Using fluxmeters to measure cadmium concentrations in drainage from cropping systems

Col Gray

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Contents

1. Executive Summary

How cadmium (Cd) leaching losses are calculated is a key change to the recent upgrade of CadBal, a Cd balance model for estimating Cd accumulation in New Zealand agricultural soils. Cadmium leaching is now calculated by multiplying the drainage flux for a land management unit (LMU) by a model estimate of the soil solution Cd concentration. The soil solution Cd concentration is estimated using an empirical model based on soil pH, soil organic matter content and the total soil Cd concentration. However, to date there has been little validation of this approach to estimate Cd leaching because very few studies have measured Cd in drainage water collected under field conditions.

Access was recently granted to archived drainage samples collected from the Foundation of Arable Research's (FAR) fluxmeter network; established to measure nutrient loss from cropping farms across New Zealand. The aim of this project was to analyse the archived drainage samples for Cd to obtain data on Cd leaching losses from cropping soils and compare the measured Cd leaching values with Cd leaching calculated using the approach used in the CadBal model.

- Results showed that Cd concentrations in drainage from the seven fluxmeter sites were generally below the method detection limit of 0.05 µg L^{-1}, with only the occasional detection of Cd in drainage from two sites and no detection from four other sites. The exception was site 1, where the average Cd concentration in drainage from the six fluxmeters located at the site ranged from 0.06 to 0.18 µg L^{-1}.

- The mean annual Cd load (± SE) measured from site 1 was 0.33 ± 0.08 g ha^{-1}, at the lower end of the range of Cd leaching loads previously reported, and confirms that Cd leaching from soils amended with Cd from P fertiliser is generally very low.

- The amount of Cd leaching measured at site 1 (0.33 g ha^{-1}) was similar to the amount estimated using the drainage flux combined with an estimate of soil solution Cd concentrations for the site (0.41 g ha^{-1}).

- The lack of data on the rate of Cd leaching measured from the topsoil, which is the depth the CadBal model assesses the rate of Cd accumulation in soil, makes a robust validation of the leaching approach used in CadBal problematic.

- It is recommended this data gap be filled by undertaking paired measurements of Cd leaching from the topsoils of a range of soils, along with pH, total Cd and soil OM content that can be used to estimate soluble Cd concentrations to calculate Cd leaching in CadBal.

2. Background

Cadmium (Cd) is a naturally occurring contaminant in many phosphorus (P) fertilisers (McLaughlin et al. 1996). Extensive P fertiliser use has resulted in an accumulation of Cd in agricultural soils in New Zealand. Elevated Cd concentrations in soils can have adverse effects on food quality, soil health and the environment (MAF 2011). In response to this risk, many countries, including New Zealand have developed Cd balance models to assess the current and future rates of Cd accumulation in agricultural soils. This type of data is critical in helping inform policy decisions on how Cd should be best managed in agricultural systems.

In New Zealand, the only Cd balance model available is CadBal, a model that estimates the rate of total Cd accumulation in agricultural soils based on the initial soil Cd concentration for a site and a series of estimates of Cd inputs and losses. The CadBal model was developed more than 20 years ago (Roberts and Longhurst 1996). In 2020 there was an upgrade of the model (Gray and Cavanagh 2020). A key change to the model was an upgrade to how Cd leaching losses are calculated. Instead of a Cd leaching value being assigned to a site on the basis of the soil order at the site (Taylor and Pohlen 1962), it is now calculated by multiplying the drainage flux for the site by an estimate of the soil solution Cd concentration (Gray and Cavanagh 2020). The soil solution Cd concentration is estimated using an empirical model that includes soil pH, soil organic matter content and the total soil Cd for the site (Gray and Cavanagh 2020).

Despite the use of the same approach to estimate Cd leaching losses in Cd balance models throughout the world (e.g. Sterckeman et al. 2018; Römkens et al. 2018; Six and Smolders 2014; De Vries and McLaughlin 2013), there has been little validation of the model output. This is to a large degree due to the scarcity of studies that have measured Cd concentrations in drainage water collected under field conditions. Using Cd leaching data from the few field trials that are available, McLaughlin et al. (2021) reported Cd leaching losses calculated using two different models both developed in Europe were 2 to 250 greater than measured values. In comparison, Gray and Cavanagh (2020) reported a reasonably good comparability between Cd concentrations estimated using the approach in the CadBal model and Cd measured in drainage water at some sites, but at other sites, modelled Cd concentration values were significantly higher than Cd measured in drainage water.

