Analysis of samples from the Winchmore long-term fertiliser trial for total soil cadmium contents

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1. Executive Summary

Access to reliable data on soil cadmium (Cd) concentrations for soils that have received long-term inputs of phosphorus (P) fertiliser is important to help manage Cd in New Zealand agricultural systems. Two studies that analysed soil Cd concentrations in samples from the Winchmore long-term phosphate fertiliser trial suggested different trends in rates of Cd accumulation. Based on a mass balance approach, one study suggested that soil Cd concentrations may have plateaued over recent years. Using more recent data, the other indicated soil Cd concentrations were still increasing.

The aim of this study was to re-analyse soil samples previously analysed for Cd at the Winchmore trial, and also analyse new samples to help clarify the trend in soil Cd concentrations.

Results in the highest P fertiliser treatment indicated soil Cd concentrations were significantly ($P < 0.05$) greater in the most recent analysis. When this new analysis was combined with all the soil Cd data from previous studies and statistically analysed, results indicate soil Cd concentrations in the two fertiliser treatments are increasing over time. It is recommended future soil samples collected from the Winchmore trial are analysed for soil Cd to determine if concentrations continue to increase.

2. Background

Recent analysis (Kelliher et al. 2017) of topsoil samples (2009 and 2016) for total cadmium (Cd) from the Winchmore long-term fertiliser trial indicate Cd is still accumulating in soil (Figure 1). This is in contrast to decreasing and then plateauing, which had previously been reported by McDowell (2012). It is uncertain why Cd concentrations decreased from 1994 to 1998 and then plateaued between 1999 to 2009. This is because although Cd inputs in fertiliser have decreased from 1996 (Fertiliser Matters 2005), Cd losses from surface runoff (McDowell 2010), leaching (Kelliher et al. 2017) and plant/animal uptake are unlikely to have been sufficient to result in a significant decrease in topsoil Cd status.

