Agriculture, Ecosystems and Environment 165 (2013) 80–87

Contents lists available at SciVerse ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Natural background and anthropogenic contributions of cadmium to New Zealand soils

R.W. McDowell[a,*], M.D. Taylor[b], B.A. Stevenson[c]

[a] AgResearch, Invermay Agricultural Centre, Private Bag 50034, Mosgiel, New Zealand
[b] Waikato Regional Council, 401 Grey St, Private Bag 3038 Waikato Mail Centre, Hamilton 3240, New Zealand
[c] Landcare Research, Private Bag 3127, Hamilton 3240, New Zealand

ARTICLE INFO

Article history:
Received 2 August 2012
Received in revised form
20 December 2012
Accepted 23 December 2012
Available online 17 January 2013

Keywords:
Reference
Fertiliser
Phosphorus
Superphosphate

ABSTRACT

The need to manage the potentially biotoxic metal-cadmium (Cd) in soil, relative to proposed limits, requires knowledge of how much Cd is present naturally under minimally disturbed conditions (MDC). Two data sets were collated, one of MDC soils sampled under native bush ($n = 293$) and another of different land uses (arable, dairy, drystock, horticulture, forestry, and urban; $n = 1043$) from which was estimated the background and anthropogenic contributions of Cd. The concentration of total Cd in MDC soils was strongly correlated to 11 different variables (e.g. pH, total carbon), but to total phosphorus most of all ($r = 0.712$, $P < 0.001$). Phosphorus concentration was used in an equation to show on average that background concentrations (up to a maximum of the 95th percentile of the MDC data set; 0.48 mg kg^{-1}) accounted for about half of the Cd in the land use data set. The New Zealand fertiliser management strategy currently sets absolute limits – irrespective of soil type or background contributions. However, given that anthropogenic inputs of Cd have been shown to be more bioavailable to plants, our approach could be used to highlight and initiate further investigation of anthropogenic enrichment that is more soil specific.

1. Introduction

Cadmium (Cd) is a potentially biotoxic metal that enters the human food chain via plants grown on Cd-enriched soil and animals that eat the resulting forage or ingest a small quantity of Cd-enriched soil (Lee et al., 1996; Ryan et al., 1982). In New Zealand, a multi-stakeholder Cd working group was established with the aim of managing and mitigating the build up of Cd in soil. This group developed a Cd management plan which included a Tiered Fertiliser Management System (TFMS) to ensure that Cd concentrations enriched by anthropogenic inputs do not reach unsafe levels (Anon., 2011). The TFMS has four tiers: (1) if, during a 5-yearly screening of soil, the total Cd concentration is <0.6 mg kg^{-1}, there is no restriction placed on the application of P fertiliser; (2) P fertiliser applications rates and products are restricted for soils with a Cd concentration ≥0.6 mg kg^{-1} and <1.0 mg kg^{-1} to ensure that Cd does not exceed an acceptable threshold (tier 4) within 100 years; (3) for soil Cd concentrations ≥1.0 mg kg^{-1} and <1.4 mg kg^{-1}, P fertiliser application rates are further managed by the use of a Cd balance model to ensure that an acceptable threshold is not exceeded within 100 years, and (4) above tier 4 (1.8 mg kg^{-1}) no further accumulation of Cd is allowed (Rys, 2011; Report of the Cadmium Working Group, 2011; Warne, 2011). However, knowledge on background concentrations is required to identify those soils naturally rich in Cd, thereby determining the anthropogenic influence and so provide the starting point from which remedial or management strategies are initiated.

In many countries, soils are likely to be contaminated by the long-range weather transport and precipitation of Cd which impairs the ability to define a true background concentration (Salminen and Tarvainen, 1997). In contrast, New Zealand, being 3000 km downwind of Australia, is relatively isolated from atmospheric sources of Cd, and has relatively little heavy industry or mining. The major anthropogenic source of Cd in New Zealand is the application of phosphorus-based fertilisers (Williams and David, 1973). In New Zealand, superphosphate was traditionally made from Cd-rich phosphate rock from Nauru. While fertiliser manufacturers have shifted to production from phosphate rocks with less Cd, historic applications have enriched the national mean concentration in the top 7.5 cm of soil to 0.35 mg kg^{-1}, with a range from near zero to 2.52 mg kg^{-1} (Report of the Cadmium Working Group, 2008).

