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CURRENT STATE AND TREND OF CADMIUM LEVELS IN SOIL, FRESHWATER AND SEDIMENTS ACROSS THE WAIKATO REGION

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Abstract
The Waikato Regional Council has monitored cadmium (Cd) in soils, groundwater and the Waikato river and carried out numerous investigations in aquatic sediment. Soil Cd monitoring shows a non-significant (at 95% confidence limit) decreasing trend in concentration of cadmium for the average of 150 soil quality monitoring sites since 2007, although 3% of samples remained above Tier 2 levels (1.4 mg/kg). According to the Tiered Fertiliser Management System, sites above Tier 0 require some form of phosphate fertiliser management to ensure that Cd contamination is kept below concentrations of concern for the next 100 years. Fertiliser industry soil monitoring showed similar results. Regional Council groundwater monitoring detected Cd in 16% of the groundwater samples with the highest Cd concentration 50% of the drinking water standard limit of 4 µg/L. These samples tended to be from high intensity farming areas. Results for the Waikato River samples were all below the detection limit (0.01 µg/L). Cadmium was enriched in peat lake sediments compared with background soil concentrations, while the estuarine and marine sediments within the Lower Firth of Thames were enriched compared with the west coast estuaries. In all cases, cadmium concentrations were below the ANZECC sediment low guideline for protection of aquatic ecosystems (1.5 mg/kg).

A reduction in fertiliser Cd levels compared to levels pre-1990's and the more efficient use of fertiliser are thought to contribute significantly to the reduced accumulation of soil Cd. However, mineral P fertilisers continue to be an important source of contaminant Cd to agricultural soils. Despite fertiliser industry driven reductions in fertiliser cadmium levels, Cd is still being applied to land. If this Cd is not accumulating in soil surface, it is being transferred to plants and the food chain, and moving deeper into the soil profile and/or the wider environment. Although current Cd levels in NZ soil and the current rates of application along with monitoring of Cd within the wider environment does not provide evidence for significant adverse effects, continued monitoring is necessary to provide sufficient warning should the situation change. Ongoing implementation of the Cadmium Management Strategy is likely to ensure that there remains minimal risk to human health and the environment over the foreseeable future. The fertiliser industry are encouraged to seek ways to further reduce Cd loading in agricultural soils, including the potential for use of alternative raw materials, utilising recycled P.

Background and Introduction
Cadmium (Cd) is a heavy metal that occurs naturally in soils at trace levels. The median Cd value for New Zealand non-agricultural soils is 0.07 mg/kg (Cavanagh 2014), while the median Cd value measured by Waikato Regional Council in soil quality monitoring samples under native forest in 2015 is 0.10 mg/kg.

The use of phosphate fertilisers over long timeframes in New Zealand has led to a gradual accumulation of Cd in fertilised soils, where it is predominately bound to minerals and organic matter in the topsoil (CWG 2008). Yet it is mobile enough for a proportion of added Cd to transfer to water (median partitioning coefficient, k_d 240 L/kg, Taylor 2016) or be taken up by plants (median transfer factor, TF 0.131, Taylor 2016). Cadmium in the environment is a human and ecological health issue that may, over time, suppress animal and microbiological life, have implications for human health and excessive levels of Cd in soils can restrict land use flexibility (CWG 2008). Cadmium is considered a priority contaminant in New Zealand (MfE 2011) and the fertiliser industry introduced voluntary limits on Cd levels in phosphate fertilisers in the mid 1990's.

There are several tools available to central government agencies and territorial authorities to help them manage Cd in the environment. The National Environmental Standards for Assessing and Managing Contaminants in Soil for the Protection of Human Health, (NESCS) provides a nationally consistent set of soil contaminant standards that apply to various land use scenarios and provides guidance for territorial authorities. Draft ecological soil guideline values have been developed for the protection of ecological receptors as of June 2016 and are currently undergoing a consultation process (Cavanagh & Munir 2016). Food Standards Australia New Zealand set standards at a level well below intake levels where toxic effects are likely to be observed and are set to protect health over a life time's exposure at the level of the food standards. The current standard for Cd in a range of key crops grown in NZ is 0.1 milligram per kilogram of food fresh weight, (as consumed, or in the case of dried products, prior to drying).

Plant uptake is influenced by a combination of many environmental factors including the amount of Cd; soil characteristics, such as pH and the presence of adsorption sites; the presence or absence of competing cations, such as zinc; plant related factors, such as the crop species and cultivar, the types of plant tissue and leaf age (Alloway 2008, CWG 2008). So, there is no simple relationship between soil Cd levels and plant uptake, although there are management options available to help reduce plant uptake including increasing soil pH and organic matter content (Gray et al. 1999, Gray & McLaren 2006).

