Agriculture, Ecosystems and Environment 144 (2011) 95–101

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

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

Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer

L.A. Schipper[a,*], G.P. Sparling[a], L.M. Fisk[a], M.B. Dodd[b], I.L. Power[c], R.A. Littler[d]

[a] Department of Earth and Ocean Sciences, University of Waikato, Hamilton 3240, New Zealand
[b] Agresearch Grasslands, Private Bag 11008, Palmerston North 4442, New Zealand
[c] Agresearch Ruakura, Private Bag 3105, Hamilton 3240, New Zealand
[d] Department of Statistics, University of Waikato, Hamilton 3240, New Zealand

ARTICLE INFO

Article history:
Received 28 April 2011
Received in revised form 14 July 2011
Accepted 2 August 2011
Available online 18 September 2011

Keywords:
Pasture
Soil
Phosphorus
Fertiliser
Cadmium
Uranium

ABSTRACT

In New Zealand, phosphate (P) fertilisers used in agriculture are the main sources of the potentially toxic elements cadmium (Cd) and uranium (U), which occur as unwanted contaminants. New Zealand is developing draft soil guideline values (SGV) for maximum concentrations of Cd. To assess when soils under pasture for sheep production might reach a particular SGV, we analysed archived soil samples from a 23 yr P fertiliser trial. The pasture sites were at Whatawhata, North Island, New Zealand, and had received P fertiliser at the rates of 0, 30, 50 and 100 kg P ha^{-1} yr^{-1}. From 1983 to 1989, P was applied as single superphosphate, from 1989 to 2006, P was applied as triple superphosphate. Soils from replicate paddocks were sampled annually to a depth of 75 mm on easy (10–20°) and steep (30–40°) slope classes. Total P, Cd and U were analysed by ICP-MS after acid digestion. Data were analysed by fitting trend lines using linear mixed models for two slope classes and for two sampling periods 1983–1989 and 1989–2006 when the soil sampling method and fertiliser type had been changed.

The changes in total P, Cd and U were directly related to the type and amount of P fertiliser applied, the control treatment showed no significant change in P, Cd or U. At 50 and 100 kg P ha^{-1} yr^{-1} there were generally linear increases in total P and total U, and the same trend line applied to both time periods, but the rate of increase in P was greater on the easy slope class. For Cd, a "broken stick" model was needed to explain the data. Pre-1989, Cd increased in the 50 and 100 kg P ha^{-1} yr^{-1} treatment (0.036–0.045 mg kg^{-1} yr^{-1}, respectively): post 1988 the rate of increase declined markedly on those two treatments (0.005–0.015 mg kg^{-1} yr^{-1}, respectively), and declined absolutely in the 30 kg P ha^{-1} yr^{-1} treatments. The maximum content of Cd was in the 100 kg P ha^{-1} yr^{-1} treatment which reached 0.931 mg Cd kg^{-1} on the easy slope. For U there were steady linear increases for the 30, 50 and 100 kg P ha^{-1} treatments, and no significant difference between the steep and easy slopes, nor the two sampling periods, the maximum concentration obtained was 2.80 mg U kg^{-1} on the 100 kg P ha^{-1} treatment. The results suggest that at rates of P fertiliser likely to be applied to hill farms (<50 kg P ha^{-1} yr^{-1}), and using P fertiliser with low Cd content, then the Cd concentration in this soil will never reach a SGV of 1 mg kg^{-1}.

1. Introduction

Phosphate fertilizers have been applied to New Zealand agricultural land since the introduction of European agriculture in the late 1800s. In their natural state most New Zealand soils are of low fertility and phosphate fertilizers and lime were necessary to establish productive legume-based pastoral agriculture following forest clearance (Syers et al., 1986). The development of aerial topdressing around 1940 allowed even steep hilly terrain to be fertilized (During, 1984). There is an on-going requirement for increased food production, and the current trend in New Zealand is for increased intensification of land use with greater use of fertilisers and irrigation (Parliamentary Commissioner for the Environment, 2004).