One reason for the low Cd concentrations measured in drainage, particularly from several of the soils in the Gray et al. (2003) study used in the comparison, could be the design of the barrel lysimeters that were used to collect drainage. The lysimeters used a base plate fixed to the bottom of the soil core and a tube to collect drainage under gravity. This design creates an environment where there is no unsaturated water flow in the soil core (Degryse and Smolders 2006). This can induce saturated conditions at the interface of the soil and base plate in which anaerobic conditions can develop. Gray et al. (2003) reported higher pH values in drainage than the bulk soil, which has been suggested to be indicative of anaerobic conditions and may have resulted in reduced Cd mobility (Six and Smolders 2014).

The Foundation of Arable Research (FAR) has a network of passive-wick tension fluxmeters that were installed on commercial cropping farms across New Zealand to measure nutrient loss in drainage water (Wallace et al. 2020). A feature of the fluxmeters is that they are designed so drainage is pulled out of the soil from a hanging water column created via a wick. This means that the lower soil-boundary remains unsaturated. Potentially, Cd concentrations measured in drainage collected using fluxmeters where suction has been applied are more representative of field conditions than previous measurements using barrel lysimeters. However, it should be recognised that fluxmeters like barrel lysimeters are also subject to some practical limitations, with the wick potentially retaining soil colloids, possibly resulting in the exclusion of colloidal transport of Cd (McLaughlin et al. 2021). Although, the extent of colloidal transport of Cd in soils still remains uncertain.

The aim of this project was to measure Cd concentrations in drainage samples collected using fluxmeters from the FAR monitoring network. This will provide data on Cd leaching losses from cropping soils which are not currently available in New Zealand. Measured Cd leaching data can then be compared with Cd leaching data calculated using the approach used in the CadBal model.

3. Material and Methods

3.1 Fluxmeter sites

In 2014/15, 12 passive-wick tension fluxmeters were installed on 12 commercial cropping farms in four regions of New Zealand. Over the last six years, drainage from the fluxmeters has been collected and analysed for nitrogen (N) and phosphorus (P). Following analysis, subsamples of drainage from selected fluxmeters have been frozen and archived. In this study, archived drainage samples collected over one year of monitoring from six of the 12 fluxmeters installed at seven sites were analysed for Cd. A summary of the regions and cropping rotation at the seven sites is given in Table 1.

3.2 Design and installation of the fluxmeters

A detailed review of the design and functionality of the fluxmeters is provided by Gee et al. (2009) and Meissner et al. (2010). Briefly, the fluxmeters are 1200 mm long and 200 mm wide at the convergence zone at the top of the unit (Figure 1). In the convergence zone, fine silica sand is packed on top of diatomaceous earth to filter out sediment material before drainage water is collected in a reservoir at the base of the fluxmeter. A passive wick is in contact with the sand. This wick ensures that water only enters the reservoir when soil moisture is at or above field capacity, preventing preferential flow into or around the fluxmeter. Polyethylene tubes are attached to each fluxmeter to allow the extraction of drainage water under suction during sampling events (Figure 1).

Table 1: The region and summary of the crop rotation at the seven fluxmeter sites. The crop highlighted in bold is what was growing during the period drainage samples were analysed.

Site	Region	Cropping rotation
1	Canterbury	ryegrass seed-ryegrass pasture-wheat-barley-**plantain-wheat-** ryegrass seed
2	Canterbury	barley-white clover seed-clover pasture-carrots-winter wheat-**ryegrass-peas**-rape
3	Canterbury	ryegrass seed-ryegrass pasture-beans-oats-kale seed-**peas-carrot seed**-oats
5	Manawatu	maize-oats-fodder beet-**oats seed-oats grazed**-maize-ryegrass-barley-ryegrass
7	Hawke Bay	carrots-Italian ryegrass-peas-Italian ryegrass-**peas-beans**-barley-Italian ryegrass
9	Hawke Bay	peas-beans-barley-Italian ryegrass-peas-**sorghum-winter wheat**-ryegrass/clover
10	Waikato	Italian ryegrass-potatoes-onions-Italian ryegrass-**potatoes**-shallots-maize

The installation of the fluxmeters involved augering 200 mm diameter holes to a depth of 2200 mm. Soil removed from the upper 1000 mm was collected in buckets in 100 mm depth increments for subsequent repacking on top of the fluxmeter. Soil from below 1000 mm was discarded. Fluxmeters were lowered into holes and the soil was repacked back in 100 mm layers to the original density of the soil prior to disturbance.