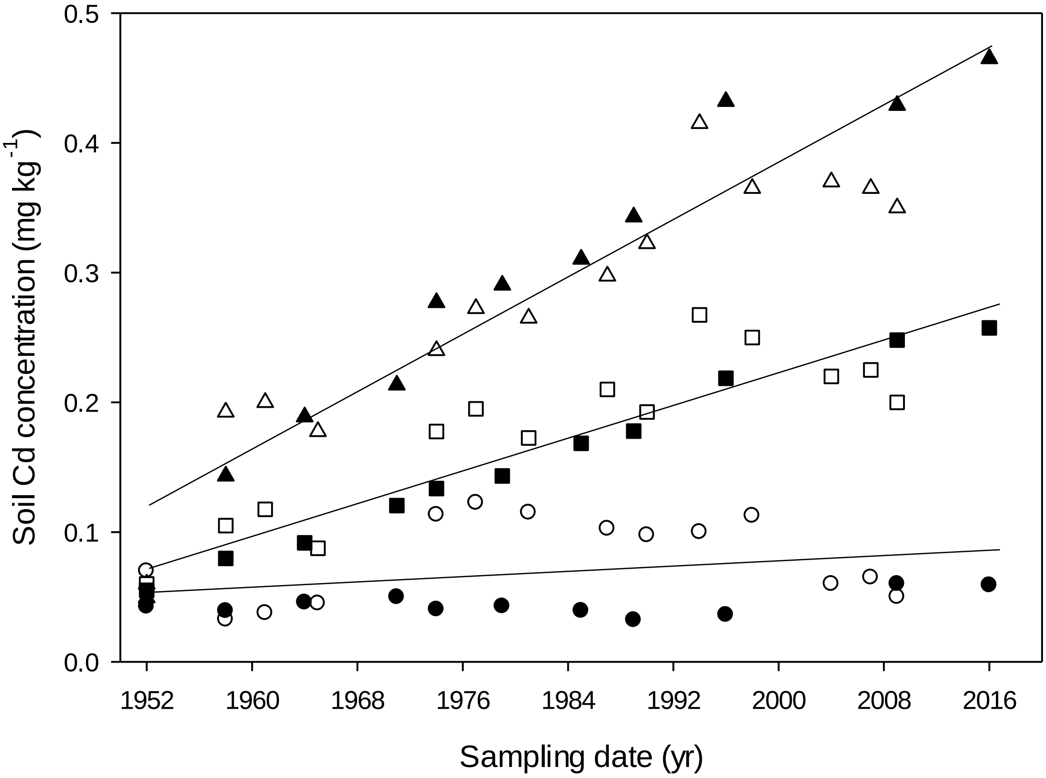

Figure 1. Relationship between sampling date and mean soil cadmium concentrations in soil (0 - 7.5cm) from plots which received no fertiliser (○ from McDowell (2012) and ● Kelliher et al. (2017)) or plots receiving phosphorus applications of 17 (□ and ■) and 34 kg P ha^{-1} y^{-1} (△ and ▲). Also shown are regression lines fitted to the data for the plots.

Interestingly, the decreases in Cd concentrations reported by McDowell (2012) occurred in all treatments, including the control. This systematic trend could indicate a possible change in how the soil was sampled during this period (i.e. deeper cores resulting in dilution of soil Cd). This would seem unlikely however, as results for other measured contaminants (uranium and fluorine) increased between 2004 and 2009 (McDowell 2012; Gray 2017). Another reason could be an analytical change when this batch of samples was analysed for Cd, which resulted in lower results.

This project addresses some of the uncertainty around Cd analysis of soil samples previously analysed at Winchmore, while also undertaking additional analyses to provide a larger dataset for identifying trends in soil Cd over time. The aims are:

1. Re-analyse soils from the McDowell (2012) study for total Cd contents for dates where samples began to deviate from the regression lines in Figure 1 (i.e. 2004, 2007 and 2009). This provides some insight into whether there was an analytical issue associated with the analysis of those samples which resulted in low Cd values.
2. Analyse archived soils for total Cd from three fertiliser treatments in the Winchmore trial (Nil, 17 and 34 kg P ha^{-1} yr^{-1}) on four sampling dates (2001, 2005,

2012 and 2014). This provides additional data for identifying trends in soil Cd contents.

3. Statistically analyse the data to determine trends in total soil Cd over time.

3. Methods

3.1 Soil samples

Soil samples (0 – 7.5 cm depth) were retrieved from the AgResearch soil archive for each treatment and replicate (four) from the long-term phosphate fertiliser trial i.e. Nil, 17 and 34 kg P ha^{-1} yr^{-1}. These were sampled in the spring of 2001, 2004, 2005, 2007, 2009, 2012 and 2014. Soils had been air dried and sieved (< 2mm) prior to storage.

3.2 Soil cadmium analysis

Total recoverable Cd concentrations in samples were determined following nitric acid/ hydrochloric digestion (US EPA 2002) using inductively coupled plasma-mass spectrometry. Quality control measures included the use of blanks, duplicate samples and a certified reference material AGAL-10 (Australian Government Analytical Laboratories, Sydney, Australia). For blank samples, Cd concentrations were less than the detection limit of 0.010 mg Cd kg^{-1}. Duplicate results were within 10%. Recovery of Cd from the certified reference material was within the limits of the certified value.

3.3 Statistical analysis

Linear regression models with year as a continuous variable and “P fertiliser added” and “data source” were fitted as factors. The interactions between the three variables were included in the model to show the changes in response to time with the other variables. All models were fitted in R (R Core Team (2017)).

4. Results and Discussion

4.1 Re-analysis of soil samples

A comparison of soil Cd concentrations measured by McDowell (2012) and the same samples analysed again in the present study (i.e. 2004, 2007 and 2009) is shown in Figure 2. Results indicate that in the control and 17 kg P ha^{-1} yr^{-1} treatments there is no significant difference in soil Cd concentrations between the two sets of analyses. In comparison, in the 34 kg P ha^{-1} yr^{-1} treatment soil Cd concentrations were significantly ($P < 0.05$) higher in the most recent analysis. It was postulated that the difference between the McDowell (2012) and Kelliher et al. (2017) results may have resulted from different analytical procedures (i.e. a different acid digestion method and instrumentation). While Cd data were the same for the control samples in the most recent analysis and the McDowell (2012) data, we cannot rule out inefficiencies in digestion/extraction in Cd-enriched topsoils, especially given the variation in older control soils.