Some Cd leaches down the soil profile (Tyler 2004) and appears to be soil specific, e.g. high mobility of Cd has been observed in sandy soils (McLaughlin et al. 1996). A comprehensive attempt to understand Cd leaching was presented in Gray et al. (2003). They found the range of Cd leached was quite wide (0.27 - 0.86 g/ha/y) but no statistical relationships between the amounts of Cd leached and major soil characteristics were established.

A Cadmium Management Strategy has been developed (Cadmium Working Group 2011, Appendix 2), under the auspices of the Chief Executives Environment Forum. The Cadmium Management Strategy, in many ways an international first, is aimed at managing the accumulation of Cd in agricultural soils to ensure that there remains minimal risk to human health and the environment over the long-term (the next 100 years at least). It was established to stand for seven years and be reviewed in 2017/18 to determine progress and future direction.

Identifying trends in Cd in New Zealand farmed soils and the wider environment is necessary to help manage the risks associated with Cd and to inform the review of the Cadmium Management Strategy. This paper presents the combined results and trends identified from monitoring of cadmium by the Waikato Regional Council and the fertiliser industry.

Methods

Waikato Regional Council's routine monitoring programmes include the monitoring of Cd in soils, surface water and groundwater. Fertiliser industry routine monitoring programmes include the monitoring of Cd in soils and phosphate fertiliser.

Soil monitoring :150 soil quality sites have been monitored by Waikato Regional Council for Cd since 2005 (Figure 1). Samples are composites of 40-50 plug samples, 0-10 cm depth by 2.5 cm wide, from a 50 m transect (Kim & Taylor 2009) and analysed following national guidelines (Hill & Sparling 2009; Kim & Taylor 2009). Where the same site had been sampled at different times, changes in Cd concentrations over time were assessed.

Fertiliser industry soil data represent aggregated farm samples from the Waikato conducted under the Tiered Fertiliser Management System (TFMS) collected as part of routine industry evaluation of soil fertility. Soil sampling of pastoral soils were to a depth of 75 mm, representing a conservative 'screening' sample for soil Cd concentrations, and arable and horticultural soils were sampled to a depth of 150 mm, representing a 'definitive' assessment of soil Cd concentration under the TFMS. Composite soil samples were collected along transects representative of farm blocks.

Soil analysis results for both regional council and industry data represent a near total soil Cd (acid recoverable extraction methods).

Soils data were compared with the TFMS. The TFMS requires monitoring of soil Cd with a series of soil Cd trigger values which give rise to increasingly stringent controls on choice and rate of phosphate fertiliser products used to control Cd accumulation (Table 1).

Table 1: The tiered management approach to cadmium accumulation in soil.

Tier	Soil cadmium (mg Cd/kg)	Management required
Tier 0	< 0.6	Soil cadmium is within the range of natural background concentrations. No restriction on phosphate fertiliser type or application.
Tier 1	0.6 to <1.0	Some restrictions on phosphate fertiliser application rates, and implementation of appropriate management practices.
Tier 2	1.0 to <1.4	Increased restrictions on phosphate fertiliser type and application rates, and implementation of appropriate management practices.
Tier 3	1.4 to <1.8	Further restrictions on phosphate fertiliser type and application rates, and implementation of appropriate management practices.

Groundwater monitoring**:** Routine, regional monitoring of groundwater, by Waikato Regional Council, began in 1995 and has included Cd in the trace element analysis. There are currently about 106 wells monitored. An additional, substantial groundwater monitoring investigation which included Cd in groundwater was undertaken during the period 2008–2012, with 762 samples analysed (Nokes & Weaver 2014). These samples were predominantly from wells within the regional groundwater quality monitoring networks (Figure 1).

***Surface water monitoring*:** The Waikato river water quality monitoring programme began in 1995 and includes analysis of Cd and other trace elements from six sampling sites along the river on a five yearly basis (Figure 2).

***Sediment monitoring*:** Sediment investigations undertaken by Waikato Regional Council over the period 2003 to 2016 include sediments of 22 lakes, river sediments from the Waihou, Piako and Ohinemuri rivers, the estuarine sediments of the west coast and the estuarine sediments of the Firth of Thames, all include analysis for Cd, (Figure2).