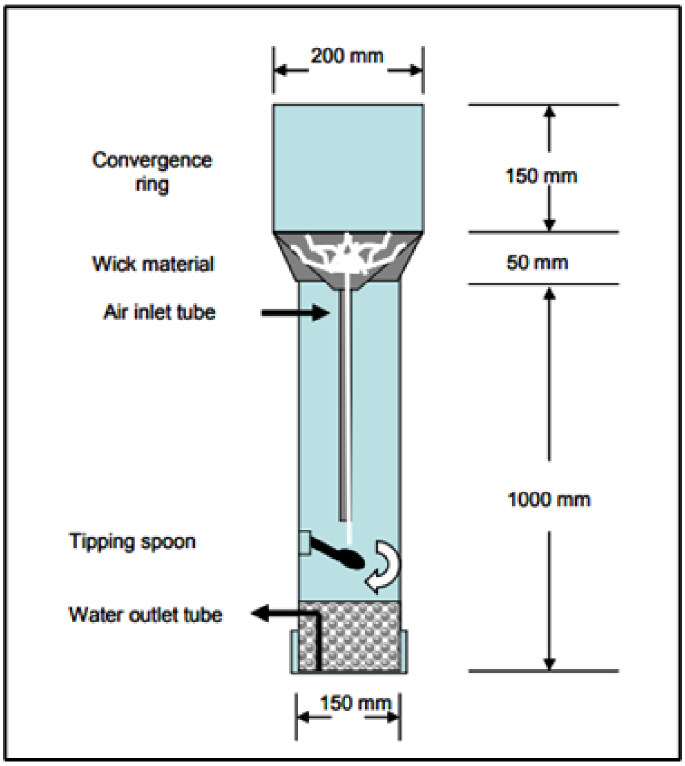

Figure 1: Passive wick fluxmeter used to monitor water and cadmium fluxes. Note that a tipping spoon was not used in the fluxmeters for this study.

3.3 Sample collection and analysis

Drainage was extracted from fluxmeters using a suction pump. A water balance model was used to assist in predicting the timing of sampling (Norris et al. 2016). At each sampling event, the volume of drainage was recorded, and a sub-sample was frozen and archived. The archived drainage samples used in this study were defrosted, shaken to homogenise each sample and filtered through a 0.45 µm membrane and analysed for Cd by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Topsoil samples (0 – 20 cm) collected from each site were air-dried and ground (<2 mm) prior to chemical analysis. Soils were analysed for pH 1:2.5 (soil/water ratio) (Blakemore et al. 1987), soil organic matter content (Metson et al. 1979), Olsen-P (Olsen et al. 1954) and total recoverable Cd by nitric acid/hydrochloric digestion using USEPA method 200.2 (Martin et al. 1994) followed by analysis using ICP–MS.

3.4 Quality control

Drainage samples were analysed for Cd by Hill Laboratories Ltd, an International Accreditation New Zealand accredited laboratory. Quality control measures for Cd analysis included use of blanks, analysis of duplicate samples, spiked blanks and the participation in an inter-laboratory comparison programme. Inter-laboratory comparison reference water quality control samples were included in analysis runs. Concentrations of Cd in procedural blanks were less than the detection limit of 0.05 µg Cd^{-1}. Duplicate results were within 5% of each other. The recovery of Cd from spiked blanks and reference materials were within the limits of the certified values.

