (Gray and Cavanagh 2018). In the previous version, crop offtake of Cd was only able to be calculated for four food crops (potato, onion, lettuce, wheat) using the average Cd concentration (mg Cd kg^{-1}) reported for that crop and a default dry matter (DM) yield (kg ha^{-1} y^{-1}). Offtake of Cd in pasture (mixed ryegrass/clover) was calculated using a pasture Cd concentration based on a relationship between pasture Cd concentration and total soil Cd concentration reported by Roberts et al. (1995a), and a default pasture DM yield for either a sheep/beef or dairy system. Furthermore, to account for removal of Cd in animal products and transfer of Cd to non-productive parts of the LMU, Cd offtake was based on 15% of the total pasture DM yield.

There are limitations with this approach, in particular the link between crop offtake of Cd and the soil Cd concentration not being accounted for. For example, if Cd concentrations increase in soil over time, Cd loss through plant offtake is likely to be under-estimated. International Cd balance models (e.g. Six and Smolders 2014; De Vries and McLaughlin 2013; Sheppard et al. 2009a) use a plant uptake factor (PUF), the soil Cd content (mg kg^{-1}) and plant yield (kg ha^{-1}) to estimate plant offtake of Cd (mg ha^{-1}) (equation 4).

Where:

$$\text{CO (mg Cd ha}^{-1}\text{ yr}^{-1}) = [\text{Cd}]_{\text{total soil}}{}^{n} \times (\text{PUF} \times \text{Y} \times \text{BR}) \quad (4)$$

Where:

$$\text{PUF} = \text{plant uptake factor} = [\text{Cd}]_{\text{plant}}/[\text{Cd}]_{\text{total soil}}{}^{n} \quad (5)$$

Where:

$[\text{Cd}]_{\text{plant}}$ = plant Cd concentration (mg kg^{-1})

$[\text{Cd}]_{\text{total soil}}{}^{n}$ = total soil Cd concentration (mg Cd kg^{-1} soil) at year n

Y = crop yield (kg ha^{-1} dry matter)

BR = proportion of the crop yield removed at harvest (%)

The review recommended that CadBal is updated to include equation 4. The outputs of equation 4 were compared with the pasture Cd offtake outputs calculated using the previous model, to assess the sensitivity of the outputs in equation 4 to variation in PUF values for different crops.

4.4.1 **Model testing**

To assess the importance of different parameters (e.g. plant species, crop rotation length, P fertiliser inputs, soil type) that are relevant to calculate crop offtake of Cd using different PUF values, testing was undertaken for a range of agricultural systems scenarios (Table 2).

Scenarios 1 to 3 were based on Cd offtake in a mixed ryegrass/clover pasture calculated using the method used in the previous version of the CadBal model. Predicted soil Cd concentrations were modelled using 15% (scenario 1), 5% and 1% (scenarios 2 and 3, respectively) of pasture removed to assess their importance on crop offtake. Scenarios 4 to 10 were based on a range of common pasture and food crop species grown within New Zealand agricultural systems. Crop Cd offtake was modelled using the new equation 4 (above) with both a low PUF (a) and a high PUF (b) based on the 5th and 95th percentile respectively of PUF values reported for each crop species. Comparison between PUF values was made to illustrate the relative impact of variation within and between crop uptake on predicted soil Cd concentrations.

The input parameters used in the different scenarios are summarised in Table 3. Information on fertiliser application rates and DM yields for the different crops in the scenarios were based on data reported for different pasture and food crops from Reid and Morton (2019), Morton et al. (2017) and Nicholls et al. (2012) (Table 3). The PUFs used were from Cavanagh et al. (2015; 2017), with additional information sourced from the international literature (Table 3). Information on crop rotations was sourced from industry representatives and researchers. For scenarios 1 to 8, a fertiliser Cd concentration of 184 mg Cd kg^{-1} P (the average Cd concentration measured in single superphosphate (SSP) fertiliser between 2003 to 2015 (Abraham 2018) was used (Table 3). For scenarios 9 and 10, a fertiliser Cd concentration of 100 mg kg^{-1} was used, which is the assumed upper limit for nitric-acid derived fertilisers such as Nitrophoska (FANZ 2019), which are more typically applied to food crops. Calculations were all based on an initial total soil Cd concentration of 0.6 mg kg^{-1}, a soil bulk density of 1000 kg m^{-3}, and a soil depth of 0.15 m. The effect of different parameters on predicted soil Cd concentrations were modelled after 20 and 50 years. Inputs and losses of Cd from other sources were ignored.

Table 2. Summary of the description of the different scenarios tested.

Number	Scenario description	Variation
1	mixed ryegrass/clover pasture	15% grazing pasture removal, existing Cadbal formula
2	mixed ryegrass/clover pasture	5% grazing pasture removal, existing Cadbal formula
3	mixed ryegrass/clover pasture	1% grazing pasture removal, existing Cadbal formula
4a	Ryegrass pasture	1% grazing pasture removal, low PUF
4b	Ryegrass pasture	1% grazing pasture removal, high PUF
5a	Ryegrass, chicory	Alternate years of each plant, 1% grazing pasture removal, low PUF
5b	Ryegrass, chicory	Alternate years of each plant, 1% grazing pasture removal, high PUF
6a	Ryegrass, chicory	Chicory every 4 years, 1% grazing pasture removal, low PUF
6b	Ryegrass, chicory	Chicory every 4 years, 1% grazing pasture removal, high PUF
7a	Ryegrass, lucerne	Ryegrass 2 years and lucerne 7 years Mix of grazing and cut and carry for lucerne – with an average 33% plant removal for lucerne, low PUF
7b	Ryegrass, lucerne	Ryegrass 2 years and lucerne 7 years Mix of grazing and cut and carry for lucerne – with an average 33% plant removal for lucerne, high PUF
7c	Wheat, lucerne	Wheat 2 years and lucerne 7 years Mix of grazing and cut and carry for lucerne – with an average 33% plant removal for lucerne
7d	Kale, lucerne	Kale 2 years and lucerne 7 years Mix of grazing and cut and carry for lucerne – with an average 33% plant removal for lucerne
8a	Wheat, peas	Alternate year rotations, low PUF
8b	Wheat, peas	Alternate year rotations, high PUF
9a	Potatoes-onions-brassica-spinach-lettuce	2 year rotation, assuming brassica is winter crop, low PUF
9b	Potatoes-onions-brassica-spinach-lettuce	2 year rotation, assuming brassica is winter crop, high PUF
9c	Potatoes-onions-brassica-spinach-lettuce	2 year rotation, assuming brassica is winter crop Fertiliser application rates based on P offtake for specified yield low PUF
9d	Potatoes-onions-brassica-spinach-lettuce	2 year rotation, assuming brassica is winter crop Fertiliser application rates based on P offtake for specified yield high PUF
9e	Potatoes-onions-brassica-spinach-lettuce	2 year rotation, assuming brassica is winter crop PUF based on the median for volcanic soils
9f	Potatoes-onions-brassica-spinach- lettuce	2 year rotation, assuming brassica is winter crop PUF based on the median for non-volcanic soils
10a	spinach-lettuce-spinach-lettuce-maize	2 year rotation, assuming 1 lettuce crop is winter crop, low PUF
10b	spinach-lettuce-spinach-lettuce -maize	2 year rotation, assuming 1 lettuce crop is winter crop, high PUF

Table 3. Summary of the different phosphorus (P) fertiliser application rates, cadmium (Cd) concentrations in P fertiliser, crop dry matter (DM) yield and plant uptake factors (PUFs) used in the scenario testing. The input parameters used in the different scenarios are from the Reid and Morton (2019); Morton et al. (2017); and Nicholls et al. (2012). PUF data are from Cavanagh et al. (2015; 2017); Rietra et al. (2017); Lin et al. (2015); Smolders et al. (2008); Alexander et al. (2006).

Crop	P fertiliser application (kg ha^{-1})	Maintenance P fertiliser[1] (kg ha^{-1})	Cd input in P fertiliser (mg Cd kg^{-1} P)	Crop yield (t ha^{-1} DM)	Low PUF	High PUF	Volcanic soil PUF[2]	Non-volcanic soil PUF[2]
Ryegrass	30		184	10	0.16	0.24		
Chicory	35		184	10	0.74	4.7		
Lucerne	60[3]		184	12	0.09	0.64		
Kale	30		184	15	0.5	3.2		
Wheat	40		184	10.8	0.14	2.6		
Peas	20		184	5	0.3[4]	3[4]		
Spinach	9	9	100	1.8	1.7	6.5	2.8	4.5
Lettuce	110	9	100	1.5	0.34	4.23	0.42	3.1
Lettuce (winter)	5		100	0.9	0.34	4.23	0.42	3.1
Cabbage (winter)	19	19	100	6.8	0.3	0.4		
Potatoes	140	37	100	23	0.123	1.40	0.28	0.73
Onions	100	22.5	100	10	0.113	1.37	0.32	0.68
Maize	40		100	20	0.1	0.1		

[1]Used in scenarios 9c and 9d to assess influence of fertiliser application rate on estimated soil Cd
[2]Used in scenarios 9e and 9f
[3]An application rate of 30 kg P ha^{-1} was also used for comparison in scenario 7
[4]Guesstimate to provide illustration of the relative influence of plant uptake and fertiliser application rates for scenario 8

4.4.2 **Results**

4.4.2.1 Grazing crops

There was little difference (< 3%) in soil Cd concentrations predicted by scenario 1 and scenarios 2 and 3 when the percentage of DM removed decreased from 15% to 1% (Table 4). There was also no difference between soil Cd concentrations predicted using the plant uptake relationship in the existing version of the CadBal model with 1% DM pasture removal (scenario 3) and soil Cd concentrations predicted using the updated CadBal model that included equation 4 with either a high (scenario 4a) or low PUF (scenario 4b).

Table 4. Comparison of predicted soil cadmium (Cd) concentrations (mg kg^{-1}) after 20 and 50 years for scenarios 1 to 4 and the % difference compared to scenario 1.

Scenario	Predicted soil Cd (mg kg^{-1})	% difference from scenario 1	Predicted soil Cd (mg kg^{-1})	% difference from scenario 1
	Yr 20		Yr 50	
Scenario 1	0.666	0	0.765	0
Scenario 2	0.672	0.90	0.780	1.96
Scenario 3	0.674	1.14	0.784	2.48
Scenario 4a	0.674	1.18	0.785	2.57
Scenario 4b	0.674	1.17	0.784	2.54

Despite the inclusion of chicory in the rotation (scenarios 5 and 6), which has a much higher PUF than ryegrass (Table 3), predicted soil Cd concentrations were only slightly higher than those predicted by scenario 4a, which was a ryegrass only system (Table 5). The higher Cd offtake in chicory was probably offset by the slightly higher Cd input in P fertiliser (Table 3). There was also little difference in predicted soil Cd concentrations using either a low or high PUF for scenarios 5 to 6.

Predicted soil Cd concentrations were up to 18% higher in scenarios that included lucerne (scenarios 7a to 7d) compared to the ryegrass only system (scenario 4a) (Table 5). This is because although the lucerne scenario included a cut and carry component, and therefore a significant proportion of Cd would be removed in harvested material compared to the ryegrass system, this is offset by the higher P fertiliser application rate required for lucerne (60 kg P ha^{-1} yr^{-1}) than for ryegrass (30 kg P ha^{-1} yr^{-1}).

It was also found that halving the rate of P fertiliser application for lucerne from 60 to 30 kg P ha^{-1} yr^{-1} has a greater effect on predicted soil Cd concentrations after 50 yr than the variation in plant uptake (15% versus 4%). The crop grown between lucerne rotations (ryegrass, wheat or kale), had little effect on predicted soil Cd concentrations, probably due to the low proportion of plant Cd removed in these systems.

Table 5. Comparison of predicted soil cadmium (Cd) concentrations (mg kg^{-1}) after 20 and 50 years for scenarios 4 to 7 and the % difference compared to scenario 4a.

	Soil Cd (mg kg^{-1}) Yr 20	% difference from scenario 4a	Soil Cd (mg kg^{-1}) Yr 50	% difference from scenario 4a	Reduced fertiliser application[1]	% difference[3]
Scenario 4a	0.674	0	0.785	0		
Scenario 5a	0.680	0.9	0.799	1.8		
Scenario 5b	0.678	0.6	0.794	1.2		
Scenario 6a	0.677	0.4	0.792	0.9		
Scenario 6b	0.676	0.3	0.789	0.6		
Scenario 7a	0.727	7.9	0.926	18.1	0.786[2]	85
Scenario 7b	0.714	6.0	0.888	13.2	0.752	85
Scenario 7c	0.724	7.4	0.919	17.2	0.786	86
Scenario 7d	0.711	5.5	0.882	12.4	0.752	85

[1]Fertiliser application rate of 30 kg P ha^{-1} used for lucerne instead of 60 kg P ha^{-1}
[2]Soil Cd concentration (mg kg^{-1}) at 50 yr when reduced P fertiliser applied
[3]The % difference from predicted Cd concentration at 50 yr using fertiliser application rate of 60 kg P ha^{-1}

4.4.2.1 Food crops

In scenarios that included food crops, where the crop yield is based on the edible crop and 100% of this yield is assumed to be removed at harvest, plant offtake of Cd can be large, even resulting in predicted decreases in soil Cd over time (Table 6). This is despite typically higher rates of P fertiliser applied compared to grazed systems (Table 3). Furthermore, as can be seen by comparing predicted soil Cd concentrations in scenarios using low and high PUFs, the variation in plant uptake can also be significant. For example, predicted soil Cd concentrations were 60% higher in a wheat and pea crop rotation after 50 yr using a low PUF (scenario 8a) than a high PUF (scenario 8b).