With a largely rural economy P fertilizers are considered to be the major contributor to elevated trace metal contents in soils in New Zealand (Roberts et al., 1994; Gray et al., 1999), with few significant inputs from the atmosphere or industrial production (see review by Loganathan et al., 2003). The phosphate rocks used to manufacture P fertilizer contain elevated levels of some trace elements, of which cadmium (Cd) and uranium (U) are of concern because of their concentrations and toxicity. These unwanted elements become even more concentrated in the fertilizer during processing (Rothbaum et al., 1986; Syers et al., 1986; Chien et al., 2003; Loganathan et al., 2003). New Zealand has traditionally

* Corresponding author.
E-mail address: Schipper@waikato.ac.nz (L.A. Schipper).

0167-8809/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.agee.2011.08.002

sourced phosphate rocks from Christmas Island and Nauru, which are particularly high in Cd and U, and superphosphate made from those sources typically contained 34–69 μg Cd g^{-1} fertiliser (Rothbaum et al., 1986). Superphosphate samples measured in 1995 (Taylor, 1997) contained 8–37 μg U g^{-1} fertiliser nearly all present as ^{238}U.

Top-dressing with P fertilizer can result in enriched concentrations of Cd and U in surface soil (Rothbaum et al., 1979, 1986; Yamaguch et al., 2009; Loganathan and Hedley, 1997; Gray et al., 2003b). Typical Cd concentrations in New Zealand agricultural top soils were 0.44 mg kg^{-1} (range 0.04–1.53 mg kg^{-1}), and 0.20 mg kg^{-1} (range 0.02–0.77) in non-agricultural soils (Longhurst et al., 2004). The Cd concentrations in New Zealand soils (Roberts et al., 1994; Longhurst et al., 2004) are at the lower end of the worldwide range of 0.01–10 mg kg^{-1} reported by Ure and Berrow (1982). Cd has no essential biological function and is highly toxic to plants and animals and accumulates in the liver and kidneys of grazing animals (Alloway, 1990a,b; Roberts et al., 1994; Roberts and Longhurst, 2002). Most countries in the Organisation for Economic Co-operation and Development (OECD) have set maximum permitted Cd contents in selected foodstuffs: the maximum residue level for meat and offal for human consumption in New Zealand is 1.25 mg Cd kg^{-1} fresh weight for kidneys and 2.25 mg Cd kg^{-1} fresh weight for liver (New Zealand Food Safety Authority, 2011). The tolerable Cd intake for human adults is 1 μg kg^{-1} body weight per day (Fertiliser Matters, 2010). A former guideline for maximum soil Cd content for the disposal of biosolids to land was 1 mg total Cd kg^{-1} soil, and this value has sometimes been adopted for land intended for agricultural use. New soil guideline values (SGV) are being developed as a National Environmental Standard where the SGV values differ depending on the land use, proportion used for food production and soil pH (Ministry for the Environment, 2010). No SGV is yet suggested for wholly agricultural land, currently the nearest equivalent is a rural residential land use with 50% agricultural production. The SGV, stated to be “for reference purposes only” varies between 1 mg Cd kg^{-1} at a soil pH of 5, up to 8 mg Cd kg^{-1} at a soil pH of 8.

There is generally more U in soils and rocks than there is Cd (De Boulois et al., 2008; Gavrilescu et al., 2008). Uranium is classified as “very toxic” (Health and Safety Executive, 1995), causing skin, lung, intestinal and bone marrow disorders, particularly where individuals have been chronically exposed by skin contact, direct ingestion or inhalation of dust (such as in mines and processing). U is taken up by plants but most U ingested in food and water is excreted and does not remain in the body (Taylor, 1997). All 3 main isotopes of U (^{235}U, ^{236}U, ^{238}U) are radioactive alpha emitters with long half-lives (Jones et al., 1990). There is public confusion about the health risk from natural levels of radioactivity from U probably because of association with the fissile isotope ^{235}U used (after enrichment) by the nuclear industry, and depleted uranium, used mainly for munitions. For the general population, chemical toxicity by inhalation of dust or ingestion is considered a greater hazard than radioactive toxicity (Menzel, 1968). It is generally agreed that U binds to soil clays and to organic matter, and is only moderately mobile under oxidizing conditions (Taylor, 1997). In long-term pastures top-dressed with P fertilizer in England and New Zealand, most of the U applied in the fertiliser was found to remain in the surface soil (Rothbaum et al., 1979).