4. Results and Discussion

4.1 Soils

The soils at the fluxmeter sites represented five soil orders (Hewitt 2010). Soils were slightly acid, except for site 5 which was slightly alkaline, and soil organic matter contents were low (< 5%) (Blakemore et al. 1987). Olsen P concentrations ranged from 11 mg L^{-1} at site 1 to 33 mg L^{-1} at site 10. With the exception of site 10, total soil Cd concentrations were lower than the mean Cd concentration of 0.28 mg kg^{-1} reported for cropping soils in New Zealand (Cavanagh 2014) and below or only marginally higher than the natural background Cd concentration for New Zealand soils of 0.09 mg kg^{-1} (Abraham 2018). The soils were mainly silt loam or loam textures (Table 2).

Table 2: Soil order, soil texture and mean (± standard deviation; n = 3) values for soil pH, organic matter (OM) content, total soil cadmium (Cd) concentration and Olsen P at the seven fluxmeters sites (0 – 20 cm).

Site	Soil order	Soil texture	pH	OM (%)	Total Cd (mg kg^{-1})	Olsen P (mg L^{-1})
1	Pallic	Silt loam	6.1 ± 0.1	4.3 ± 0.2	0.16 ± 0.01	11 ± 1
2	Pallic	Silt loam	6.0 ± 0.1	4.1 ± 0.5	0.15 ± 0.01	13 ± 1
3	Pallic	Loam over clay	5.8 ± 0.1	4.8 ± 0.3	0.18 ± 0.01	27 ± 1
5	Gley	Sandy loam	7.4 ± 0.1	2.4 ± 0.3	0.05 ± 0.01	25 ± 3
7	Recent	Silt loam	6.5 ± 0.2	2.0 ± 0.2	0.13 ± 0.01	24 ± 3
9	Brown	Silt loam	5.9 ± 0.1	2.6 ± 0.0	0.09 ± 0.01	21 ± 2
10	Allophanic	Loam	6.4 ± 0.2	3.7 ± 0.1	0.47 ± 0.05	33 ± 1

4.2 Rainfall and drainage

Rainfall for each site was obtained using data from the nearest NIWA climate station to the fluxmeter site. Rainfall ranged between 786 mm at site 3 to 1299 mm at site 10 and was 5 to 35% above the long-term average for all sites. Drainage was more variable than rainfall, with values ranging between 120 mm at site 2 to 622 mm at site 5 (Table 3).

Table 3: Annual rainfall (+ the % of the long-term average rainfall for the site), drainage, and average (± standard error) cadmium (Cd) concentration in drainage measured at the seven fluxmeter sites.

Site	Rainfall (mm)	Drainage (mm)	Cd concentration (µg L^{-1})
1	921 +23	231	0.11 ± 0.04
2	1007 +35	120	<0.05
3	786 +28	303	<0.05
5	1183 +20	622	<0.05
7	838 +5	304	<0.05
9	1200 +8	238	<0.05
10	1299 +15	270	<0.05

4.3 Cadmium concentrations and loads

Cadmium concentrations in drainage were generally below the method detection limit of 0.05 µg L^{-1}, with only the very occasional detection of Cd in drainage from sites 2 and 3, and no detection from sites 5, 7, 9 and 10. The very low number of detects in drainage from sites 2 and 3 precluded any meaningful statistical analysis of these samples. The exception however was site 1, where the average Cd concentration in drainage from the six fluxmeters at the site ranged from 0.06 to 0.18 µg L^{-1} from nine drainage events, with an overall average Cd concentration of 0.11 µg L^{-1} (Table 3). It is unclear why Cd was only measured at site 1, as topsoil properties (i.e. pH, OM, texture) known to affect Cd solubility were broadly similar between many of the sites (Table 2). Rather, subsoil properties appear to be more important in controlling the concentration and transport of Cd, presumably via sorption processes.

The annual Cd load (± standard error; n = 6) measured from site 1 was 0.33 ± 0.08 g ha^{-1}. For context, this compares to the amount of Cd added to the soil 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 5.5 g ha^{-1} yr^{-1}. The annual Cd load from site 1 is at the lower end of the range of values (0.02 to 1.80 g ha^{-1} yr^{-1}) that have been measured in drainage from soils amended with P fertiliser in studies both in New Zealand (Gray et al. 2021; McDowell 2019; Gray et al. 2017; Gray and McDowell 2016; Carrick et al. 2014; McLaren et al. 2004; Gray et al. 2003) and overseas (Imseng et al. 2018; Filipović et al. 2016; Cambier et al. 2014; Bengtsson et al. 2006) that used lysimeters, suction cups or drainage collected from hydrologically-isolated field plots (Table 4). It is also lower than the load (2.3 g ha^{-1}) reported by Salmanzadeh et al. (2017), who estimated the Cd leaching due to irrigation by measuring differences in total soil Cd concentrations in 22 paired dryland and irrigated soils in New Zealand.