As well as variation in crop uptake, the rate of P fertiliser application also affected predicted soil Cd concentrations. For example, when maintenance P rates are used (Scenario 9c and 9d), predicted soil Cd concentrations were 55 to 77% lower than when P fertiliser rates were based on the assumed recommended rate (Table 6). Similarly, if the recommended P fertiliser application rate for lettuce in scenario 10a and 10b is based on a 90% yield at an Olsen P concentration of 40 mg L^{-1} (i.e. 20 kg P ha^{-1}), predicted soil Cd concentrations are 66 to 80% lower than those when P is applied at the recommended rate (110 kg P ha^{-1}) to achieve a 100% yield at the same Olsen P. These modelled scenarios demonstrate the interaction between fertiliser application rate, expected yield and crop offtake of different plant species.

Table 6. Comparison of predicted soil cadmium (Cd) concentrations (mg kg^{-1}) after 20 and 50 yr for different scenarios and % different between low and high plant uptake factors (PUFs), and the % difference in predicted soil Cd concentrations from the application of different rates of P fertiliser for scenario 9.

Scenario	Soil Cd (mg kg^{-1})		Soil Cd (mg kg^{-1})		Reduced fertiliser application[4]	
	Yr 20	% low PUF	Yr 50	% low PUF	% difference Yr 20	% difference Yr 50
Scenario 8a	0.641		0.699			
Scenario 8b	0.513	80	0.422	60		
Scenario 9a	0.812		1.110			
Scenario 9b	0.566	70	0.538	49		
Scenario 9c[1]	0.626		0.661		77	60
Scenario 9d[1]	0.436	70	0.294	44	77	55
Scenario 9e[2]	0.772		0.996			
Scenario 9f[3]	0.683	88	0.772	78		
Scenario 10a	0.677		0.784			
Scenario 10b	0.576	85	0.548	70		

[1]Fertiliser application rates based on P offtake for specified yield
[2]PUF based on median for volcanic soils
[3]PUF based on median for non-volcanic soils
[4]Fertiliser application rates based on P offtake in harvested crop

4.4.3 Recommended agricultural systems and PUF values for crop offtake in CadBal

Based on the results of the model testing and simplicity for the user, two agricultural systems are available in the updated CadBal model to estimate crop offtake of Cd. The first is based on a crop being grown on an annual basis for one or more years and includes grazed systems. The second is based on short rotation crops and allows for more than one crop to be grown in a single year or crop rotation cycle.

4.4.3.1 Grazed and annual crops

This system will be used to model Cd offtake for a single crop grown for one or more years, including crops grazed by livestock (Table 7). While it is recognised that plant uptake of Cd can vary greatly both within and between crops, median PUF values have been assigned based on New Zealand data for grazed crops (i.e. pasture (a mix of ryegrass/clover), chicory, plantain, fodder beet, kale, ryegrass, lucerne, maize) and annual food crops (i.e. potatoes and wheat) (Cavanagh et al. 2015; 2017). This assumes that over time, plant uptake of Cd will vary within the observed range. Separate PUFs are provided for high and low Cd accumulating plant species and for volcanic (Allophanic and Granular soils) and non-volcanic soils, where data is available, reflecting the difference in plant Cd uptake between the groups (Cavanagh et al. 2015).

Table 7. Plant uptake factors (PUF) to be used in the updated CadBal model for grazed and annual crops separated for volcanic and non-volcanic soils and low and medium Cd accumulating crops. Data are from Cavanagh et al. (2015; 2017); Rietra et al. (2017); Lin et al. (2015); Smolders et al. (2008); Alexander et al. (2006).

Crop type	Volcanic soils PUF	Non-Volcanic soils PUF
High PUF: chicory, plantain, fodder beet, kale	0.67	2.30
Low PUF: pasture, ryegrass, lucerne, maize	0.09	0.24
Potato	0.28	0.73
Wheat (barley, oats)	0.50	
Low PUF: kumara, beans, peas, sweetcorn	0.39	
Medium PUF: carrots, broccoli, cauliflower, cabbage, beetroot, Asian greens, leeks, turnips, swedes	1.75	

Given the absence of New Zealand data on Cd uptake for many food crops, these have firstly been broadly grouped as either low or medium Cd accumulators based on data reported in international studies (Table 7). Existing New Zealand data has then been used to assign a single PUF (i.e. not differentiated as volcanic or non-volcanic soils) for each group. For the low Cd accumulator plants (kumara, beans, peas, sweetcorn) the median PUF for potatoes and onions is used. For the medium Cd accumulator plants (carrots, broccoli, cauliflower, cabbage, beetroot, Asian greens, leeks, turnips, swedes) the median PUF for lettuce, kale and fodderbeet (bulb) is used.

It should be noted that when crops are grazed by livestock, only a small proportion (1%) of Cd is removed in crop biomass from the LMU, and therefore crop selection is not critical. However, greater variation in predicted soil Cd concentrations may arise in cut and carry systems or where annual food crops are grown and there is significant removal of crop biomass. To account for this variation, the user will be required to select the proportion of the crop that is removed (2 to 100%) from their LMU in any given year.

4.4.3.2 Short rotation crops

This system is used to model Cd offtake where the crops grown have a short growing period, i.e. where more than one crop may be grown on the LMU within a year. In this system, the user has the flexibility to choose up to six crops grown in a rotation period of up to three years. The recommended PUFs for the different short rotation crops are given in Table 8. The values are based on New Zealand data for potatoes, onions, spinach, lettuce and wheat (Cavanagh et al. 2015; 2017). The same approach as described above was used to assign values for the low, medium and high Cd accumulating crops, with silverbeet based on the median PUF value for spinach. The assumption for short rotation crops is that 100% of the yield is removed, based on the edible portion only.

Table 8. Plant uptake factors (PUF) to be used in the updated CadBal model for short rotation crops separated for volcanic and non-volcanic soils and low, medium and high Cd accumulating crops. Data are from Cavanagh et al. (2015; 2017); Rietra et al. (2017); Lin et al. (2015); Smolders et al. (2008); Alexander et al. (2006).

Plant type	Volcanic soils	Non-volcanic soils
Potato	0.28	0.73
Onion	0.32	0.68
Spinach	2.8	4.5
Lettuce	0.42	3.1
Wheat (barley, oats)	0.5	
Low PUF: kumara, beans, peas, sweetcorn	0.39	
Medium PUF: carrots, broccoli, cauliflower, cabbage, beetroot, Asian greens, leeks, turnips, swedes	1.75	
High PUF: silverbeet	4.2	

4.4.4 **Summary**

To calculate crop offtake of Cd in the updated CadBal model, the user is required to firstly select either a grazed or annual crop or a short rotation crop grown on their LMU.

For grazed or annual crop systems, the user is then required to select a crop type from a lookup table for which a default PUF will be assigned. For grazed crops, a default value of 1% biomass removal will be assigned for that crop. For crops that are not grazed e.g. a cut and carry system or an annual food crop, the user can select the proportion (2 to 100%) of the crop biomass that is harvested from their LMU. The user is then required to select the P fertiliser rate and P fertiliser product applied to that crop from a dropdown list, along with the dry matter or fresh weight yield for the crop and the rate and concentration of lime or FDE if applied to their LMU.

For short rotation crops, the user can select up to a maximum of six crops grown in a rotation period of either one, two or three years. The crop types are available from a lookup table for which a default PUF will be assigned. The assumption for short rotation crops is that 100% of the edible yield is removed. For each crop, the user needs to select the P fertiliser rate and P fertiliser product applied to that particular crop from a dropdown list, input the anticipated dry matter or fresh weight yield (based on the edible portion) for each crop, and the application rate and Cd concentration of lime if applied to their LMU.

4.5 Rate of phosphate fertiliser application

The user is required to enter the rate of inorganic P fertiliser applied to their LMU in units of kg P ha^{-1} yr^{-1}. This can be the amount of P fertiliser from a single product or from the application of more than one P fertiliser product during the year if it is applied to different crops which have different P fertiliser requirements.

4.6 Cadmium concentrations in phosphate fertiliser products

Cadmium in P fertiliser is the single largest Cd input into agricultural soils in New Zealand. It is therefore essential accurate data on Cd concentrations in different P fertiliser products are available for input into CadBal. It is recognised it is a challenge having access to data on Cd concentrations for specific P fertiliser products, simply because Cd concentrations will constantly vary depending on the blend of phosphate rocks and processes used in their manufacture. However, the TFMS (FANZ 2019) report assumed upper Cd limits in different P fertiliser 'product groups' that are in use in New Zealand (Table 9). The upper Cd limits vary from 100 mg Cd kg^{-1} P for nitric acid derived products such as nitrophoska, up to 280 mg Cd kg^{-1} P for both phosphate rock and sulphuric acid derived products.

In the updated model, a lookup table with the different P fertiliser product groups and their assumed upper Cd limits in units of mg Cd kg^{-1} P are available for the user to select. In addition, there is also the option for the user to enter their own 'other' Cd concentration for their P fertiliser product e.g. the average Cd concentration measured in SSP by the Fertmark fertiliser quality assurance programme.

Table 9. Maximum cadmium (Cd) limit (mg Cd kg^{-1} P) in different phosphate fertiliser product groups (FANZ 2019).

Product group for phosphate fertiliser	Assumed upper limit for Cd concentration (mg Cd kg^{-1} P)	Phosphate fertiliser product
Direct application phosphate rock	280	Direct application phosphate rock/reactive phosphate rock
Sulphuric acid derived products	280	Single superphosphate Sulphur super Potash super Serpentine superphosphate Superphosphate blends
Phosphoric acid derived products	220	Triple superphosphate Di-ammonium phosphate Mono ammonium phosphate
Nitric acid derived products	100	Compound fertiliser prills

4.7 Lime inputs

In the existing version of the CadBal model, Cd in lime products is not an option as an input, despite the fact it is an input in some Cd balance models in Europe (Sterckeman et al. 2018; Six and Smolders 2014). There is little published data on Cd concentrations in New Zealand lime products, and the data that is available is variable. Roberts et al. (1995b) reported a concentration of 4 mg Cd kg^{-1} in lime used in South Auckland market gardens, sourced from Waitomo and Redvale. This is high compared to the mean Cd concentration of 0.25 mg Cd kg^{-1} reported by Kim (2005) for three different brands of lime sold for home gardens in the Waikato.

To get a better understanding of Cd concentrations in lime products and whether Cd from lime should be considered an input in the CadBal model, bulk samples of lime were obtained from 12 quarries of variable size (total output of lime 20,000 to 200,000 T yr^{-1}) located across the North and South Islands of New Zealand. In addition, Cd concentrations in lime samples collected from the same quarry over several months were also analysed as a check on the variability in Cd over time. Total recoverable Cd was determined by microwave digestion of ground lime samples in concentrated nitric acid using AOAC Official Method 200.6 (AOAC 2006), followed by Cd analysis using inductively coupled plasma mass spectrometry (ICP–MS). Cadmium concentrations in samples were corrected for moisture content which ranged between 0.1 to 6.8%.

Total Cd concentrations ranged from 0.02 to 0.50 mg kg^{-1} (Table 10) with a median and mean concentration of 0.15 and 0.23 mg kg^{-1}, respectively. This is very similar to the mean Cd concentration reported by Kim (2005) and in lime products from Northern Europe. Erstad (1992) reported Cd concentrations in 16 different lime products in Norway ranged from <0.01 to 0.33 mg Cd kg^{-1}. In Finland, Cd concentrations in liming materials range between 0.06 to 0.15 mg kg^{-1} (Mäkelä-Kurtto et al. 2007).

Table 10. Cadmium (Cd) concentrations (mg kg^{-1} dry weight) in lime products sampled from 12 quarries across New Zealand.

Sample name	Cd concentration (mg kg^{-1} dry weight)
A	0.46
B	0.22
C	0.09
D	0.11
E	0.10
F	0.11
G	0.11
H	0.02
I	0.45
J	0.18
K	0.50
L	0.35

It was also found that Cd concentrations in lime samples collected over several months from the same site remained remarkably consistent over time (Table 11).

Table 11. Cadmium (Cd) concentrations (mg kg^{-1} dry weight) in four lime products sampled from the same quarry over two or three months.

Sample name	Cd concentration (mg kg^{-1} dry weight)		
	October 2019	November 2019	December 2019
H	0.02	0.02	n.d.
I	0.45	0.47	0.48
J	0.18	0.17	0.18
L	0.35	0.35	n.d.

n.d. not determined

To determine the significance of Cd inputs to soil from lime compared to other sources, a Cd input was calculated assuming a lime application rate of 500 kg ha^{-1} yr^{-1} (with 100 % $CaCO_3$) that had a Cd concentration of 0.15 mg Cd kg^{-1}. The application rate was based on the amount of lime required to neutralise the acidity generated in a productive legume/grass pasture (Morton 2019). The Cd concentration in lime was the median value for data reported in Table 10. It was calculated that an annual application of lime would add 75 mg Cd ha^{-1} yr^{-1}. For context, this compares to the amount of Cd from an annual application of P fertiliser of 30 kg ha^{-1} that has a Cd concentration of 184 mg Cd kg^{-1} P (Abraham 2018) of 5520 mg Cd ha^{-1} yr^{-1}.

In the updated model, a Cd input from the application of lime has been added. The user will be able to select a median default concentration for lime of 0.15 mg Cd kg^{-1} based on data from this study, although the user also has the flexibility to enter their own 'other' lime Cd concentration in units of mg Cd kg^{-1}.

4.8 Rate of lime application

The user is required to enter the rate of lime applied to their LMU in units of kg lime ha^{-1} for each year lime is applied.