Attempts at quantifying background concentrations have been beset with issues surrounding contamination of background sites.

* Corresponding author. Tel.: +64 3 489 9262; fax: +64 3 489 3739.
E-mail address: richard.mcdowell@agresearch.co.nz (R.W. McDowell).

0167-8809/$ – see front matter
http://dx.doi.org/10.1016/j.agee.2012.12.011

For instance, Zhang et al. (2011) state that due to contamination a "baseline concentration can be used to represent element concentrations specific for a given region and time period, but does not always represent a true background (*viz*. reference) concentration". Kabata-Pendias and Dudka (1991) concluded that Cd concentrations in excess of 0.5 mg kg^{-1} indicated anthropogenic input. However, Garrett (1995) contended such concentrations were possible "in areas of natural geochemical enrichment". The main natural source of Cd to soil is the weathering of parent materials rich in sulphides. The total concentration of Cd is then determined by the concentration of the soil's Al-, Fe- and Mn-sesquioxides (and their interaction with other elements), clay and organic matter. Without information on these parameters, or surrogates, background concentrations have largely relied on mean values. In New Zealand, the mean background concentration has been measured in a number of studies: Roberts et al. (1994) put this at 0.2 mg kg^{-1}; Anon. (2007) at 0.1 mg kg^{-1}; and Taylor et al. (2007) at 0.16 mg kg^{-1}. However, the range of concentrations in baseline soils ranged from less than the detection limit (0.01 or 0.1 mg kg^{-1}) to 0.77 mg kg^{-1}. The aim of this study was to investigate the variation in background concentrations of Cd in relation to soil properties and compare these against soils in different agricultural land uses revealing the anthropogenic load and informing us about the relevance of mitigation strategies such as the New Zealand TFMS. Although we have taken care to acquire data that was most likely to represent background conditions, insufficient information was available on these to say this with 100% certainty. Hence, we refer to our background sites as under minimally disturbed conditions (MDC), a term regularly used in freshwater science (Soranno et al., 2011).

2. Materials and methods

2.1. Soil samples

Data for nearly 1800 soil samples were collated with total acid extractable Cd as the common analyte, but supplemented with chemical and physical data obtained from published studies or the reanalysis of archived soils. These soils were later split into a MDC data set that included only those soils likely sampled under native bush, which established the natural background, and a data set of different land uses (arable, dairy, drystock, horticulture, forestry, and urban). A third data set (Roberts et al., 1994) was used for validation of the analysis of MDC data and termed MDC-validation. Unless otherwise indicated, total Cd, hereafter termed Cd, was analysed via graphite furnace atomic adsorption spectroscopy with Zeeman correction (GFAAS), inductively coupled plasma-mass spectroscopy (ICP-MS), or optimal emission spectroscopy (ICP-OES) of *aqua regia* digests (Andrews et al., 1996). The detection limit for each machine was 0.05, 0.01 and 0.005 mg kg^{-1}, respectively. Soils within the database that were archived, and available for analysis, were digested with *aqua regia* for Al, As, Ba, B, Ca, Cd, Cu, Fe, K, P, Pb, Mg, Mn, Mo, Ni, U, V and Zn using ICP-OES. Where soils had been previously analysed for Cd, the revised concentration compared well (R^2 = 0.98, P < 0.001, slope = 1.01) when above the detection limit. Except where indicated, all soils had data on land use, soil order, pH (in water; 1:2.5 soil to water ratio), total C and N by LECO combustion, and Olsen P. The soil orders are, according to the New Zealand soil classification of Hewitt (1998), and in parentheses, the corresponding FAO classification (IUSS Working Group WRB, 2006) are: Allophanic soils (Andisols); Brown soils (Cambisols); Gley soils (Gleysols); Granular soils (Ferrasols); Podzols (Podzols); Pumic soils (Vitric Andosols); Recent soils (Arenosols and Fluvisols); and Ultic soils (Acrisols). A summary of the datasets and archived soils follows.

