Salmanzadeh, M., Hartland, A., Stirling, C., Balks, M., Schipper, L. and George, E., 2016. Use of cadmium isotopes to distinguish sources of cadmium in New Zealand agricultural soils: preliminary results. In: *Integrated nutrient and water management for sustainable farming*. (Eds L.D. Currie and R.Singh). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 29. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 4 pages.

USE OF CADMIUM ISOTOPES TO DISTINGUISH SOURCES OF CADMIUM IN NEW ZEALAND AGRICULTURAL SOILS: PRELIMINARY RESULTS

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Background

In New Zealand's agricultural soils, phosphate fertiliser applications are the main source of cadmium (Cd). In 1997, the NZ fertiliser industry discontinued sourcing rock phosphate from Nauru (about 450 mg Cd/ Kg P) and began producing superphosphate from other rock phosphate sources (such as Morocco), which have generally lower concentrations of Cd. Research on the concentration of Cd in soils from the long-term irrigation trials at the Winchmore research farm (Canterbury) indicates that Cd accumulation rates have started to slow in the period since 1997 (Fig. 1) (McDowell 2012).

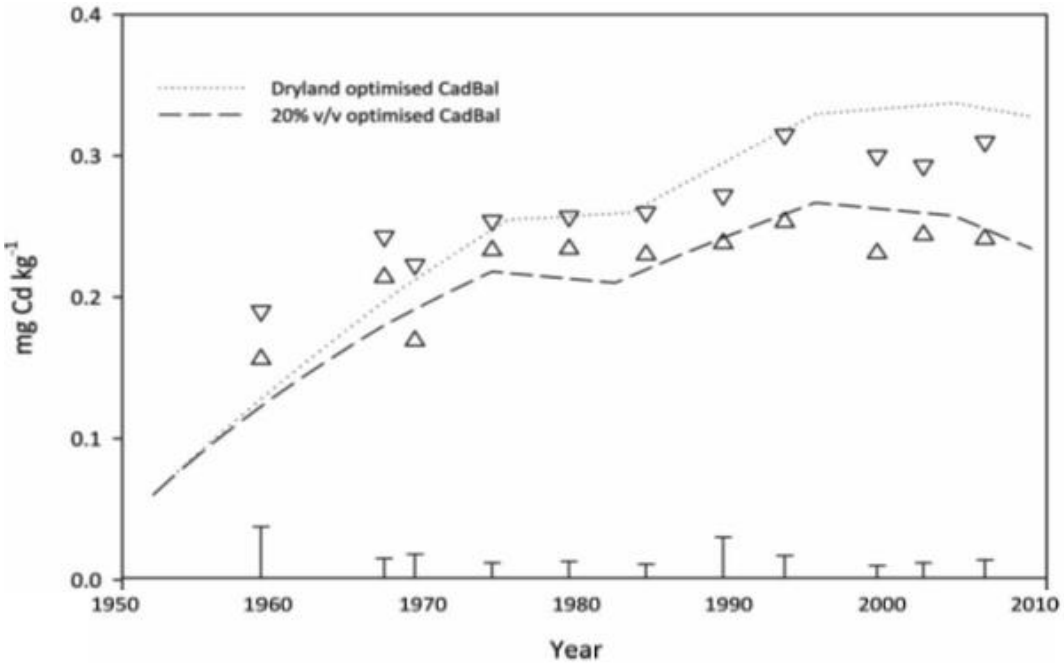

Fig. 1. The mean of Cd concentration in soil at the Winchmore long-term irrigation trial (symbol) and the CadBal model (lines) (McDowell 2012)

The objective of this research is to assess the potential of Cd stable isotope ratios ($\varepsilon^{114/110}$Cd) to distinguish the contribution of different sources (new fertiliser and old fertiliser) in causing this plateau in Winchmore soil samples. We investigate the hypothesis that the decrease in the rate of Cd accumulation is linked to the lower Cd inputs in the contemporary phosphate fertiliser supply. Stable isotopes are the footprints of elements and can be used to trace the fate of Cd in soils.