The very low amount of Cd measured in drainage confirms that Cd derived from P fertiliser is generally immobile in soil, particularly below 100 cm which was the sampling depth of the fluxmeters. Kelliher et al. (2017) for instance measured Cd concentrations in soils from the long-term P fertiliser Winchmore trial in Canterbury by sampling to 100 cm, and reported that while only 36% of the fertiliser Cd added was found in the top 7.5 cm, almost 100% of the fertiliser Cd added was retained in the top 50 cm of the soil. A similar result was found by Salmanzadeh et al. (2016) for three soils under pasture in the Waikato region (Horotiu, Bruntwood and Te Kowhai soils) that had the same P fertiliser history. Using the supplemental data published by Salmanzadeh et al. (2016) and assuming the bulk density was the same for all of the samples, the total Cd stock measured in the top 7.5 cm for all three soils was 33% and between 96 to 98% in the top 50 cm. Loganathan and Hedley (1997) reported < 5% of the Cd applied from an annual application of P fertiliser to a Pallic soil under pasture in a trial in the Manawatu leached below a depth of 20 cm over a 10 year period.

*Table 4: Summary of studies that have measured cadmium (Cd) leaching losses or movement of Cd down the soil profile amended with phosphorus (P) fertiliser. * Soil classification is the World Reference Base for Soil Resources.*

Soil classification (Hewitt 2010)	Cadmium loss (g Cd ha^{-1} yr^{-1})	Notes	Reference
Pallic, Brown Brown, Pumice, Allophanic	0.27 – 0.86	Field-based lysimeter study (50 x 25 cm) investigating cadmium leaching from different soil types under pasture over a period of two years.	Gray et al. (2003)
Recent	0.5 – 0.8	Laboratory-based lysimeter study (50 x 70 cm) using a stony soil that received periodic irrigations (12–18 mm depth at 35–40 mm/h applied every 3–4 days) and were treated with single superphosphate, cow urine, and farm dairy effluent.	Carrick et al. (2014)
Pumice	0.57 – 0.92	Field-based lysimeter study (50 x 70 cm) investigating the effect of application of farm dairy effluent on Cd leaching from a pasture soil that had a coarse or fine textured subsoil.	Gray et al. (2021)
Pallic	0.53 – 1.80	Laboratory-based lysimeter study (18 cm pots) investigating the effect of application of either potassium or calcium chloride on leaching and plant uptake of cadmium.	McDowell (2019)
Recent	0.27 – 0.32	Field trial using hydrologically-isolated plots (1 x 20 x 0.8m). Plots grazed (fodder beet) with dairy cows for either 6 or 24 hrs to determine the effect of urine inputs (*viz* chloride) on cadmium mobility.	Gray et al. (2017)
Organic	0.14 – 0.39	Laboratory-based lysimeter study (21 x 30 cm) where soils sown with ryegrass were amended to 3 soil pH values (4.5, 5.5, 6.5) and received varying amounts of single superphosphate (up to 200 kg P ha^{-1}).	Gray and McDowell (2016)
Pallic, Gley, Recent, Brown, Pumice		A survey of the amount of total soil Cd that has moved down the soil profile (0 – 0.1 m) due to irrigation of 22 paired dryland and irrigated sites under pasture	Salmanzadeh et al. (2017)
Pallic	0.27	Field-based lysimeter study (50 x 70 cm) investigating heavy metal leaching from a pasture soil amended with biosolids over a period of three years. Results are from the control treatment (no biosolid applied) under pasture.	McLaren et al. (2004)
Cambisol*	0.02 – 0.99	Field based study that measured cadmium losses in drainage water collected using suction cups from three arable monitoring sites in Switzerland positioned at 50 cm depth.	Imseng et al. (2018)
Regosol*, Gleysol*, Cambisol*	0.13 – 0.35	Field based study that measured cadmium fluxes from three arable sites over five years in Sweden using suction cup lysimeters positioned at 50 cm depth.	Bengtsson et al. (2006)
Luvisol*	0.11 – 0.14	Field based study that measured Cd losses in drainage over nearly six years, collected using wick lysimeters positioned at 45 cm depth from three arable plots in France.	Cambier et al. (2014) and Filipović et al. (2016)