1. *500 soils archive*: Four-hundred samples were obtained from the 1998–2000 sampling of the "500 soils" project archived by Landcare Research (see Hill et al., 2003). These samples were of the top 10 cm from different land uses throughout New Zealand. Among the 400 soils still in the archive, data for Cd were available for the Bay of Plenty, Waikato, Taranaki, and Marlborough regions, either as published studies (e.g. Taylor et al., 2010), or as part of unpublished reports (Anon., 2005, 2007). Some of these samples, and all the samples from the Northland, Auckland, Wellington and Canterbury regions, were digested and reanalysed. Additional data were available for: exchangeable cations (Ca, Mg, K, and Na); NO_3-N and NH_4-N extractable by 2 M KCl; anaerobically mineralisable N; bulk density; macroporosity @ – 10 kPa; and aggregate stability (the methods for each of these are available in Blakemore et al., 1987). However, a preliminary correlation analysis of these data showed no significant correlation with Cd and hence the acquisition of these additional samples for the other datasets was not pursued. Among those soils from the 500 soils project, 62 were classified as under MDC.
2. *Published studies*: Soils were reanalysed of 5 topsoils (0–10 cm depth) from the Otago region under pasture, production forestry and native land use collected by McDowell and Stewart (2006). Data (excluding Olsen P) from a study of 105 MDC sites (0–10 cm depth) in the Auckland region were also included (Anon., 2001). Data were available for all variables except those measured in *aqua regia* (exclusive of Cd) for samples of fertilised pasture and native (broadleaf or podocarp forest) land use under two contrasting soil types and at depths of 0–3.5, 3.5–7.5, 7.5–15 and 15–30 cm from Zanders et al. (1997).
3. *Unpublished West Coast study*: Twenty samples of topsoil (0–10 cm depth) taken from native (largely podocarp) bush sites in the lower West Coast region (within 100 km of Haast) ranging in elevation from 10 m to 500 m above sea level were reanalysed.
4. *MAF database*: Data were obtained from samples taken of the 0–10 cm depth of 50 dairy, 293 drystock, 272 arable, 54 forestry, 10 urban, and 85 native land use sites around New Zealand and collated by the New Zealand Ministry of Agriculture and Forestry (MAF; unpublished). Of these soils, 20 arable, 31 dairy, 30 drystock, 12 horticulture, 12 forestry, and 30 native soils were available for reanalysis – otherwise Cd data were obtained via GFAAS or ICP-MS. A total of 64 samples from the MAF database recorded a Cd concentration at or below the respective detection limit.
5. To validate our analysis of the MDC data set, a database of 398 soils from the 0–7.5 cm depth was used. This database, held by AgResearch and published in Roberts et al. (1994) and Longhurst et al. (2004), contained data for As, Pb, Cd, Cu and P of 312 pastoral (drystock and dairy) sites receiving varying rates of P fertiliser and 86 non-pastoral sites. The non-pastoral sites used for the validation step (MDC-validation) were mostly (90%) from under native bush (B. Longhurst, AgResearch-Ruakura, New Zealand; *pers. comm.*), but included some samples that were taken from retired or non-fertilised land.

The number of samples in the MDC database totalled 293, while the land use database totalled 1043 samples.

2.2. Database analysis

The MDC database contained data from the 500 soils archive, data for soils under broadleaf and podocarp forest from Zanders et al. (1997), background sites from Anon. (2001), and soils under podocarp forest from an unpublished study of soils from the West Coast. The land use dataset contained all remaining soils, except for the validation soils. Among the 293 samples in the MDC dataset, 85 were at or below the detection limit and set at half the detection