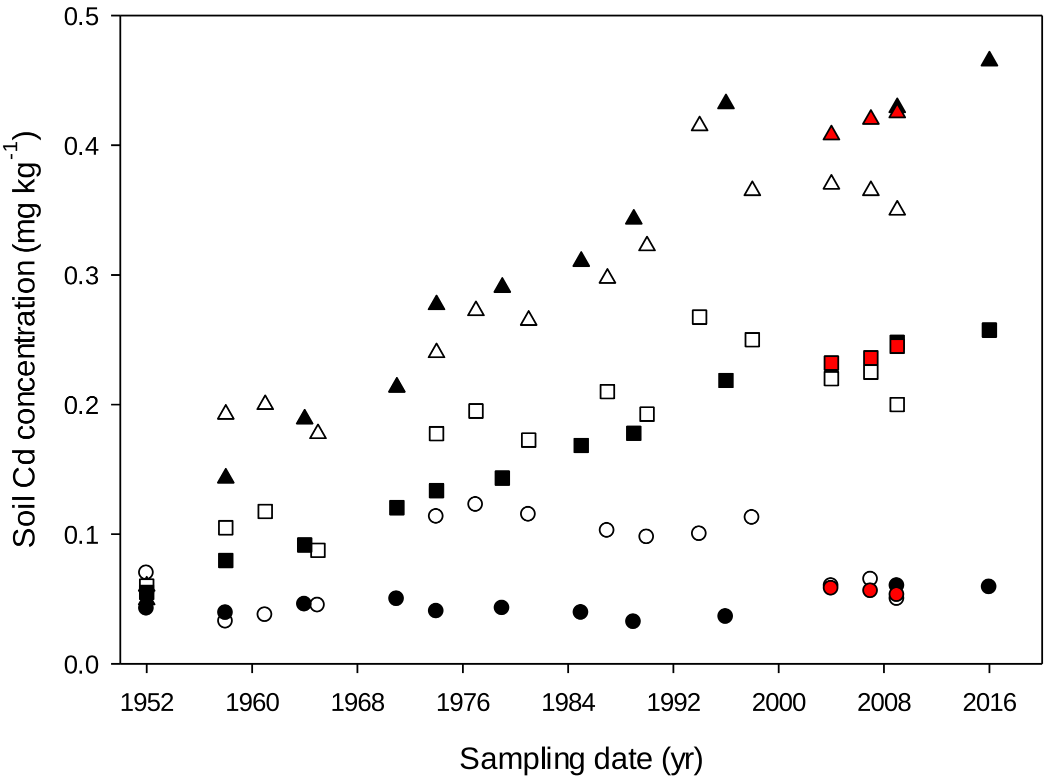

Figure 2. Relationship between sampling dates and mean soil cadmium concentrations in plots which received no fertiliser (○ from McDowell (2012) and ● Kelliher et al. (2017) and ● this study) or phosphorus applications of 17 kg P ha^{-1} y^{-1} (□, ■ and ■) and 34 kg P ha^{-1} y^{-1} (△, ▲ and ▲).

4.2 Additional soil analysis

Results from the analysis of additional samples from 2001, 2005, 2012, and 2014 from the three treatments are shown in Figure 3. When this Cd data is combined with the re-analysed samples in the present study (i.e. 2004, 2007 and 2009), the data of McDowell et al. (2012) and all the previous Cd data, it indicates that soil Cd concentrations in the two fertiliser treatments increased over time. Soil cadmium concentrations in the control treatment remained fairly constant.