Materials and Methods

Twelve fertilised soil samples from each of the years 1959, 1967, 1979, 1993, 2002 and 2015 as well as one control (unfertilised) soil sample were selected. All the soil samples were from 0-7.5 cm of plot number 15 (dryland treatment, irrigation trial) of Winchmore research farm. The irrigation trial of Winchmore farm was established on 1949 and received 250 kg ha^{-1} of Single superphosphate in winters annually (McDowell 2012). In addition to soil samples, rock phosphate and fertiliser samples from Nauru rock phosphate, Christmas Island rock phosphate, old fertiliser (mid 1980s) and new fertilisers (2000, 2007 and 2015) were analysed. Two replicates of each sample were selected and all the soil and fertiliser samples were dried and sieved (< 2mm). The samples were digested using aqua regia, aimed at releasing anthropogenic Cd, leaving the silicate soil matrix largely intact, and then the total concentration of Cd was determined using ICP-MS (Schipper *et al.* 2011). The required volumes of each digested sample were transferred to the University of Otago for Cd isotope determination. After preparing the aliquots of each sample, the isotope ratios of Cd ($\varepsilon^{114/110}$Cd) were measured using multiple-collector ICP-MS (MC-ICPMS) (Gault-Ringold & Stirling 2012).

Results and Discussion

The total concentration of Cd extracted from Winchmore research farm soils has decreased since 1997 (Fig. 2). Also, the total concentration of Cd in fertiliser samples has decreased and the concentration of Cd in the newest fertiliser sample (fertiliser 2015) was about 9 ppm, approximately a factor of 4 lower than Cd concentrations from fertilisers applied in the mid-1980's (Fig. 3).

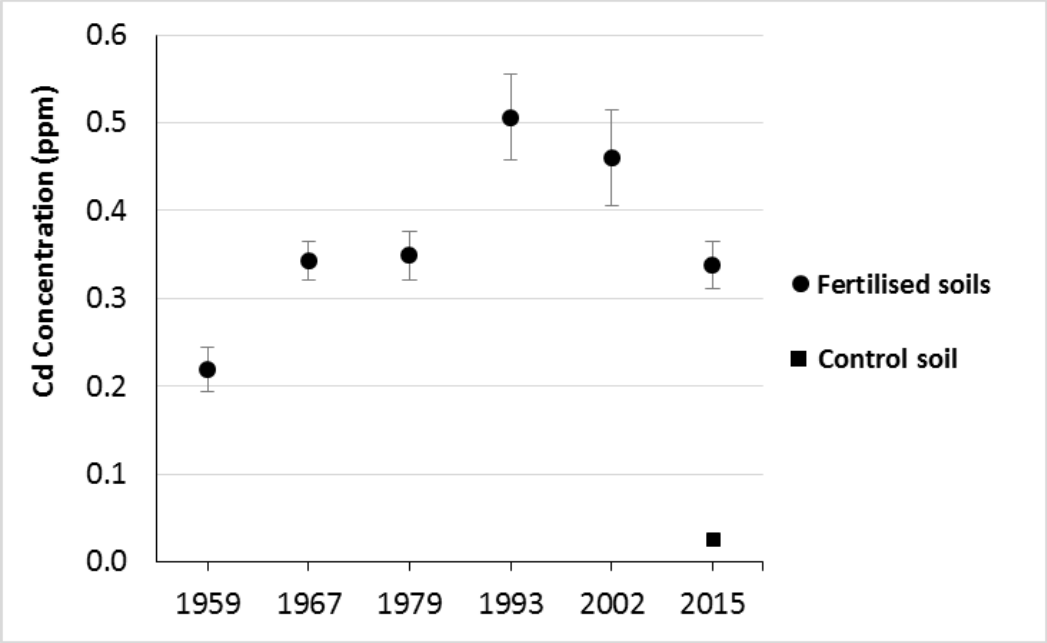

Fig. 2. Mean of total concentration of Cd in fertilised and control soil samples (error bars are ± 2SD from the mean)