4.9 Farm dairy effluent

In the existing version of the CadBal model, Cd in FDE or pond solids is not a Cd input option. Grazing animals typically only retain a small proportion of the Cd they ingest from soil and plants, with up to 99% excreted in dung and returned to the soil (Lee et al. 1994; 1996a). If this dung is captured along with wastewater and stored as FDE, it potentially could contain a small amount of Cd. If the FDE along with the pond solids from an effluent pond is returned to the same paddocks the animals grazed, it is simply a re-cycling of Cd in the soil-plant-animal system. Alternatively, if the FDE and the solids are not returned to the same paddock, and the application is restricted to a dedicated LMU, this could be considered a net Cd input.

A factor that may affect the Cd concentration in the effluent and pond solids is the farms dairy production system. This is because the type of system affects the amount of imported feed given to the animal. System 5 dairy production systems described by DairyNZ indicate between 25 to 40% (up to 55%) of the total feed (e.g. Palm Kernel Extract, maize silage/grain, barley, wheat, oats etc) can be imported (i.e. not grown on farm). There is no published information on the Cd content of these imported feeds (and their associated effluent). However, it could be that FDE and solids from animals given these feeds may have higher Cd concentrations than animals that feed on predominantly ryegrass/clover pastures, which have lower Cd concentrations.

To determine whether FDE and pond solids should be considered a Cd input in the updated CadBal model, effluent and solid samples were collected and analysed for Cd from a range of sites across New Zealand.

4.9.1 **Farm dairy effluent**

Bulk FDE samples were collected from 19 sites representing farm dairy systems 2 to 5 as described by DairyNZ (Table 12). Samples were mostly collected from the effluent pond after it had been mechanically stirred, although samples at some sites were taken from the sump or the irrigator. One site (Farm A) was sampled three times at monthly intervals to investigate variability in FDE Cd concentrations over time. Total recoverable Cd concentrations in FDE samples were determined by digestion in concentrated nitric acid (APHA 3030 E 23rd ed. 2017) and analysed for Cd by ICP-MS.

Cadmium concentrations in FDE ranged between <1.1 to 5.8 µg L^{-1}, with 14 of the 19 samples having Cd concentrations below the method detection limit of 1.1 µg L^{-1} (Table 12). There was no difference in Cd concentrations in FDE between farm dairy systems, or the location from where the sample was taken (i.e. pond, irrigator or sump). There was also no difference in Cd concentrations in FDE sampled over time from site Farm A, for which Cd concentrations were all < 1.1 µg L^{-1} (data not shown).

Table 12. Cadmium (Cd) concentrations (µg L^{-1}) in farm dairy effluent (FDE) and in pond solids (mg kg^{-1} dry weight) from different dairy farming systems.

Site	Farm dairy system	Sampling location	Cd concentration FDE (µg L^{-1})	Cd concentration Pond solids (mg kg^{-1} dry weight)
Farm A	2	Pond	<1.1	0.09
Farm B	2	Pond	<1.1	0.09
Farm C	3	Pond	<1.1	0.06
Farm D	3	Pond	<1.1	0.35
Farm E	3	Pond	<1.1	0.39
Farm F	3	n.s	<1.1	0.09
Farm G	2	n.s	<1.1	0.03
Farm H	2	n.s	<1.1	0.03
Farm I	5	n.s	<1.1	0.06
Farm J	5	n.s	<1.1	n.d
Farm L	5	n.s	<1.1	n.d
Farm 1	5	Irrigator	<1.1	n.d
Farm 2	2	Sump	5.8	n.d
Farm 3	2	Sump	<1.1	n.d
Farm 4	2	Pond	1.2	n.d
Farm 5	5	Irrigator	1.5	n.d
Farm 6	3	Sump	<1.1	n.d
Farm 7	5	Pond	3.6	n.d
Farm 8	3	n.s	2.0	n.d

n.s not specified; n.d not determined

To determine the significance of Cd inputs to soil from FDE compared to other sources, Cd inputs were calculated assuming an application rate of FDE of 40 mm ha^{-1} yr^{-1} that had a Cd concentration of 0.55 µg Cd L^{-1}. The application rate was based on the maximum N limit of 150 kg ha^{-1} allowed by many regional councils in New Zealand for applying FDE to land assuming a median N concentration in the FDE of 390 mg N L^{-1} (Longhurst et al. 2017). The median Cd concentration in effluent was calculated from the results in Table 12, assigning a value of half the method detection limit for sites that had Cd concentrations < 1.1 µg L^{-1}. It was calculated that an annual application of FDE could supply the equivalent of 220 mg Cd ha^{-1}. For context, this compares to the amount of Cd from an annual application of P fertiliser of 30 kg ha^{-1} that has a Cd concentration of 184 mg Cd kg^{-1} P (Abraham 2018) of 5520 mg Cd ha^{-1} yr^{-1}.

In the updated model, a Cd input from the application of FDE has been added. The user will be able to select the median default concentration for FDE of 0.55 µg Cd L^{-1} found in this study, although also has the flexibility to enter their own 'other' FDE Cd concentration in units of µg Cd L^{-1}.

4.9.2 **FDE pond solids**

Farm dairy effluent pond solids were collected from nine of the same sites used to collect FDE (Table 12). Total recoverable Cd concentrations were determined by digesting solids in concentrated nitric/hydrochloric acids as described in the USEPA method 200.2 (Martin et al. 1994) and analysed for Cd by ICP-MS. Cadmium concentrations were corrected for moisture content.

Cadmium concentrations in pond solids ranged from 0.03 to 0.39 mg kg^{-1} dry weight (Table 12), with a median Cd concentration of 0.09 mg Cd kg^{-1} dry weight. As found in the effluent samples, there didn't appear to be any difference in Cd concentrations between farm dairy systems.

It is difficult to determine the significance of Cd inputs from pond solids compared to other sources because factors such as the amount of pond solids produced, along with the rate and frequency of land application can vary widely (Longhurst et al. 2000). As a result, we used a scenario of an 'average Waikato dairy farm' (details in Appendix A Table A1; Bob Longhurst, personal communication) to estimate the amount of pond solids produced per annum.

The scenario estimated 29 m^3 of solids were produced per year. Assuming they had a bulk density of 500 kg m^{-3}, and land application was restricted to a three-hectare block, an annual application would be equivalent to about 4800 kg ha^{-1}. This is consistent with observations of estimated rates of solids application of between 2500 to 5000 kg ha^{-1} found at some sites in the North Island (Bob Longhurst, personal communication). Using a median Cd concentration in solids of 0.09 mg Cd kg^{-1} from the results reported in Table 12, it was calculated an annual application of solids could supply the equivalent of 432 mg Cd ha^{-1}. For context, this compares to the amount of Cd from an annual application of P fertiliser of 30 kg ha^{-1} that has a Cd concentration of 184 mg Cd kg^{-1} P (Abraham 2018) of 5520 mg Cd ha^{-1} yr^{-1}.

In the updated model, a Cd input from the application of FDE pond solids has been added. The user will be able to select the median default concentration for pond solids of 0.09

mg Cd kg^{-1} found in this study, although also has the flexibility to enter their own 'other' pond solids Cd concentration in units of mg Cd kg^{-1}.

4.10 Rate of FDE application

The user is required to enter the depth that FDE is applied to their LMU in units of mm FDE ha^{-1} for each year it is applied.

4.11 Rate of FDE pond solids application

The user is required to enter the rate that FDE pond solids are applied to their LMU in units of kg pond solids ha^{-1} for each year pond solids are applied.

4.12 Irrigation

In the existing version of the CadBal model, Cd in irrigation water was not an input. Except for a model used in Australia (De Vries and McLaughlin 2013), irrigation is also not an input in Cd balance models used overseas (Römkens (et al. 2018; Sterckeman et al. 2018; Six and Smolders 2014).

Irrigation is widely applied in several regions of New Zealand, particularly Canterbury, which makes up over 64% of the total irrigated area across the country (Ministry for the Environment 2017). There is no published data available on Cd concentrations in irrigation water in New Zealand. However, Cd concentrations reported in surface (Taylor 2016) and groundwater samples (Noakes and Weaver (2014) from sites that potentially could be used for irrigation are in most instances below the method detection limit for Cd.

To assist in determining whether Cd in irrigation water should be considered a Cd input in the CadBal model, groundwater samples were collected and analysed for Cd from wells that were consented for irrigation from Canterbury, Marlborough and Wellington regions. In addition, data on Cd concentrations was supplied by the Waikato Regional Council from irrigation wells located across the Waikato. Cadmium concentrations in water samples were analysed by ICP-MS that had a method detection limit (DL) of 0.05 µg Cd L^{-1}.

It was found that Cd concentrations were below the DL in all samples from Canterbury, Marlborough and Wellington as well as 81% of the samples from the Waikato region

(Table 13). Of the 25 samples above the DL from the Waikato region, 15 of the samples had Cd concentrations of 0.1 µg L^{-1}, with a highest Cd concentration of 0.8 µg L^{-1}.

Table 13. Summary of cadmium (Cd) concentrations (µg L^{-1}) measured in groundwater samples used for irrigation from Wellington, Marlborough, Canterbury and the Waikato regions.

Region	Year	Number of groundwater wells	Cadmium concentration (µg L^{-1})
Wellington	2019	25	All samples < 0.05 µg L^{-1}
Marlborough	2019	19	All samples < 0.05 µg L^{-1}
Canterbury	2019	21	All samples < 0.05 µg L^{-1}
Waikato	2016/17	131	106 samples < 0.05 µg L^{-1} 15 samples 0.1 µg L^{-1}

The results are consistent with Cd concentrations in samples that have previously been reported in national surveys of groundwater quality across New Zealand. Noakes and Weaver (2014) summarised Cd concentrations measured in groundwater samples collected by Regional Councils and from the Ministry for the Environment's National Groundwater Quality Monitoring sites (Daughney and Randall 2009). They found that the majority of the median Cd concentrations reported in the national groundwater monitoring sites were below the limit of detection of the test method used. Cadmium concentrations in 87% of 1283 samples analysed by Regional Councils were also below the limit of detection, with only three samples exceeding 50 percent of the maximum acceptable value of 4 µg Cd L^{-1}. In a more recent survey of 30 shallow groundwater wells in Taranaki, Bedford et al. (2017) reported 27 samples had Cd concentrations below the method detection limit of 0.1 µg L^{-1}, while the highest Cd concentration was 0.6 µg L^{1}.

No specific analysis of surface water samples used for irrigation were made in this study. However, data on Cd concentrations monitored at six surface water quality sites along the Waikato River for the last 20 years (1995-2015), indicate Cd concentrations are consistently below the DL of 0.01 µg L^{-1} (Taylor 2016). Cadmium concentrations in surface water samples collected from rivers in the Wellington region were also below the method DL (Taylor 2016).

Given the very high proportion of both surface and groundwater samples with low Cd concentrations (below detection), a Cd input from irrigation water has not been included in the updated CadBal model.

4.13 Atmospheric inputs

In the existing version of the CadBal model, default values for Cd inputs from atmospheric accession were available for six locations across New Zealand, based on data from a survey by Gray et al. (2003a). Input values ranged from 90 to 360 mg Cd ha^{-1} yr^{-1} (Table 14). The user could also select a 'New Zealand average' of 220 mg Cd ha^{-1} yr^{-1} or use their own input data. Since the study of Gray et al. (2003a), no additional data on atmospheric inputs of Cd to agricultural soils have been collected.

While there is no data on atmospheric inputs of Cd in several regions of New Zealand (BOP, West Coast, Otago, Tasman-Marlborough), the current data is probably adequate, and the New Zealand average (220 mg ha^{-1} yr^{-1}) could be used for regions where data are unavailable. As a result, in the updated model, Cd inputs from atmospheric accession have been retained unchanged, with the user being able to select a Cd input in units of mg ha^{-1} yr^{-1} for their region from a lookup table in the CadBal model (Table 14).

Table 14. Atmospheric accession of cadmium (Cd) (mg ha^{-1} yr^{-1}) at six regions in New Zealand across two years of monitoring (Gray et al. 2003a).

Region	Cd (mg ha^{-1} yr^{-1})
Northland	210
Waikato	270
Taranaki	90
Manawatu-Whanganui	360
Canterbury	210
Southland	90
New Zealand average	220
Other	

4.14 Erosion loss

International Cd balance models do not calculate Cd losses and inputs via soil erosion and deposition because they are considered simply a redistribution of Cd within the landscape (Six and Smolders 2014; De Vries and McLaughlin 2013). In the existing version of the CadBal model, Cd loss through soil erosion, as suspended sediment and dissolved Cd in overland flow events is calculated, although Cd inputs via soil deposition are not included. An important distinction however between international Cd balance models and CadBal is their scale of operation. International models that have estimated Cd accumulation in soils have been made at a national (Sterckeman et al. 2018; de Vries and McLaughlin 2013) or multinational scale (Römkens et al. 2018; Six and Smolders

2014). In comparison, the existing CadBal model used in New Zealand is designed to complete a Cd balance at a LMU scale. At this scale, while studies have reported instances of re-distribution of soil (i.e. erosion and deposition) (e.g. Basher et al. 1995; 2002), they have also reported a net soil loss (Basher et al 2004).

As highlighted in the review of the CadBal model (Gray and Cavanagh 2018), if Cd loss from soil erosion is to remain an output in CadBal, then equally Cd inputs through the movement of soil between LMUs should also be potentially considered e.g. soil deposition on to flat land at the base of a hillslope. However, at present, an accurate method to calculate Cd input and loss from soil deposition and soil erosion at the LMU scale remains problematic (Gray and Cavanagh 2018). As recommended in the review, a detailed assessment of the significance of Cd inputs/losses from soil deposition/erosion needs to be investigated as a separate piece of work, and any recommended updates made to the CadBal model when this work is completed.