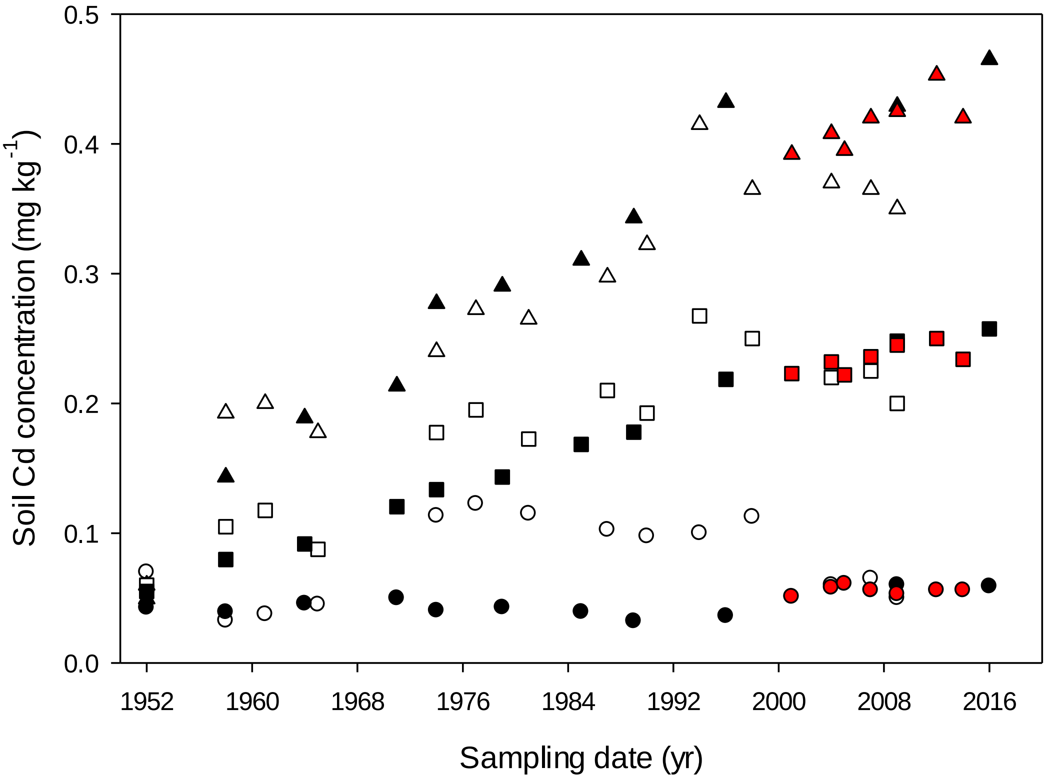

Figure 3. Relationship between sampling date and mean soil cadmium concentrations in plots which received no fertiliser (○ from McDowell (2012); and ● Kelliher et al. (2017) and ● from this study) or phosphorus applications of 17 kg P ha^{-1} y^{-1} (□, ■ and ■) and 34 kg P ha^{-1} y^{-1} (△, ▲ and ▲).

5. Key findings

- Results indicate significantly higher soil Cd concentrations in the 34 kg P ha^{-1} yr^{-1} fertiliser treatment than previous analysis of the same soils had suggested.
- When all soil Cd data from the previous studies are combined with the new analysis and statistically analysed, results indicate soil Cd concentrations in the two fertiliser treatments are increasing over time.

6. Acknowledgements

Funding for this work was provided by the Fertiliser Association of New Zealand (FANZ).

7. References

Fertiliser Matters 2005. Cadmium in New Zealand: an update. Auckland, New Zealand Fertiliser Manufacturer's Research Association. Newsletter 34.

Gray CW 2017. Fluorine accumulation and loss from a pasture soil. AgResearch Client Report for FANZ: RE500/2017/007.

Kelliher F, Gray CW, Noble A 2017. Superphosphate fertiliser application and cadmium accumulation in a pastoral soil. New Zealand Journal of Agricultural Research 60: 4, 404–422.

McDowell RW 2010. Is cadmium loss in surface runoff significant for soil and surface water quality: a study of flood-irrigated pastures? Water, Air and Soil Pollution 209: 133–142.

McDowell RW 2012. The rate of accumulation of cadmium and uranium in a long-term grazed pasture: implications for soil quality. New Zealand Journal of Agricultural Research. 55: 133–146.

R Core Team (2017). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.