4.4 Comparison of measured versus estimated Cd leaching loads

Because no Cd leaching was measured at six of the seven sites, a comparison between measured and estimated Cd leaching losses calculated using the approach used in the CadBal model was only able to be made at site 1. To estimate soil solution Cd concentrations, we used the relationship reported between soil solution Cd concentration and topsoil properties for 40 New Zealand agricultural soils (Equation 1; Gray and Cavanagh 2020). Where $\text{Log}[\text{Cd}]_{\text{soil soln}}$ is the average concentration of Cd in soil solution ($\mu\text{g L}^{-1}$), pH is measured in water, log soil OM is soil organic matter content (%), and log $[\text{Cd}]_{\text{total soil}}$ is the total soil concentration (mg kg^{-1}).

$$\text{Log}[\text{Cd}]_{\text{soil soln}} = 6.246 - 0.987\ \text{pH} - 0.513\ \log \text{OM} + 0.818\ \log\,[\text{Cd}]_{\text{total soil}}$$

$$R^2\text{adj} = 0.84 \qquad (1)$$

Using the mean topsoil values for pH, total Cd concentration and OM content (Table 2) as input parameters in Equation 1 and the drainage reported for the site (Table 3), the predicted annual Cd leaching loss was 0.41 g ha^{-1}. This compares to the measured value of 0.33 ± 0.08 g ha^{-1}.

Cadmium transport in soils, like other solutes, is subject to a range of both physical (macropore flow) and chemical (Cd sorption and desorption processes) non-equilibrium conditions that can either enhance or impede Cd concentrations in drainage (Garrido et al. 2008; Degryse and Smolders 2006; Bergkvist and Jarvis 2004). As a consequence, it is always is going to be challenging for a soil solution Cd concentration that has been estimated using topsoil properties and is in equilibrium with the solid phase in the topsoil to accurately reflect the Cd flux in a soil that will likely vary temporally over the drainage season (Degryse and Smolders 2006; Bengtsson et al. 2006) and with the depth that drainage is being sampled, as Cd leaching tends to decrease with soil depth (McLaughlin et al. 2021). This appears to have been the case in this study for the six sites where no Cd was detected in drainage, despite modelled soluble Cd concentrations in the topsoil of between 0.005 to 0.365 $\mu\text{g L}^{-1}$. It seems any soluble Cd present in the topsoil was readily attenuated, likely by sorption processes in the subsoil as it was transported through the soil, to the extent it was below the Cd detection limit at the 100 cm fluxmeter sampling depth. This highlights that ideally modelled and measured Cd leaching should be evaluated using data that has been collected from the same soil depth (McLaughlin et al. 2021). Nonetheless, when non-equilibrium conditions were not important, such as site 1, the drainage flux combined with an estimate of soil solution Cd concentrations appears to provide an adequate indication of the amount of Cd loss via leaching.

5. Conclusions

This study found that Cd leaching losses from seven long-term cropping soils were generally very low, with Cd detected in drainage at only one site. This is consistent with earlier studies that found Cd derived from P fertiliser is largely immobile in soil. The amount of Cd leaching measured at site 1 (0.33 g ha^{-1}) was similar to the amount estimated using the drainage flux combined with an estimate of soil solution Cd concentrations for the site (0.41 g ha^{-1}).

Further work is still required however to obtain more data on Cd leaching collected under field conditions to allow evaluation with modelled Cd leaching data (McLaughlin et al. (2021). The focus should be on measuring Cd leaching from the topsoil, the soil depth CadBal uses to assess the rate of Cd accumulation in soil, along with measurements at the same depth for pH, total Cd and soil OM content that are used in the model to calculate Cd leaching. This would allow a more robust assessment of the approach that Cd balance models such as CadBal use to estimate Cd leaching from soils.

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