In the interim, the CadBal model will remain estimating Cd losses via soil erosion using a combination of the sediment yield (kg ha^{-1} yr^{-1}) for a LMU and the total soil Cd concentration (mg kg^{-1}). However, the sediment loss data has been updated using data compiled in the review by Gray and Cavanagh (2018) for a range of different landuse activities (Table 15). The exception being for market gardening/arable cropping where because of the paucity of sediment loss data from this landuse and the uncertainty in the contribution re-distribution of soil that can occur within sites, the sediment load data in the existing version of the CadBal model has been retained.

Table 15. Median sediment loads (kg ha^{-1} yr^{-1}) from sheep, dairy, winter crop, mixed (largely sheep and beef), deer and market garden landuse.

Landuse	Sediment load kg ha^{-1} yr^{-1}
Sheep	595
Dairy	131
Winter crop	1012
Mixed (largely sheep and beef)	988
Deer	2068
Market garden/arable cropping	500

The user is required to enter the sediment load in units of kg ha^{-1} yr^{-1} for the landuse of their LMU based on default values in a lookup table in the CadBal model (Table 15).

4.15 Cadmium leaching loss

A key recommendation in the review of the existing CadBal model was how Cd leaching was calculated. In the existing CadBal model, a Cd leaching value is assigned to the LMU on the basis of its soil characteristics and specifically soil order (Taylor and Pohlen 1962). There are however a number of limitations to this approach, including i) Cd leaching data is limited to four of the 15 soil orders in New Zealand ii) there is no link between the amount of Cd in the soils and the amount of Cd that could potentially be lost by leaching, and iii) it does not consider the drainage characteristics of soils. This approach is also at variance with many of the international Cd models which use the drainage leaving the topsoil or cultivated depth, multiplied by an estimate of the soil solution Cd concentration (Römkens et al. 2018; Eggen et al. 2019; Sterckeman et al. 2018; Salo et al. 2018; Six and Smolders 2014; De Vries and McLaughlin 2013; Sheppard et al. 2009; Keller and Schulin 2003).

There are two challenges in using this approach to calculate Cd leaching losses in a updated CadBal model. The first is obtaining an accurate measure of drainage leaving the topsoil or cultivated depth for a LMU, and the second is obtaining an accurate measure of the soil solution Cd concentration.

4.15.1 **Drainage**

Drainage can be estimated by constructing a simple daily water balance for a LMU using climate (rainfall, evapotranspiration), management (irrigation) and soil data (water holding capacity) (Woodward et al. 2001). Alternatively, the nutrient budget model OVERSEER® uses a water balance approach to calculate drainage on a daily time step and reports this on an annual basis for a range of different block types (pastoral, fodder crop, cut and carry, crop, effluent and fruit block). The principles applied and the equations used to calculate drainage in OVERSEER® are outlined in the hydrology technical manual (Wheeler 2018).

The Technical Advisory Group for this project supports the approach of using drainage data reported in OVERSEER® as an input parameter to calculate Cd leaching, because this data would typically be easily accessible to a user of the CadBal model and is an accurate measure of drainage. Alternatively, they could also use drainage data calculated using a soil water balance set up specifically for their LMU.

However, if this data is not available, it was suggested by members of the Technical Advisory Group that drainage could be estimated using rainfall + irrigation for a given LMU. To test the relationship, Ravensdown Ltd provided rainfall and irrigation data along with predicted drainage data modelled in OVERSEER® for over 20,000 different blocks (*viz* LMU's). It was found there were reasonably good relationships between rainfall + irrigation and predicted drainage modelled in OVERSEER® for crop, flat pasture and hill pasture blocks (Table 16).

Table 16. The relationship between rainfall + irrigation (mm) and predicted drainage (mm) modelled in OVERSEER® for different land management units (LMU).

LMU	slope	intercept	R^2	Number
Crop	0.761	-347	0.88	8044
Flat pasture	0.884	-591	0.94	28083
Hill pasture	0.643	-323	0.90	3167

If drainage data is not available for a LMU based on data from OVERSEER® or a soil water balance model, a user can therefore select the slope of the landuse activity that best represents their LMU i.e. flat < 3° or hill > 3°, enter the annual rainfall (mm) and annual irrigation (mm) applied to their LMU (restricted to pasture hill/flat and crop), and drainage will be calculated based on the relationships in Table 16, and used in the calculation of Cd leaching in CadBal.

4.15.2 **Soil solution**

Ideally in-situ soil solution Cd measurements should be used in calculations of Cd leaching loss from soil (Degryse et al. 2009), although in most instances these data are not available. Rather, soil Cd solution concentrations are predicted using empirical models. For example, several studies (Six and Smolders 2014; De Vries and McLaughlin 2013) calculate the mean concentration of Cd in soil solution $[Cd]_{soil\ soln}$ (mg L^{-1}) from the total soil Cd content $[Cd]_{total\ soil}$ (mg kg^{-1}) and the soils Cd K_D value (equation 10):

$$[Cd]_{soil\ soln} = [Cd]_{total\ soil}/K_D \qquad (10)$$

where K_D (L kg^{-1}) is the solid/liquid distribution coefficient (i.e. partitioning of Cd between the soil solid phase (mg kg^{-1}) and the soil solution phase (mg L^{-1}) (equation 11).

$$K_D = [Cd]_{total\ soil}/[Cd]_{soil\ soln} \quad (11)$$

The K_D model assumes a 1:1 linear relationship between Cd in the soil and Cd in the soil solution (Six and Smolders 2014).

However, because K_D values in soils are seldom measured, they are often predicted from combinations of soil parameters such as pH, total and dissolved organic carbon (DOC) content, cation exchange capacity (CEC), oxalate extractable iron (Fe) and aluminium (Al) and clay content (Sheppard et al. 2007; Sauvé et al. 2000a; Andersson and Christensen 1988). From a practical perspective, ideally only properties that are commonly measured in soils should be used to estimate K_D values. Six and Smolders (2014) combined data from several studies in Europe that had measured K_D values to derive a regression model that estimated K_D based on soil pH and total soil C. Using the K_D value and total soil Cd content < 1 mg Cd kg^{-1} (most representative of agricultural soils) to estimate soil solution Cd concentrations, Six and Smolders (2014) reported a good (r^2 = 0.81) comparison with measured soil solution Cd concentrations.

Other studies have used a non-linear Freundlich model to estimate soil solution Cd concentrations (Groenenberg et al. 2012; Römkens et al. 2004; Elzinga et al. 1999). Soil solution Cd concentrations (mg L^{-1}) are estimated directly from the total soil Cd content (mg kg^{-1}) or reactive soil Cd content extracted in 0.43 M nitric acid (Groenenberg et al. 2017), taking into account soil parameters such as OM (%), clay content (%), oxalate extractable Fe and Al (mg kg^{-1}), DOC (mg L^{-1}) and soil pH measured either in water or $CaCl_2$ (equation 12).

$$Log[Cd]_{soil\ soln} = constant + \log\ [Cd]_{total\ soil} + \log\ (OM) + \log\ (clay) + \log\ (Al/Fe\ oxalate) + \log\ (DOC) + pH \quad (12)$$

The non-linear model has recently been used by Römkens (personal communication) to estimate soil solution Cd concentrations to calculate leaching fluxes in a Cd balance study across Europe. The model used by Römkens included soil pH measured in 0.01 M $CaCl_2$, soil OM (%), and total soil Cd content (mg kg^{-1}) and predicted 72% of the variation in soil solution Cd concentrations.

Two New Zealand studies have previously reported non-linear models that estimated soluble Cd concentrations in soils, although both have limitations. One study used a dilute salt (0.01 M calcium nitrate) as a proxy measure of the soil solution Cd concentrations (Gray et al. 1999). In-situ measurements of soil solution are preferred over dilute salts because properties such as the ionic strength and pH of the soil solution are not changed, and the DOC concentration is not diluted (Degryse et al. 2009). If these properties are modified, they can significantly affect soil solution Cd concentrations. The second study did measure in-situ soil solution Cd concentrations, although soil pH, total C and total soil Cd could only explain 50% of the variation in soil solution Cd concentrations (Gray and McLaren 2006). Furthermore, a significant proportion (42%) of the soils were from Thailand and highly contaminated with Cd (up to 218 mg kg^{-1}) from mining activity and were alkaline (pH 7.6). These are not relevant to agricultural soils in New Zealand which are generally acid (Morton 2019), with average total soil Cd concentrations of 0.45 mg kg^{-1} (Abraham 2018).

In response, a study was undertaken to derive a model that could predict in situ soil solution Cd concentrations using commonly measured soil parameters. Soil solution Cd concentrations were derived using both i) a non-linear Freundlich model and ii) a linear model to estimate soil K_D values and the total soil Cd concentration (equation 10). The ability of each model to predict soil solution Cd concentrations was then validated using an independent set of soils and compared to Cd concentrations that have been measured in drainage from field trials.

4.15.2.1 Material and methods

Topsoil samples used for the derivation of models to estimate soil solution Cd concentrations were collected from 40 agricultural sites across New Zealand, representing eight soil orders and three land use activities (Appendix B Table B1). An additional set of topsoil samples were collected from 30 agricultural sites to validate the models. These soils also represented a range of soil orders and land use activities (Appendix B Table B2). A summary of the methods of soil and soil solution analysis, quality control and data analysis are given in Appendix B.

4.15.2.2 Results and discussion

The properties of the soils used in the derivation dataset are given in Table 17 (full dataset in Appendix B Table B1). Soil pH ranged from 5.0 to 7.0 and the OM content from 1 to 67 %. Total soil Cd concentrations ranged from 0.07 to 1.14 mg kg^{-1} with a mean concentration of 0.43 mg kg^{-1}. This is similar to the mean concentration (0.45 mg kg^{-1}) reported in a recent survey of Cd agricultural soils in New Zealand and is fivefold higher than the background Cd concentration of 0.09 mg kg^{-1} (Abraham 2018). Total soil Cd concentrations were positively correlated to total soil P (r = 0.88 P < 0.001), indicating the main source of Cd in these soils was likely from P fertiliser (McLaughlin et al. 1996) (Appendix B Figure B1). Soil solution Cd concentrations ranged from 0.05 to 3.30 µg L^{-1} with a mean concentration of 0.61 µg L^{-1} and median of 0.45 µg L^{-1} (Table 17).

Table 17. Summary of soil pH, soil organic matter (OM), 0.43 M nitric (HNO_3) acid extractable Cd, total Cd, soil solution Cd and Cd K_D values from the derivation dataset.

	pH	OM (%)	HNO_3 Cd (mg kg^{-1})	Total Cd (mg kg^{-1})	Soil solution Cd (µg L^{-1})	K_{Dbatch} (L kg^{-1})
Min	5.0	1.0	0.02	0.07	0.05	24
Max	7.0	66.7	1.10	1.14	3.30	2480
Mean	5.9	10.5	0.36	0.43	0.61	343
Median	5.9	7.9	0.31	0.39	0.45	237

4.15.2.3 Non-linear model

Using a non-linear model, regression analysis indicated that soil solution Cd concentrations (µg L^{-1}) could be best predicted by soil pH, log soil OM (%) and log total soil Cd content (mg kg^{-1}) (equation 13). Each parameter is highly significant (P < 0.001), and the standard errors are given in parentheses.

$$\text{Log}[Cd]_{soil\ soln} = 6.246\ (\pm 0.487) - 0.987\ (\pm 0.070)\ pH - 0.513\ (\pm 0.128)\ \log OM + 0.818\ (\pm 0.133)\ \log [Cd]_{total\ soil}$$

$$R^2adj = 0.84\ (\pm 0.168) \qquad (13)$$

Soil pH was found to be the most important soil parameter, explaining 68% of the variation in soil solution Cd, followed by soil OM (9%) and total soil Cd content (7%). Many studies have shown combinations of these soil parameters to be important in predicting soil solution Cd concentrations (Meers et al. 2005; Zhao and McGrath 2002). Sauvé et al. (2000a) reported soil pH and total soil Cd explained 76% of the variation in soil solution Cd concentrations in 64 soils from North America. Others have found the inclusion of additional parameters such as oxalate extractable Fe and Al and DOC were also important (Groenenberg et al. 2012). The inclusion of these soil parameters was not considered in the present study because they are not routinely measured in soil testing undertaken by New Zealand landowners. Furthermore, they could not be accurately estimated using soil parameters reported in soil datasets available in New Zealand.

The inclusion of reactive Cd, based on an extract such as 0.43 M HNO_3, instead of total Cd has also sometimes been used in models to estimate Cd in soil solution (Römkens et al. 2018; Dikjkstra et al. 2004). Reactive Cd is considered to be a pool of Cd that is totally reversibly sorbed in soil (Groenenberg et al. 2017; Houba et al. 1985). The replacement of total Cd with reactive Cd was tested in the current study, but it did not significantly improve the prediction of soil solution Cd concentration (data not shown). This was probably because on average, a high proportion (84%) of the Cd in our soils was reversibly sorbed, indicating it was not strongly retained within mineral constituents in the soil. A similar finding has been reported by others including De Vires et al. (2011) who found about 70% of the total Cd in Australian soils was readily extracted in 0.43 HNO_3 and Römkens et al. (2009) who reported between 80 to 90% for soils in Taiwan.