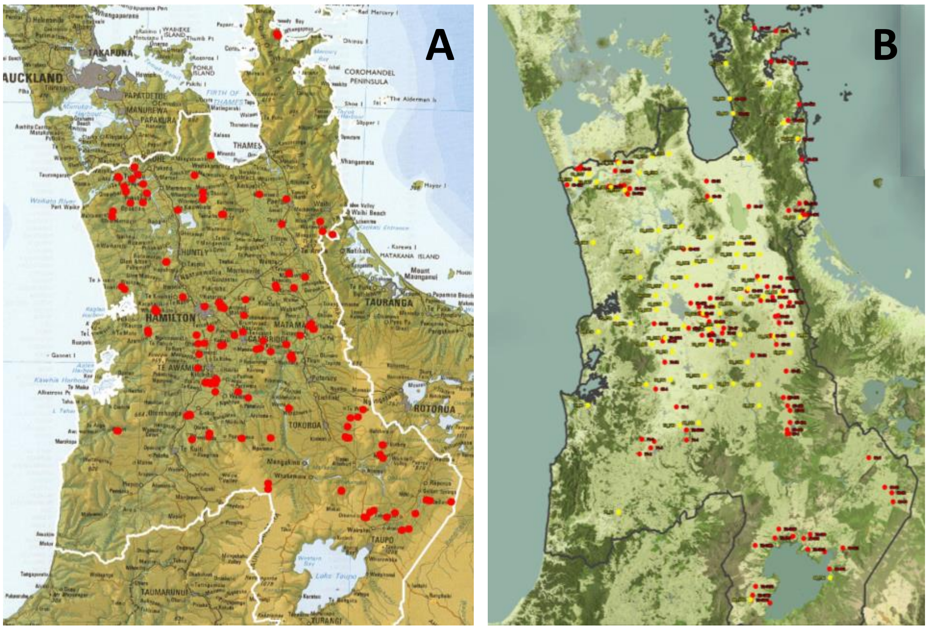

Figure 1. Waikato Regional Council monitoring sites for (A) soil and (B) groundwater.

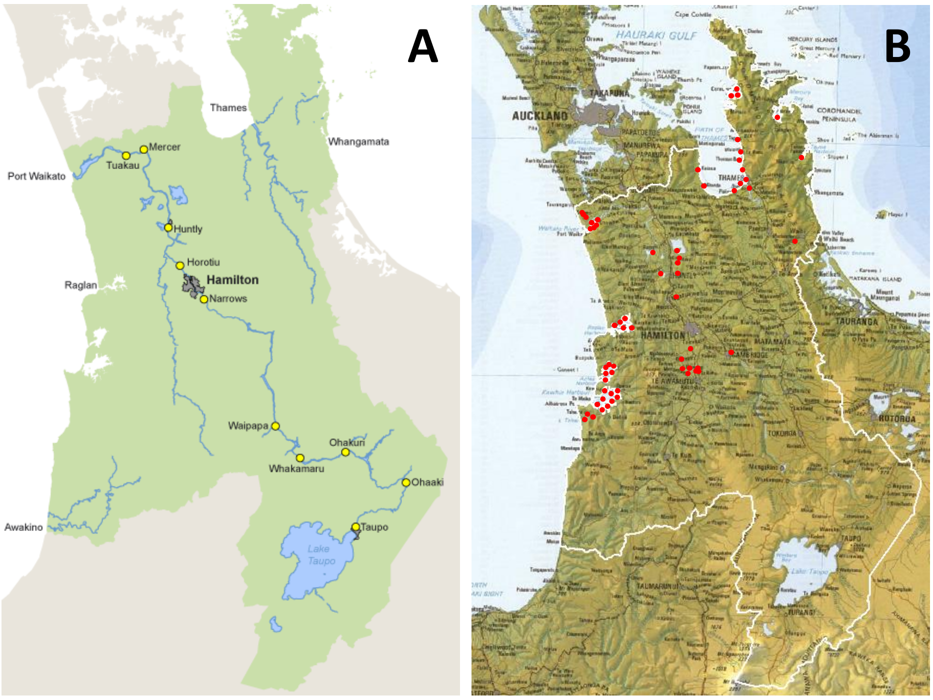

Figure 2. Waikato Regional Council monitoring sites for (A) Waikato River surface water and (B) locations where sediment samples were taken.

Phosphate Fertiliser monitoring: The Cd content of phosphate fertiliser currently has a voluntary limit of 280 mg Cd/kg P and is monitored at the manufacturing sites by the fertiliser companies, with independent auditing by Quality Consultants New Zealand Ltd (QCONZ).