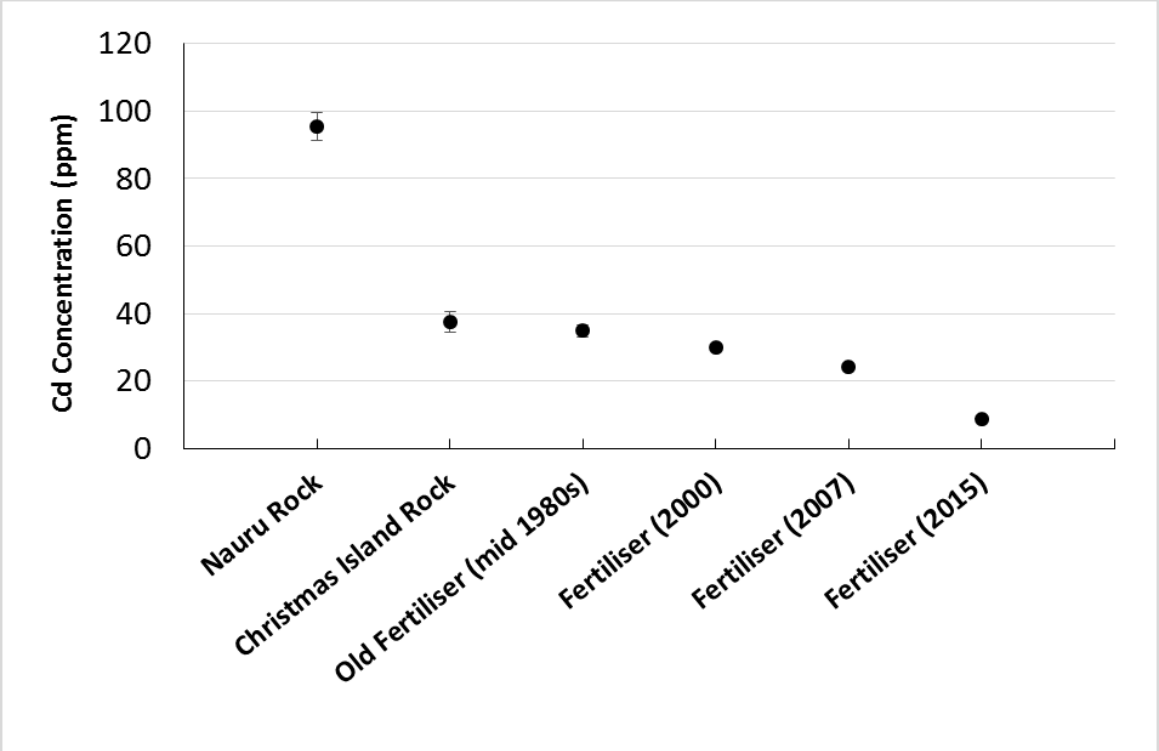

Fig. 3. Mean of total concentration of Cd in fertiliser and rock phosphate samples (error bars are ± 2SD from the mean)

The Cd isotope results show that the $\varepsilon^{114/110}$Cd composition of Cd released from fertilised soils, natural soils and new fertilisers can be distinguished (Fig. 4). The isotope ratios of fertilised soil samples did not change significantly through time and it seems that soil samples of Winchmore research farm are still affected by old fertilisers. Circles in Fig. 4 show that the Cd isotope ratios of soil samples are more similar to the Cd isotope ratios of old fertilisers.