4.15.2.4 Linear model

Cadmium sorption for all soils was highly linear. Examples of sorption isotherms for four soil orders are given in Appendix B Figure B2. The linearity has been noted by others investigating Cd sorption at low Cd concentrations in studies in New Zealand (Gray et al. 1999; Kim and Fergusson 1992) and overseas (Boekhold et al. 1993; Christensen 1989) and is indicative of a constant partition coefficient between the soil and the solute. K_{Dbatch} values ranged from 24 to 2480 L kg^{-1} (Table 17), with a median of 237 L kg^{-1}. This is higher than the median value previously reported by Gray et al. (1999) for 21 agricultural soils in New Zealand which was 154 L kg^{-1}. This is probably because overall the soils in the present study have both higher soil pH values and OM content. The median is lower however than the K_D value (390 L kg^{-1}) reported by Sauvé et al. (2000b), calculated from a compilation of 70 published international studies, indicating Cd sorption is comparatively low in New Zealand soils.

A comparison of K_{Dbatch} with $K_{Din\ situ}$ values is given in Appendix B Figure B3. Although highly correlated, $K_{Din\ situ}$ values were on average higher (five-fold) than the K_{Dbatch} values. A similar finding has been reported in other studies that have compared K_D values measured using both methods, thought to be due to Cd sorption-desorption hysteresis (De Vries et al. 2011). This is because $K_{Din\ situ}$ values are based on Cd desorption measurements while K_{Dbatch} values are based on Cd sorption. Significant Cd sorption-desorption hysteresis has previously been found in studies of agriculture soils in New Zealand (Gray et al. 1998). As a result, $K_{Din\ situ}$ values are considered preferable over K_{Dbatch} values when trying to predict soil solution Cd concentrations (De Vries et al. 2011).

Regression analysis indicated that $K_{Din\ situ}$ values could be best predicted by soil pH and log soil OM content (equation 14). Each parameter is highly significant (P < 0.001), and the standard errors are given in parentheses.

$$\log K_D = -3.625\ (\pm\ 0.406) + 1.0195\ (\pm\ 0.0664)\ pH + 0.6294\ (\pm\ 0.0967)\ \log OM$$

$$R^2adj = 0.87\ (\pm\ 0.17) \qquad (14)$$

As was found in the non-linear model, soil pH was the dominant soil parameter, explaining 77% of the variation in log $K_{Din\ situ}$. This is similar to what other studies have reported (De Vries et al. 2011; Sauvé et al. 2000b; Janssen et al. 1997). Several studies have also shown that like the present investigation, soil pH, in combination with soil OM improved the prediction of $K_{Din\ situ}$ (Six and Smolders 2014; Lee et al. 1996b). Other studies (De Vries et al. 2011) have found that in addition to soil pH and OM content, the inclusion of DOC improved the prediction of soil solution Cd concentrations, although that was not measured in the present study.

4.15.2.5 Validation of the linear and non-linear models

Because there is a lack of relevant New Zealand data reporting soil solution Cd concentrations that could be used to validate our models, a new dataset was generated from topsoil sampled from 30 different agricultural sites. The data is summarised in Table 18 (full dataset in Appendix B Table B2). The samples had a similar range of total soil Cd (0.1 to 1.3 mg Cd kg^{-1}), soil solution Cd concentrations (0.05 to 1.70 µg Cd L^{-1}) and soil parameters such as pH (5.1 to 6.9) and OM content (3.6 to 69.3%) as the derivation dataset.

Table 18. Summary of soil pH, soil organic matter (OM), 0.43 M nitric (HNO_3) acid extractable Cd, total Cd, soil solution Cd and Cd K_D values from validation dataset.

	pH	OM (%)	HNO_3 Cd (mg kg^{-1})	Total Cd (mg kg^{-1})	Soil solution Cd (µg L^{-1})	K_{Dbatch} (L kg^{-1})
Min	5.1	3.6	0.08	0.10	0.05	41
Max	6.9	69.3	1.05	1.29	1.70	2361
Mean	5.8	12.1	0.35	0.41	0.49	373
Median	5.8	9.6	0.23	0.29	0.37	189

A comparison of predicted soil solution Cd concentrations using the non-linear model (equation 13) versus measured soil solution Cd concentrations is given in Figure 1. Using soil pH, OM and total Cd as input parameters, it was found these could predict 83% of the variation in soil solution Cd concentrations.

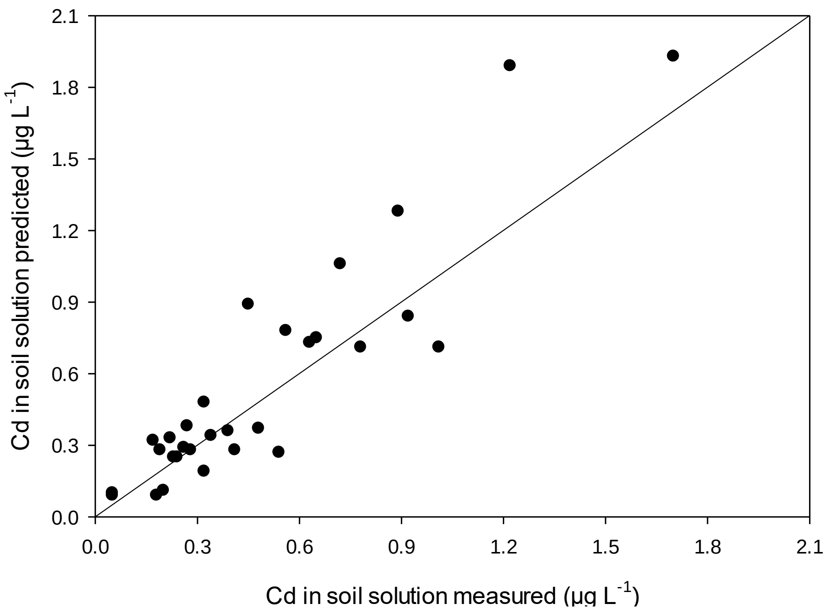

Figure 1. Comparison of measured and predicted soil solution cadmium (Cd) concentrations (µg L^{-1}) calculated using the non-linear model (equation 13) using soil data from the validation dataset. The line is the 1:1 relationship.

A comparison of soil solution Cd concentrations calculated using the linear model to predict soil $K_{Din\ situ}$ values (equation 14) and total soil Cd with measured soil solution Cd concentrations are given in Figure 2. It was found that the linear model could also predict 83% of the variation in the measured soil solution Cd concentrations.

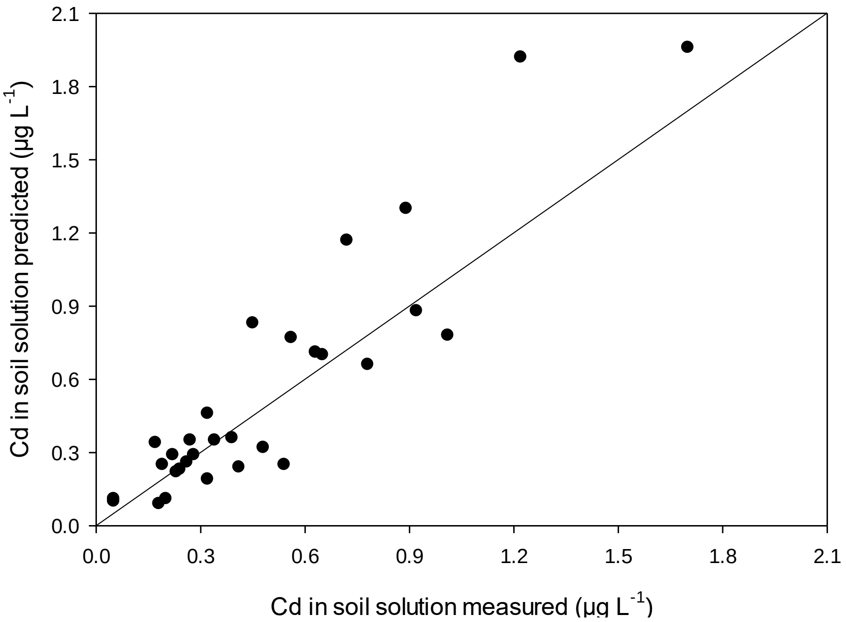

Figure 2. Comparison of measured and predicted soil solution cadmium (Cd) concentrations (µg L^{-1}) calculated using the linear model (equation 14) to predict $K_{Din\ situ}$ and total soil Cd using soil data from validation dataset. The line is the 1:1 relationship.

It appears the linear and non-linear models could both adequately predict soil solution Cd concentrations in our validation dataset.

4.15.2.6 Comparison of predicted versus measured soil solution Cd concentrations - field trials

Despite both (linear and non-linear) models being able to predict soil solution Cd concentrations in our validation dataset, it is important to find out how well soil solution Cd concentrations predicted using the models compared to Cd concentrations measured in drainage samples collected from field studies. Unfortunately, very few studies have reported Cd concentrations in drainage collected from field trials (Sterckeman et al. 2018), although there is some Cd data available from two long-term field trials in Europe (Filipović et al. 2016; Cambier et al. 2014; Bengtsson et al. 2006) and from three field trials from New Zealand that investigated the effect of cow urine (Gray et al. 2017), subsoil texture (Gray and Cavanagh 2016) and soil type (Gray et al. 2003b) on Cd leaching losses from soils.

A summary of topsoil properties (pH, OM and total soil Cd) from each study used to predict soil solution Cd concentrations using equations 13 and 14, along with the average Cd concentration measured in drainage from each study is given in Table 19. It was found that on average, Cd concentrations measured in drainage were about two-fold lower than soil solution Cd concentrations predicted using either model. There was however a lot of variability between measured and predicted Cd concentrations between sites. For example, there was a reasonably good comparability between measured and predicted Cd concentrations at the Arable plot 2 and 3, SGW, cont, pumice fine and coarse, and Pallic sites (Table 19). In contrast, relationships were poor at the Arable Plot 4, MSW, Allophanic 2, Pumice 1 and 2 sites.

The variability observed between predicted and measured Cd concentrations is perhaps not unexpected, given that depending on the soil type, Cd transport, like other solutes can be subject to a range of physical and chemical non-equilibrium conditions that can influence Cd concentrations in drainage (Garrido et al. 2008). This does make it challenging for a predicted soil Cd concentration to reflect an average Cd flux in a soil that will likely vary considerably over the period of the drainage season. For example, several studies have shown that Cd can move by preferential flow in both coarse textured (Carrick et al. 2014) and well-structured clay soils (Bergkvist and Jarvis 2004), where water and solutes move through the soil via macropores, bypassing a large part of the soil matrix. This can enhance the transport of Cd through the soil and Cd concentrations in drainage. Whereby if chemical non-equilibrium conditions (sorption and desorption reactions) occur during Cd transport, this can result in Cd concentrations in solution equilibrated with the soil that are either lower or higher than the Cd concentration in the drainage water (Degryse and Smolders 2006).

Nonetheless, when non-equilibrium conditions are not present, a satisfactory relationship between Cd measured in drainage and soil solution Cd concentrations has been reported. For example, in a field study of Cd transport in both polluted and non-polluted soils, Degryse and Smolders (2006) found soil solution Cd concentrations extracted by centrifugation from the soil at the end of the trial were within the range of Cd concentrations measured in drainage over an 18-month period.

4.15.2.7 Cadmium fluxes

It is also important to evaluate how well Cd leaching fluxes are calculated using a predicted soil solution Cd concentration and a predicted drainage value from OVERSEER® compared to measured Cd fluxes reported in New Zealand.

A soil solution Cd concentration was calculated using the non-linear model (equation 13) using the median soil pH (5.8), soil organic matter content (8.8%) and total Cd concentration (0.34 mg kg^{-1}) from the combined derivation and validation datasets (Appendix B Table B1 and B2) (n = 70). Drainage data was based on the median value from over 20,000 cropping and pasture blocks reported in OVERSEER® (Alister Metherell Ravensdown Ltd, personal communication).

Using the predicted soil solution Cd concentration (0.44 µg L^{-1}) and predicted drainage (352 mm), a Cd leaching flux of 1.55 g Cd ha^{-1} yr^{-1} was calculated. This is within the range of values (0.14 to 2.3 g Cd ha^{-1} yr^{-1}) that have previously been measured or estimated from soils amended with P fertiliser in New Zealand (Gray et al. 2017; Salmanzadeh et al. 2017; Gray and Cavanagh 2016; Gray and McDowell 2016; Carrick et al. 2014; McLaren et al. 2004; Gray et al. 2003b). It is also similar to the leaching fluxes reported by Römkens (personal communication) who, using a similar mechanistic approach to calculate Cd accumulation in arable soils across Europe, reported fluxes of between 0.14 to 5.1 g Cd ha^{-1} yr^{-1} for 25 member states, with a median flux of 1.2 g Cd ha^{-1} yr^{-1}.

4.15.3 Summary

The results of this study indicate that commonly measured parameters such as soil pH and soil OM content, along with the total soil Cd concentration can be combined to predict *in-situ* soil solution Cd concentrations. If we accept that the soil solution Cd concentration predicted using these soil parameters reflects the average Cd concentration in drainage, we propose using this approach along with a measurement of drainage, preferably taken from OVERSEER® or a soil water balance for the LMU to estimate Cd leaching flux in the updated CadBal model. Given the similarity in the linear and non-linear models used to predict soil solution Cd concentrations, it probably doesn't matter which one is selected, although preference is for the non-linear approach which is what has been used in the most recent attempt to model Cd accumulation in soils in Europe (Römkens (personal communication).

To undertake the calculation of Cd leaching loss in the CadBal model, the user will be required to provide a value for soil pH (measured in water), soil OM content (%), and total soil Cd (mg kg^{-1}) representing their LMU, along with a measure of drainage (mm) obtained from OVERSEER® or a soil water balance for the LMU. This will provide a measure of Cd leaching loss in units of mg Cd ha^{-1} yr^{-1}.

4.16 Other inputs

4.16.1 **Sludge**

Sludge (*viz* biosolids) are not typically applied in significant quantities to agricultural soils in New Zealand. As a result, Cd input from sludge has been removed from the updated CadBal model.