Monitoring results and discussion

Soil Monitoring: State of environment monitoring by Waikato Regional Council shows a non-significant (at 95% confidence limit) decreasing trend in concentration of Cd for the average of all 150 soil quality monitoring sites in the Waikato region since 2007 (Figure 3). Of the land uses receiving fertiliser, about half the pastoral land monitored by Waikato Regional Council was in tier 0 and only 1 site was in tier 4, while tier 1 had the largest number of horticultural sites (Table 2).

Table 2 : Number of samples within each Tier (Source: Waikato Regional Council).

Land use/Cd range	Tier 0 <0.6	Tier 1 0.6-<1.0	Tier 2 1-<1.4	Tier 3 1.4-<1.8	Tier 4 1.8
Pastoral	108	68	33	5	1
Horticulture	1	10	8	2	0

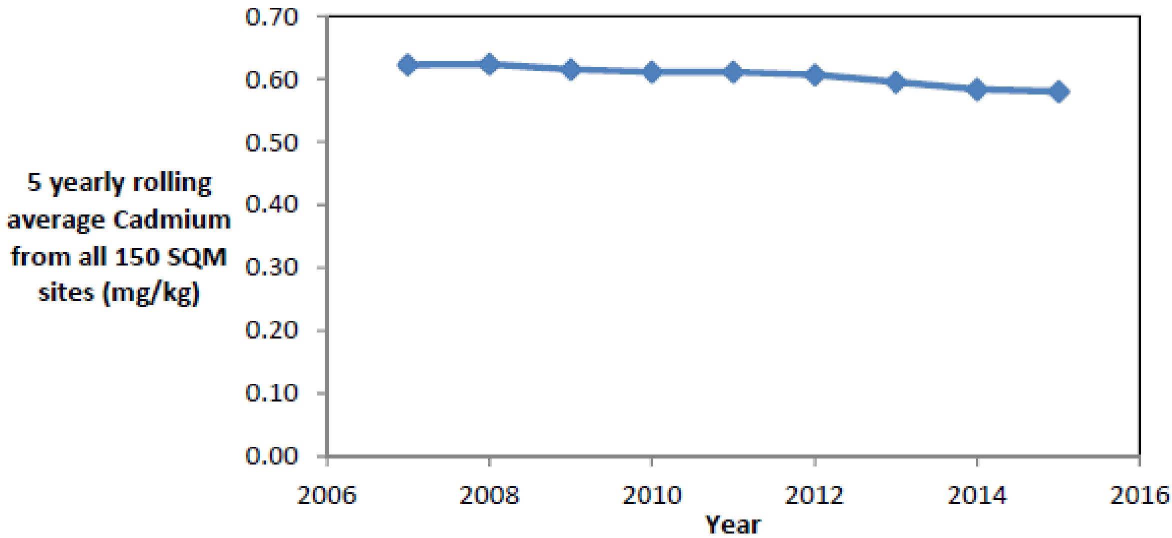

Figure 3. Rolling average soil Cd (Source: Waikato Regional Council).

The results are similar to the much wider fertiliser industry data, presented by Abraham 2016, which also show little if any change in soil Cd concentration over the period 2007 to 2015 (Figure 4). This data provides a comparison of soil Cd results reported by the fertiliser industry to those of non-industry sampling comprising Waikato Regional Council data and that of Crown Research Organisations. Further research data is provided by the Winchmore fertiliser trial over the period 1995- 2005. (Figure 5).