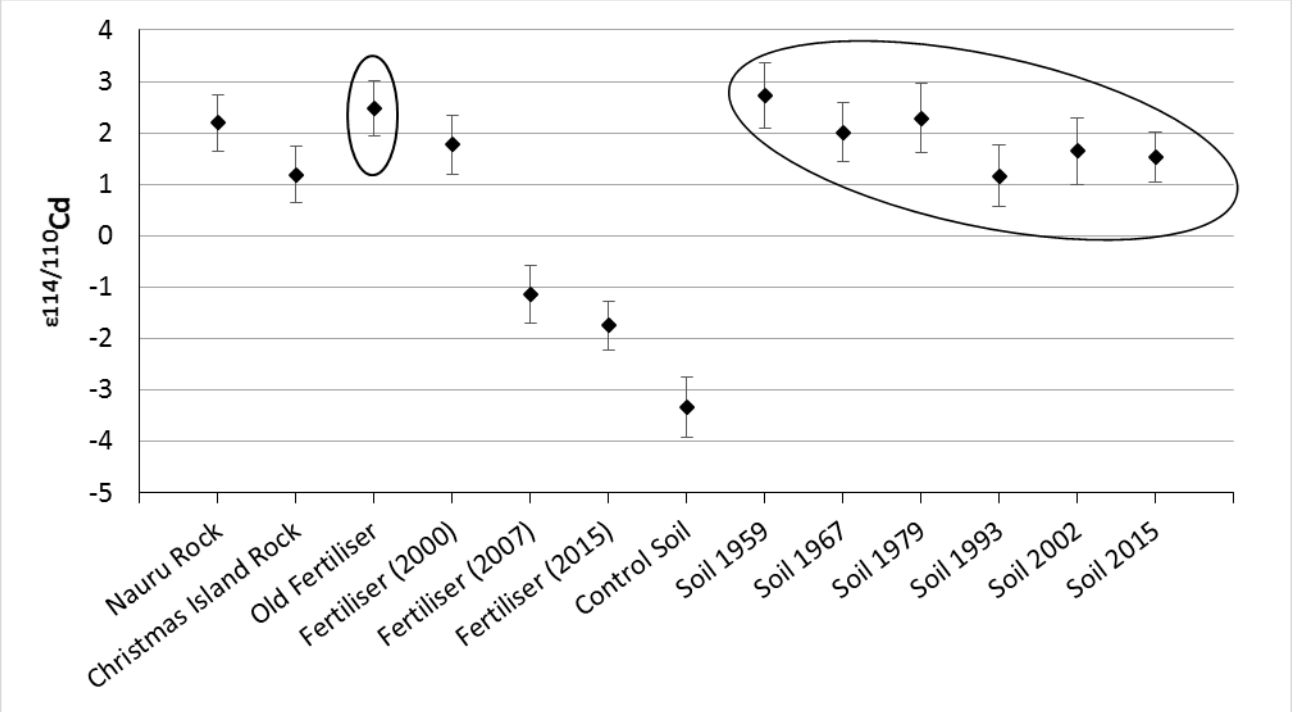

Fig. 4. Mean of isotope ratios of Cd in fertiliser, rocks and soil samples (error bars are ± 2SE from the mean)

Conclusion

The results of this research have confirmed the results of McDowell (2012) who reported the concentration of total Cd in Winchmore research farm soils. The accumulation of Cd in soil samples has shown a decreasing trend since 1997. According to the Cd isotope results, the soil samples of the Winchmore research farm are still affected by Nauru-derived phosphate fertilisers (despite the discontinued use of these fertilisers more than 19 years ago) or pre-2000 fertilisers. More analysis of existing data, as well as the acquisition of more Cd concentration and Cd isotope data for soil and fertiliser samples are required to continue this study. For example, an end-member mixing model will be used to determine the fraction distribution of different sources of Cd in the Winchmore research farm.

Acknowledgements

This research was funded by Fertilizer Association of New Zealand. We are grateful to Ray Moss from Agresearch and Ian Power from Balance Agri-Nutrients for providing the soil and fertiliser samples.

References

Gault-Ringold, M. & Stirling, C. H. 2012, 'Anomalous isotopic shifts associated with organic resin residues during cadmium isotopic analysis by double spike MC-ICPMS', *Journal of Analytical Atomic Spectrometry*, vol. 27, no. 3, pp. 449-459.

McDowell, R. W. 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*, vol. 55, no. 2, pp. 133-146.

Schipper, L. A., *et al.* 2011, 'Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer', *Agriculture Ecosystems & Environment*, vol. 144, no. 1, pp. 95-101.