4.16.2 **Compost**

The application of compost is a potential source of Cd that could be considered an input parameter in the CadBal model. Composts can contain a range of important plant nutrients (N, P, K, Zn), but also may contain small amounts of Cd (0.0003 – 0.7 mg Cd kg^{-1}) (Al Mamun et al. 2017, 2016). Data about how much compost is applied to New Zealand agricultural systems is limited, and the range in Cd concentrations is currently not available. We tried without success to obtain data on rates of compost application in sectors where compost may be used e.g. HorticultureNZ or the Foundation of Arable Research. As a result, compost has not been included as an input in the updated CadBal model.

Table 19. Comparison between measured Cd concentrations (µg Cd L^{-1}) in drainage reported in several leaching trials from Europe and New Zealand with estimated soil solution Cd concentrations (µg Cd L^{-1}) calculated for each trial using equations 13 and 14 for the non-linear and linear model, respectively.

Site name	Soil depth cm	pH	Total Cd (mg kg^{-1})	Organic matter (%)	Estimated soil solution Cd concentration (µg L^{-1}) Linear	Estimated soil solution Cd concentration (µg L^{-1}) Non-linear	Measured soil solution Cd concentration (µg L^{-1})	Reference
Arable Plot 1	0-25	6.0	0.11	2.8	0.18	0.20	0.10	Bengtsson et al. (2006)
Arable Plot 2	0-25	6.2	0.11	4.7	0.08	0.10	0.15	
Arable Plot 3	0-25	6.5	0.11	9.3	0.03	0.04	0.05	
Arable Plot 4	0-25	5.7	0.10	8.1	0.17	0.21	0.05	
SGW	0-45	6.9	0.20	2.1	0.04	0.04	0.05	Cambier et al. (2014);
MSW	0-45	7.6	0.20	1.9	0.01	0.01	0.05	Filipović et al. (2016)
Cont	0-45	6.8	0.18	1.5	0.08	0.07	0.05	
Pumice Coarse	0-7.5	6.3	0.81	15.3	0.23	0.22	0.18	Gray and Cavanagh (2016)
Pumice Fine	0-7.5	6.3	0.59	15.9	0.16	0.17	0.25	
Otama	0-15	6.6	0.26	3.7	0.09	0.09	0.18	Gray et al. (2017)
Pumice 1	0-25	5.3	0.44	18.2	1.17	1.18	0.26	Gray et al. (2003b)
Allophanic 1	0-25	5.9	0.53	21.2	0.31	0.33	0.58	
Allophanic 2	0-25	5.4	0.52	11.4	1.47	1.38	0.46	
Pumice 2	0-25	5.3	0.69	7.9	3.11	2.62	0.48	
Brown	0-25	5.6	0.41	11.0	0.74	0.73	0.32	
Pallic	0-25	5.9	0.19	5.7	0.26	0.28	0.34	

5. Sensitivity analysis

A single factor sensitivity analysis was undertaken to compare the relative effect different input parameters in the updated CadBal model had on predicted soil Cd concentrations. This approach was used in the previous update of the CadBal model (Roberts and Longhurst 2005). The analysis was not strictly statistical as the relative scale of change to variables differed. Nonetheless, it does help identify the key input parameters and the importance of obtaining good quality data in order to obtain an accurate estimate of the rate of Cd accumulation in soil using the CadBal model.

5.1 Method

A 'typical' grazed dairy system and a wheat cropping system were set up in the updated CadBal model. A summary of the input parameters and values for each system are given in Table 20 and 21, respectively. The time required for soil Cd concentrations in each system to reach a target Cd concentration were then calculated. Soil targets for the dairy and cropping systems were 1.0 and 0.6 mg Cd kg^{-1}, respectively. The CadBal model calculated it would take 71 yr for soil Cd concentrations to reach 1.0 mg kg^{-1} in the grazed dairy system (Table 20), and 203 yr in the wheat cropping system (Table 21). A single input parameter in each system was then changed, the CadBal model was re-run, and the number of years to reach the soil target for each system was recorded. This was then repeated for each input parameter.

5.2 Results and discussion

5.2.1 Grazed dairy system

As anticipated, the Cd concentration in P fertiliser and the rate of fertiliser application had by far the greatest effect on the rate of soil Cd accumulation (Table 20). This highlights the importance of having available accurate data on Cd concentrations in P fertiliser products if accurate long-term estimates of Cd accumulation in soil are to be calculated using the CadBal model.

Cadmium leaching parameters also had an important effect on the rate of soil Cd accumulation, especially soil pH and the soil OM content, as these both control Cd solubility.

As expected, parameters such as the soil depth and soil bulk density were also important, because they affect the soil mass where Cd can accumulate (i.e. the shallower the soil and lower the bulk density the quicker Cd will accumulate). In comparison, Cd inputs from lime, FDE, atmospheric accession, and Cd loss in sediment and crop offtake had less effect on the rate of soil Cd accumulation.

Table 20. Sensitivity of soil cadmium (Cd) accumulation in a grazed dairy system to changes in input parameters in the updated CadBal model.

CadBal input parameters		Unit	CadBal input value	Yr to 1 mg kg^{-1}	New CadBal input value	Yr to 1 mg kg^{-1}	Change (years)
System		Grazed dairy		71			
Soil order		Allophanic		71	Brown		
Volcanic soil		yes		71	no		
Bulk density		kg m^{-3}	764	71	1004	93	+22
Soil depth		m	0.15	71	0.075	36	-35
Initial soil Cd concentration		mg kg^{-1}	0.60	71	0.40	98	+27
Fertiliser Cd concentration		mg Cd kg^{-1} P	250	71	150	243	+172
Fertiliser P application rate		kg ha^{-1} yr^{-1}	45	71	30	171	+100
Atmospheric accession		mg ha^{-1} yr^{-1}	270	71	110	72	+1
Sediment yield		kg ha^{-1} yr^{-1}	131	71	655	76	+5
Lime Cd concentration		mg kg^{-1}	0.15	71	0.50	69	-2
Lime application rate		kg ha^{-1} yr^{-1}	500	71	1000	70	-1
FDE Cd concentration		µg L^{-1}	0.55	71	5.8	68	-3
FDE application rate		mm ha^{-1} yr^{-1}	40	71	20	71	0
FDE pond solids Cd concentration		mg kg^{-1}	0.09	71	0.39	57	-14
FDE pond solids application rate		kg ha^{-1} yr^{-1}	5000	71	2000	74	+3
Cd leaching	pH		5.6	71	6.1	45	-26
	OM	%	10	71	5	110	+39
	Drainage	mm	400	71	300	58	-13
Crop offtake	PUF		0.090	71	0.5	71	0
	Crop yield	kg ha^{-1} yr^{-1}	15000	71	10000	71	0
	Crop removal	%	1	71	1	70	-1

5.2.2 **Cropping system**

As was found in the grazed dairy system, the Cd concentration in P fertiliser had the greatest effect on the rate of soil Cd accumulation (Table 21). However, unlike the grazed system, where 99% of the Cd in crops is returned to the soil in dung, in the cropping system, parameters such as the PUF, crop yield and proportion of crop biomass removed all had an important effect on the rate of soil Cd accumulation. Compared to grazed systems, soil parameters that affect Cd leaching were again important, as was the initial soil Cd concentration, the soil depth and bulk density. Cadmium inputs in lime and atmospheric accession, and Cd loss in sediment were again less important on the rate of soil Cd accumulation.

5.2.3 **Summary**

This analysis highlights that regardless of the agricultural system, it is essential to have accurate data on Cd concentrations in P fertilisers as this is the input parameter which has the greatest effect on the rate of soil Cd accumulation. It is also important to have good estimates of the soil parameters that affect Cd leaching (pH, OM and total Cd), as well as the drainage flux. For systems where crops are harvested, accurate data on the crop yield and the proportion of the crop removed are important. Data on input parameters from lime, FDE, atmospheric accession and sediment appear to be comparatively less important.

Table 21. Sensitivity of soil cadmium (Cd) accumulation in a wheat cropping system to changes in input parameters in the updated CadBal model.

CadBal input parameters		Unit	CadBal input value	Yr to 0.6 mg kg^{-1}	New CadBal input value	Yr to 0.6 mg kg^{-1}	Change (years)
System		Wheat					
Soil order		Pallic			Brown		
Volcanic soil		no			no		
Bulk density		kg m^{-3}	1236	203	1004	165	-38
Soil depth		m	0.15	203	0.075	102	-101
Initial soil Cd concentration		mg kg^{-1}	0.15	203	0.40	113	-90
Fertiliser Cd concentration		mg Cd kg^{-1} P	185	203	100	1000	Target not reached
Fertiliser P application rate		kg ha^{-1} yr^{-1}	40	203	50	139	-64
Atmospheric accession		mg ha^{-1} yr^{-1}	210	203	110	208	5
Sediment yield		kg ha^{-1} yr^{-1}	500	203	1000	216	+13
Lime Cd concentration		mg kg^{-1}	0.15	203	0.5	194	-9
Lime rate		kg ha^{-1} yr^{-1}	500	203	1000	199	-4
Cd leaching	pH		6.0	203	6.5	168	-35
	OM	%	3.0	203	7.0	183	-20
	Drainage	mm	200	203	300	243	+40
Crop offtake	PUF		0.5	203	0.75	316	+113
	Crop yield	kg ha^{-1} yr^{-1}	10800	203	15000	278	+75
	Crop removal	%	100	203	50	157	-46

6. Testing the updated CadBal model

To assess how well the updated CadBal model predicts soil Cd concentrations, we compared the CadBal-model values to measured soil Cd concentrations previously reported (Gray et al. 2020) from the Winchmore long-term P fertiliser trial, which has received annual applications of SSP fertiliser (and therefore Cd) since 1952. The assessment was restricted to data that was collected between 1974 to 2016, due to the availability of either measured Cd concentrations in SSP fertiliser (Salmanzadeh et al. 2017; McDowell 2012), or archived SSP fertiliser from the Winchmore trial that could be analysed for Cd.

6.1 Measured soil Cd concentrations

6.1.1 Winchmore trial details

The Winchmore Research Station is located near Ashburton (43.8° S, 171.8° E). Details of the site history, establishment and management of the long-term P trial are described in other publications (e.g. Kelliher et al. 2017; Rickard and Moss 2012).

6.1.2 Samples and Cd analysis

Archived soil samples (0 – 0.075 m depth) from the control, 17 and 34 kg P ha^{-1} yr^{-1} treatments collected in the spring of 1974, 1979, 1985, 1989, 1996, 2001, 2004, 2005, 2007, 2009, 2012, 2014 and 2016 were analysed for total recoverable Cd. Cadmium in soils sampled between 1974 and 1996 were determined following a nitric acid microwave digestion (USEPA SW 846-3051) and analysed for Cd using graphite furnace atomic absorption spectrometry (Gray et al. 1999). Cadmium in soils sampled between 1996 and 2016 were determined by digesting soils in nitric/hydrochloric acids, as described in the USEPA method 200.2 (Martin et al. 1994) and analysed using ICP-MS. Archived SSP fertiliser samples that had been applied to the Winchmore fertiliser trial in 1997, 1999, 2001, 2009, 2013 and 2016 were analysed for total recoverable Cd following a nitric acid microwave digestion (USEPA SW 846-3051) by inductively coupled plasma optical emission spectrometry. The total P content was determined by colorimetric analysis after digestion in hydrochloric/nitric acid.

6.2 CadBal input parameters

A summary of the input parameters used to predict soil Cd concentrations are given in Table 22. The pasture yield data used are annual average values from the Winchmore P trial measured between 1981 and 2011 (Smith et al. 2012). Cadmium concentrations in SSP fertiliser are based on measured values representing three intervals reported to have used different blends of P rocks (and therefore had different Cd concentrations) to manufacture SSP in New Zealand (Anonymous 2008). For the first interval (1975 – 1983), a value of 155 mg Cd kg^{-1} P was used based on analysis of SSP fertiliser applied to the Winchmore trial in 1982 (McDowell 2012). For the second interval (1983 – 1996), a value of 353 mg Cd kg^{-1} P was used based on analysis of SSP fertiliser from the mid-1980s (Salmanzadeh et al. 2017). For the third interval (1996 – 2016), an average value of 169 mg Cd kg^{-1} P was used which is based on the analysis of six archived SSP fertiliser samples that were applied to the Winchmore trial (undertaken in this study).

The Cd leaching rate was based on the drainage flux and an estimation of the soil solution Cd concentration for the trial site. A drainage value of 444 mm was used that had been calculated for the Winchmore trial site using OVERSEER® version 6.3.2 (Geoff Mercer personal communication). The soil solution Cd concentration was calculated using equation (13). A soil pH of 5.65 was used based on the average value over the last 25 years from the Winchmore trial (Smith and Moss 2019). A soil OM content of 6.5% was used which was the average value between 1975 – 1987 (Nguyen and Goh 1990). The initial total soil Cd concentrations used were values measured in soils sampled in 1974 (Gray et al. 1999).

Table 22. Input parameters used in the updated CadBal model to calculate soil cadmium (Cd) concentrations (mg kg^{-1}) between 1974 and 2016 for the control, 17 and 34 kg P ha^{-1} yr^{-1} treatments from the Winchmore long-term P fertiliser trial.