There are many reports showing that Cd and U contents of fertilised New Zealand soils have increased substantially over time (Longhurst et al., 2004; Gray et al., 1999; Rothbaum et al., 1979, 1986; Loganathan et al., 1995; Taylor, 1997). P fertilisers continue to be applied to land (Parliamentary Commissioner for the Environment, 2004; Fertiliser Matters, 2005), and future concentrations of Cd and U could be expected to increase. The presence of elevated Cd and U in soils may limit the flexibility for other land uses, and there is the risk that continued accumulation of Cd and U in New Zealand soils could be used as a barrier to restrict future access for agricultural exports (Environment Waikato, 2005; MAF, 2010). Prior to 1997 the former level of Cd in New Zealand superphosphate was, on average, 48 mg Cd kg^{-1} fertiliser (Rothbaum et al., 1986; Roberts et al., 1994), but the New Zealand industry has set a voluntary target not to exceed 26 mg Cd kg^{-1} superphosphate fertiliser which has been in place since 1997 (Fertiliser Matters, 2005).

Table 1
Changes in land management and soil sampling protocols over the duration of the trial.

Year	Management history
c. 1920	Indigenous forest cleared to establish pasture. Liming and fertiliser application
1944	Earliest aerial photograph showing developed pasture
1968–1979	Top-dressed with single superphosphate at 36 kg P ha^{-1} yr^{-1}
1980–1983	P trial commenced on 20 paddocks, with four replicates at P loading of 10, 20, 30, 50, 100 kg P ha^{-1} yr^{-1}, applied as single superphosphate Between 1983 and 1988 ten soil cores 0–70 mm were taken along 5 transects on easy and steep slope classes. For our study subsamples from each of the 5 transects were combined to give a single sample for each replicate paddock and slope class
1983–1989	P trial continued with the 5 loading rates, but reduced to two replicates for each rate applied as single superphosphate. Fertiliser withheld on the other two replicate paddocks. Two of these paddocks which had received an initial loading of 10 kg P ha^{-1} yr^{-1} were selected as nominal “controls” receiving 0 kg P ha^{-1} yr^{-1}
1990–2006	Annual topdressing continued using triple superphosphate in place of single superphosphate until 2006 when the trial was terminated. Between 1993 and 2006, 15–20 soil cores to 0–75 mm depth were taken randomly from easy and steep slope classes in each paddock, then bulked for each slope class

To clarify the current rates of Cd and U accumulation or loss in New Zealand hill soils, we analysed archived soil samples from a field trial at Whatawhata Hill Farm Research Station in North Island, New Zealand, where different rates of P fertiliser had been applied annually to sheep-grazed pasture from 1983 to 2006. Our work extends the time scale of earlier reports from this site (Roberts and Longhurst, 2002) and reports for the first time the soil U contents as well as total P and Cd over a 23-yr period.

2. Materials and methods

2.1. Site and soil

Whatawhata Hill Country Research Station is situated 22 km west of Hamilton at an altitude of 45–370 m a.s.l. The P trial sites have been described previously (Roberts and Longhurst, 2002; Schipper et al., 2011) and only brief details are reported here. The climate is mild to warm and humid with an annual rainfall of around 1630 mm. The P trial was located on north-westerly facing sheep-grazed paddocks with both “easy” (10–20°) and “steep” (30–40°) slopes and an altitudinal difference of 30–50 m. The soils at Whatawhata are a mixture of Naiki (Typic Oxidic Granular Soil; or Humult) and Waingaro (Orthic Brown Soil; or Dystrochrept (Soil Survey Staff, 1992; Hewitt, 1998)).

In 1979 a long-term P fertiliser trial was established with annual topdressing of 10, 20, 30, 50, and 100 kg P ha^{-1} yr^{-1}, applied in March–April. There have been a number of changes in the management of the site and sampling protocols which are summarized in Table 1. For our study we analysed soils from 2 replicate paddocks that had received 30, 50 or 100 kg of P ha^{-1} yr^{-1} between 1983 and 2006, from the easy and steep slope classes. Two replicate paddocks that had been retired from the 10 kg P ha^{-1} yr^{-1} treatment