Input	Treatment		Data source
Agricultural system		Annual crop	
Soil order		Brown	
Bulk density (kg m^{-3})		1004	This study
Sample depth (m)		0.075	
Initial soil Cd concentration (mg kg^{-1})	Control	0.04	Gray et al. (1999)
	17 kg ha^{-1} yr^{-1}	0.13	
	34 kg ha^{-1} yr^{-1}	0.28	
Rate of P fertiliser application (kg ha^{-1} yr^{-1})	Control	0	
	17 kg ha^{-1} yr^{-1}	17	
	34 kg ha^{-1} yr^{-1}	34	
Cd concentration in P fert (mg Cd kg^{-1} P)	1975 – 1983	155	McDowell (2012)
	1983 – 1996	353	Salmanzadeh et al. (2017)
	1996 – 2016	169	This study (6 measured values)
Pasture yield (kg ha^{-1} yr^{-1} DM)	Control	5289	Smith et al. (2012)
	17 kg ha^{-1} yr^{-1}	11428	
	34 kg ha^{-1} yr^{-1}	12242	
Plant uptake factor		0.24	Table 7 this study
Sediment load (kg ha^{-1} yr^{-1})		595	Table 15 this study
Atmospheric input (mg ha^{-1} yr^{-1})		170	Gray et al. (2003a)
Cadmium leaching (g ha^{-1} yr^{-1})			As described in the text

6.3 Results and discussion

6.3.1 Measured soil Cd concentrations

Total soil Cd concentrations measured in the control treatment remained relatively constant between 1974 and 2016 (Figure 3). In comparison, Cd concentrations increased from 0.134 to 0.258 mg kg^{-1} in the 17 kg P ha^{-1} yr^{-1} treatment and from 0.277 to 0.465 mg kg^{-1} in the 34 kg P ha^{-1} yr^{-1} treatment. In line with the P fertiliser inputs, the rate of increase in soil Cd was about twice as high (1.8) in plots that received 34 kg P ha^{-1} yr^{-1} than the 17 kg P ha^{-1} yr^{-1}.

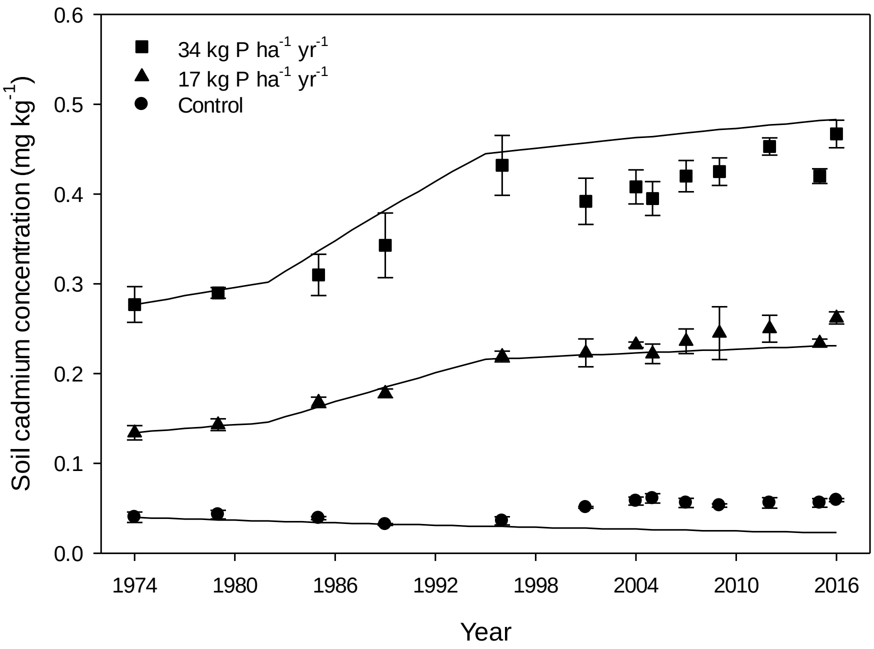

Figure 3. Mean (± 95% CI) soil cadmium (Cd) concentrations from the Winchmore long-term fertiliser trial (symbols) and the changes calculated in soil Cd (lines) by the updated CadBal model between 1974 and 2016.

6.3.2 Modelled soil Cd concentrations

Calculated soil Cd concentrations modelled using CadBal for the three fertiliser treatments are given in Figure 3. Between 1974 and 1998, there was a reasonable alignment between measured and calculated soil Cd concentrations for all three treatments. However, between 1998 – 2016, although there was still a reasonable alignment for the 17 kg P ha^{-1} yr^{-1} treatment, the control was slightly lower, and the 34 kg P ha^{-1} yr^{-1} treatment was slightly higher than measured Cd concentrations. Despite this, soil Cd concentrations predicted using CadBal in the two fertiliser treatments were within 10% of the measured values after 41 years.

6.4 Summary

Despite some uncertainty in the precise amount of Cd applied to the soil from P fertiliser and amount of Cd lost via leaching, which are the parameters which have the greatest effect on soil Cd accumulation in grazed pasture systems, there was a reasonably good relationship between measured soil Cd concentrations and Cd concentrations calculated using the updated CadBal model. It was found that after the 41 yr interval of the trial, Cd concentrations calculated by CadBal for the soils in the two fertiliser treatments were within 10% of the measured soil Cd concentrations.

7. Summary

The CadBal model has been redeveloped using a combination of Cd research published since the last update to the existing model in 2005, along with new research undertaken as part of the update. The structure of the CadBal model has remained the same as the existing model, based on the initial total soil Cd concentration for a land management unit and a series of Cd inputs and losses. However, updates have been made to some of the existing Cd input parameters, some new Cd inputs added and there have been changes to how Cd losses are modelled.

Updates to the CadBal model include new soil bulk density values to cover all soil orders in New Zealand and new data on sediment loads for different landuse activities used to estimate Cd loss by soil erosion. The model now provides default Cd concentrations for different P fertiliser groups including direct application phosphate rock, sulphuric acid derived, phosphoric derived or nitric acid derived products as categorised in the TFMS. Three new Cd inputs for lime, FDE and FDE pond solids have also been added to the model.

The main changes to the model include how Cd losses via leaching and plant offtake are calculated. The CadBal model now uses the drainage leaving the topsoil, multiplied by an estimate of the soil solution Cd concentration predicted from soil pH, soil OM content and the total soil Cd concentration to calculate Cd leaching. Crop offtake of Cd is now able to be calculated for a larger range of crop species than in the previous model, broadly grouped into either grazed and annual crops or short rotation crops. Crop offtake is calculated using the total soil Cd concentration, a plant uptake factor, the crop dry matter yield and the proportion of crop biomass removed.

A sensitivity analysis found that regardless of the agricultural system, it is essential to have accurate data on Cd concentrations in P fertilisers, as this is the input parameter which has the greatest effect on the rate of soil Cd accumulation. It is also important to have accurate data for the soil parameters that affect Cd leaching (pH, OM and total soil Cd concentration), as well as the drainage flux. For systems where crops are harvested, accurate data on the crop yield and the proportion of the crop removed are important. In comparison, data on Cd input parameters from lime, FDE, atmospheric accession and sediment appear to be less important.

A reasonably good relationship was found between calculated soil Cd concentrations using the updated CadBal model and measured soil Cd concentrations values from the Winchmore long-term P fertiliser trial. It was found that after the 41 yr interval of the trial, Cd concentrations predicted by the CadBal model for the soils in the two fertiliser treatments were within 10% of the measured soil Cd concentrations.

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10. Appendices

10.1 Appendix A

Table A1. Input parameters and calculation of the amount of pond solids produced per annum for a ‘average Waikato Dairy farm’ (Bob Longhurst, personal communication). Note: Accumulated solids total is 54m^3 per annum of which 29m^3 are removed and 25m^3 remain in the pond.

LOCATION: Hamilton	
Farm data:	
Area (effective ha)	116
Cows (no.)	342
Stocking rate (cows/ha)	2.95
Calving date (dd/mm)	19/07
Drying off (dd/mm)	13/05
Lactation (days)	278
Milk production (1,060 kg MS/	1,060
(NZ Dairy Statistics 2017-18)	
Pond data:	
Volume (m3)	1700
Depth (m)	4
Surface dimensions (m)	21*39
Surface area (m2)	820
Bottom dimensions (m)	5*23
Bottom area (m2)	115
DEC manual (2004)	
Effluent	
Daily volume (L/cow/day)	70
Daily volume (L/cow/lactation	19460
Daily volume (m3/cow/lactati	19.5
Assumptions *	
Pond level mid-point, area (m	400
Mid-point dimensions (m)	13*31
Pond volume at end	
of previous lactation (m3)	50
Rainfall - May (m3)	26
Rainfall - June (m3)	69
Rainfall - July (m3)	44
Pond volume <lactation (m3)	189
Solids in FDE (% in DM) **	0.5
Pond solids remaining (m3)	25

Scenario based on "average" Waikato dairy farm, no feed pad.												
	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN
Assumptions												
Evaporation (mm/day)	2	2	3	3	4	4.5	5	5	4.5	4	3	2
Land application (mm)	0	1.5	2.5	3.5	3.75	3.75	3.5	3.5	3	2.5	0.5	0
Land application (days/mth)	0	5	10	15	20	25	31	28	31	25	13	0
Rainfall (mm)	118.2	103.4	91.5	91.9	85	100.7	76.3	68.7	79.4	80.3	99.7	113.2
Rain to pond (m3)	96.9	84.8	75.0	75.4	69.7	82.6	62.6	56.3	65.1	65.8	81.8	92.8
Evaporation (mm/mth)	62.0	62.0	90.0	93.0	120.0	124.0	155.0	140.0	140.0	120.0	93.0	60.0
Pond evaporation (m3) *	24.8	24.8	36	37.2	48	49.6	62	56	56	48	37.2	24
Pond surface area (m2)	820	820	820	820	820	820	820	820	820	820	820	820
Net rain inputs to pond (m3)	72.1	60.0	39.0	38.2	21.7	33.0	0.6	0.3	9.1	17.8	44.6	68.8
Dairy shed (days milking)	12	31	30	31	30	31	31	28	31	30	13	0
Cows in milk	185	270	330	342	335	325	320	300	250	150	100	0
FDE (L/cow/month)	840	2170	2100	2170	2100	2170	2170	1960	2170	2100	910	0
FDE (m3/herd/month)	155	586	693	742	704	705	694	588	543	315	91	0
Pond inflows - FDE (m3)	155	586	693	742	704	705	694	588	543	315	91	0
Pond - rain (m3)	72	60	39	38	22	33	1	0	9	18	45	69
Total pond inflows (m3)	228	646	732	780	725	738	695	588	552	333	136	69
Pond outflows - LA (m3)	0	75	250	525	750	937.5	1085	980	930	625	65	0
Pond volume (m3)	416	987	1469	1724	1700	1500	1110	719	340	48	119	187
Pond solids (m3) **	25.8	2.9	3.5	3.7	3.5	3.5	3.5	2.9	2.7	1.6	0.5	0.0
Accumulated solids total (m3)	25.8	29	32	36	39	43	46	49	52	54	25	25

10.2 Appendix B - Materials and methods, soil data and results from the soil solution study

10.2.1 Materials and methods

10.2.1.1 Soil analysis

Soils were dried (35°C) to a constant weight and sieved (<2 mm) before analysis. Soil pH was determined in a 1:2.5 soil/water solution by potentiometric analysis (Blakemore et al. 1987). Soil organic matter was determined by combustion using an Elementar Vario-Max C Elemental analyser. Total soil P concentrations were determined by nitric acid/hydrochloric digestion (US EPA 2002) followed by analysis using inductively coupled plasma-optical emission spectrometry (ICP-OES). Reactive Cd was determined by extracting soils with 0.43 M HNO_3 using the method described in Groenenberg et al. (2017) followed by analysis using inductively coupled plasma-mass spectrometry (ICP-MS). Total recoverable Cd was determined by nitric acid/hydrochloric digestion (US EPA 2002) followed by analysis using ICP-MS.

10.2.1.2 Soil solution

Soil solution samples were obtained from soils using micro-rhizons samplers (Rhizon SMS MOM; Eijkelkamp) as described in Di Bonito et al. (2008). Briefly, the method involved weighing 200 g of soil into plastic pots, bringing the soil to field capacity moisture content and leaving the moist soil to equilibrate for 16 h at 20°C. This interval has been shown to be adequate to allow equilibrium of water with the soil without modifying the ionic strength or pH of the soil (Menzies and Bell 1988). The micro-rhizon samplers filter extracted soil solution at a pore diameter of 0.1 mm (Meers et al. 2005). Micro-rhizon samplers were inserted horizontally into soils, a suction applied via a syringe and soil solution extracted and analysed for Cd within 24 hrs by ICP-MS. Soil solutions were extracted from each soil in duplicate.

10.2.1.3 Determination of soil K_D values

Soil K_D values were determined using both i) a laboratory batch equilibrium method with Cd added to the soil (K_{Dbatch}) and ii) the total soil Cd content and the Cd concentration measured in soil solution ($K_{Din\ situ}$).

10.2.1.4 K_{Dbatch}

Cadmium was added as $Cd(NO_3)_2$ to 5 g soil in 30 mL of a background electrolyte of 0.01 M $Ca(NO_3)_2$. Calcium nitrate was used as the supporting electrolyte to eliminate non-specific sorption of Cd, since low affinity sorption sites would be saturated by calcium ion. Preliminary experiments to determine time of equilibration showed that after 16 hrs there was no significant change in the amount of Cd sorbed by the soil (Gray et al. 1999). Soil suspensions were shaken for 16 hrs, on a reciprocating shaker, after which the samples were centrifuged at 3500 rpm for 20 minutes, and filtered through a 0.45 µm filter membrane and Cd determined in the supernatant by ICP-MS.

10.2.1.5 $K_{Din\ situ}$

Two different $K_{Din\ situ}$ values were calculated, by dividing either the total soil Cd content or reactive soil Cd content with the soil solution Cd concentration. These were defined as

$K_{Dtotal} = [Cd]_{soil\ total}/[Cd]_{soil\ soln}$

or

$K_{Dresidual} = [Cd]_{soilresidual}/[Cd]_{soil\ soln}$

Total, reactive and solution Cd concentrations were derived as described above.

10.2.1.6 Quality control

Soils, extracts and soil solution samples were analysed by Hill Laboratories Ltd, an IANZ accredited laboratory. Quality control measures for Cd analysis included use of blanks, analysis of duplicate samples, spiked blanks and Inter-laboratory Comparison reference water quality control samples and a certified reference material AGAL-10 (Australian Government Analytical Laboratories, Sydney, Australia) for soil, along with an in-house QC soil sample. Concentrations of Cd in procedural blanks were less than the detection limit of 0.05 µg Cd L^{-1}. Duplicate results were <5%. The recovery of Cd from the spiked blanks and reference materials were within the limits of the certified values.

10.2.1.7 Data analysis

The regression coefficients for soil properties in the transfer functions for the solid solution partitioning of Cd were assessed with multiple linear regression analyses, using Genstat version 18. The raw data showed a log-normal distribution. Hence the data was log transformed (except pH) before multiple regression analysis.

Table B1. New Zealand soil order, landuse, soil pH, organic matter (OM), 0.43 M nitric (HNO_3) acid extractable cadmium (Cd), total soil Cd, soil solution Cd and K_{Dbatch} values from the sites in the derivation dataset.

Soil Order	Landuse	pH	OM (%)	HNO_3 Cd (mg kg^{-1})	Total Cd (mg kg^{-1})	Soil solution Cd (µg L^{-1})	K_{Dbatch} (L kg^{-1})
Brown	pasture	5.6	8.5	0.23	0.30	0.42	158
Recent	pasture	5.7	5.1	0.23	0.33	0.29	151
Pallic	crop	6.0	2.2	0.17	0.24	0.46	289
Pallic	crop	5.6	2.7	0.09	0.12	0.41	109
Brown	pasture	5.9	7.9	0.40	0.54	0.45	260
Recent	pasture	6.1	5.2	0.26	0.32	0.22	242
Recent	pasture	6.0	6.4	0.41	0.51	0.44	331
Brown	pasture	5.5	7.5	0.33	0.39	0.46	75
Recent	crop	6.1	4.3	0.20	0.21	0.18	353
Recent	crop	6.3	2.7	0.15	0.15	0.17	322
Pallic	pasture	5.7	3.4	0.10	0.13	0.21	106
Pallic	pasture	5.9	3.5	0.11	0.12	0.27	175
Recent	pasture	5.7	3.6	0.30	0.33	0.53	76
Recent	pasture	5.4	2.7	0.27	0.34	1.67	24
Pumice	pasture	6.0	4.5	0.41	0.44	0.71	212
Recent	pasture	6.0	4.1	0.21	0.24	0.27	250
Recent	pasture	5.4	4.8	0.22	0.30	0.48	49
Granular	crop	7.0	1.7	0.37	0.43	0.05	2000
Granular	crop	6.4	3.1	0.23	0.32	0.06	663
Allophanic	crop	6.1	4.5	0.72	0.81	0.65	356
Allophanic	crop	6.3	3.3	0.60	0.75	0.53	294
Allophanic	crop	6.5	4.7	0.43	0.41	0.09	746
Brown	pasture	6.1	7.6	0.58	0.67	0.52	406
Brown	pasture	5.8	9.9	0.68	0.75	0.85	231
Granular	crop	6.7	4.5	0.54	0.72	0.05	598
Allophanic	pasture	6.2	6.9	0.56	0.69	0.24	525
Allophanic	pasture	5.3	9.8	0.47	0.59	1.40	81
Pumice	pasture	5.9	10.6	1.10	1.14	0.73	372
Pumice	crop	5.9	8.2	0.42	0.44	0.30	262
Pumice	pasture	6.3	10.0	0.64	0.65	0.24	593
Pumice	pasture	5.8	9.1	0.20	0.25	0.26	190
Brown	pasture	5.0	6.1	0.44	0.50	2.80	68
Recent	pasture	5.7	3.5	0.30	0.38	0.96	120
Brown	pasture	5.1	4.7	0.46	0.52	3.30	46
Pallic	pasture	5.8	3.8	0.14	0.18	0.30	121
Recent	pasture	5.4	4.5	0.18	0.19	1.36	50
Pallic	pasture	5.6	3.8	0.13	0.15	0.46	56
Recent	pasture	5.6	0.6	0.02	0.07	0.62	33
Allophanic	pasture	6.2	38.8	0.69	0.78	0.13	2480
Gley	pasture	5.8	6.1	0.59	0.68	0.87	265

Table B2. New Zealand soil order, landuse, soil pH, organic matter (OM), total soil cadmium (Cd), soil solution Cd and KD_{batch} values from the sites in the validation dataset.

Soil Order	Landuse	pH	OM (%)	Total Cd (mg kg^{-1})	Soil solution Cd (µg L^{-1})	K_{Dbatch} (L kg^{-1})
Brown	pasture	5.3	3.9	0.26	0.89	58
Brown	pasture	5.1	3.4	0.22	1.22	41
Pallic	pasture	5.5	2.7	0.18	0.63	112
Recent	pasture	5.3	2.5	0.29	0.79	207
Pallic	pasture	5.9	3.5	0.20	0.54	120
Granular	pasture	6.5	7.2	0.48	0.05	584
Pallic	pasture	5.3	5.0	0.19	0.45	42
Pumice	pasture	5.8	8.2	0.81	1.01	230
Recent	pasture	5.8	6.9	0.24	0.26	307
Recent	pasture	5.8	5.2	0.17	0.23	117
Brown	pasture	5.4	7.0	0.24	0.78	84
Pallic	pasture	5.7	2.9	0.10	0.41	76
Brown	pasture	5.6	5.1	0.56	0.72	232
Brown	pasture	5.5	5.0	0.29	0.56	78
Brown	pasture	5.1	5.1	0.29	1.70	55
Recent	pasture	6.1	7.0	0.54	0.28	298
Allophanic	crop	6.9	6.9	1.29	0.05	1599
Allophanic	crop	6.2	7.5	0.86	0.17	389
Gley	pasture	5.6	4.3	0.38	0.92	101
Organic	pasture	5.8	40.3	0.71	0.19	2361
Recent	pasture	5.7	7.9	0.37	0.32	167
Brown	pasture	6.2	8.6	0.52	0.32	575
Organic	pasture	6.7	10.0	1.09	0.20	1759
Pumice	pasture	6.0	8.7	0.60	0.34	358
Organic	pasture	5.9	13.0	0.62	0.39	395
Pallic	crop	5.4	2.1	0.12	0.65	73
Pallic	crop	5.9	2.5	0.14	0.24	253
Pallic	pasture	5.6	5.3	0.14	0.22	178
Pallic	pasture	5.6	5.9	0.17	0.48	149
Recent	pasture	5.7	7.1	0.26	0.27	199

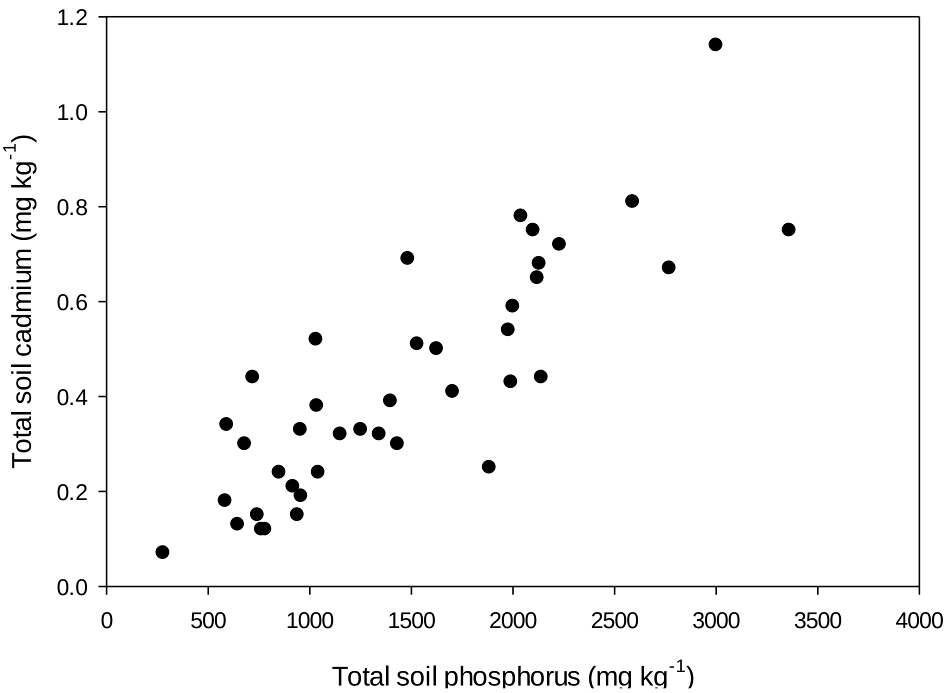

Figure B1. Correlation between total soil phosphorus (P) concentration (mg kg^{-1}) and total soil cadmium (Cd) concentration (mg kg^{-1}) from the derivation dataset (n = 40).

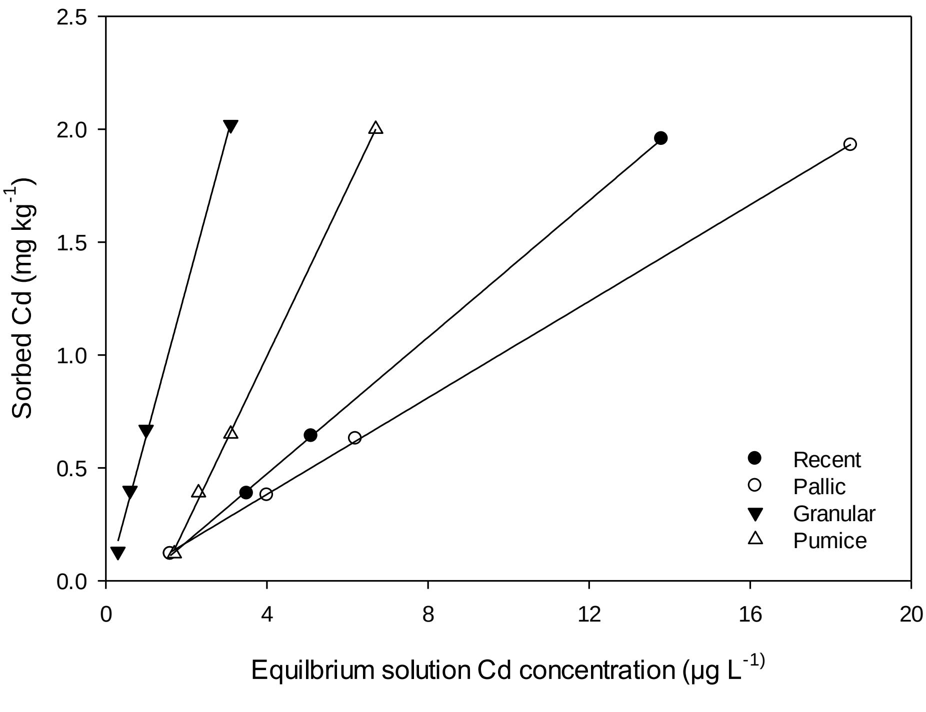

Figure B2. Example of cadmium sorption isotherms for a Recent, Pallic, Granular and Pumice soil from the derivation dataset.

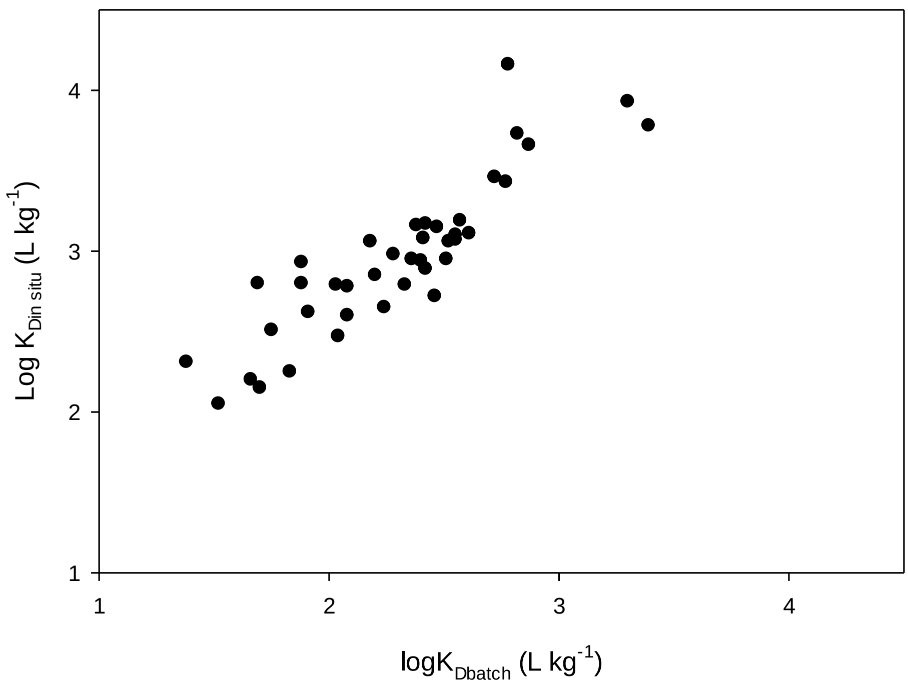

Figure B3. Comparison between log K_D (L kg^{-1}) measured using the batch method (K_{Dbatch}) versus the in situ method ($K_{D\ in\ situ}$) using the derivation dataset.