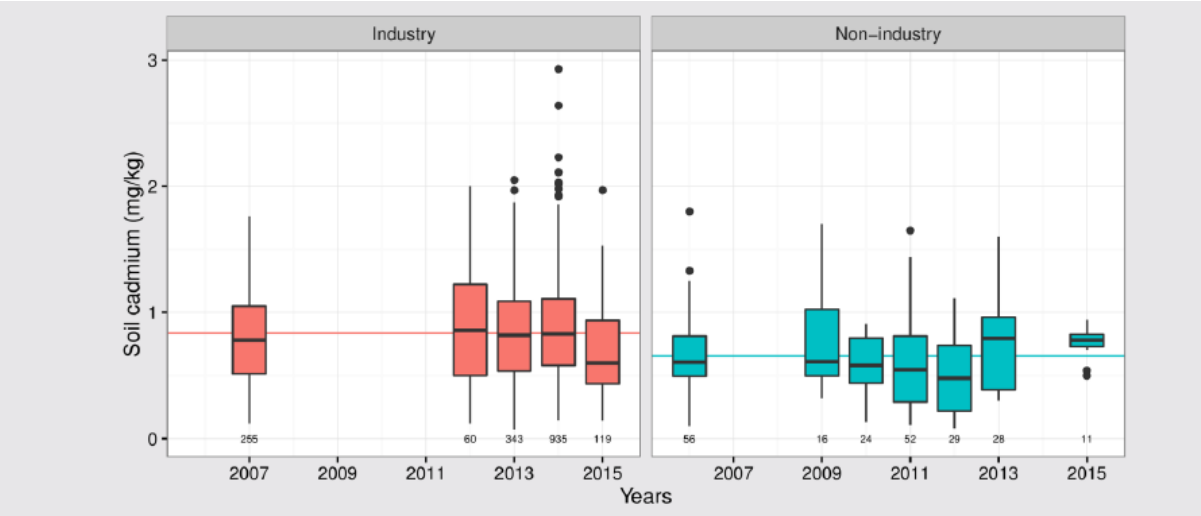

Figure 4. Comparison of non-industry and industry soil Cd data. Horizontal lines are overall median values (Source: Abraham, 2016).

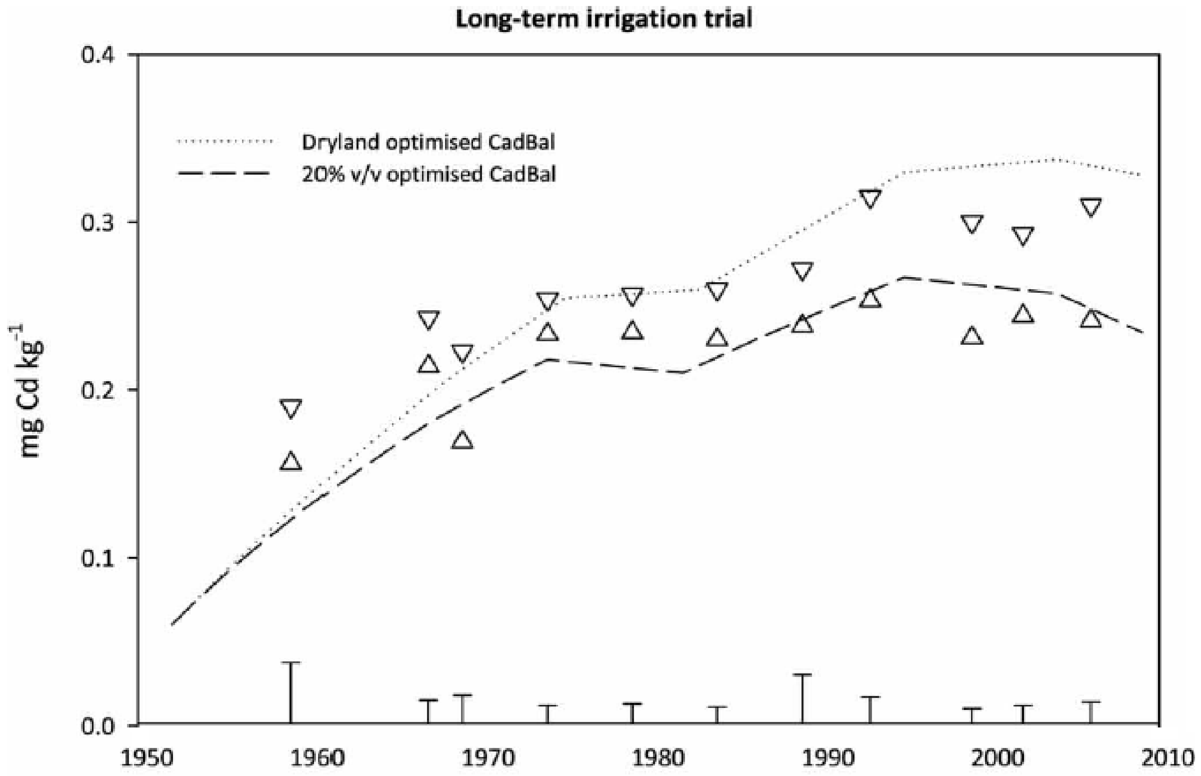

Figure 5. Soil Cd levels over about 50 years in long-term irrigation trials at Winchmore Research Station, Canterbury. Symbols indicate the mean sample value of soil cadmium from dryland (▽) and irrigated (△) treatments; dotted and dashed lines are fits of a cadmium mass-balance model which simulates soil accumulation. (Source: Abraham, 2016, adapted from McDowell, 2012).

The plateau of soil cadmium concentrations was unexpected at the start of this monitoring period. An explanation for the observed plateau in soil Cd results is a lessening of the amount of Cd in phosphate fertilisers since the mid 1990’s. NZ has traditionally sourced its phosphate from high Cd P rock, i.e. the ancient avian guano deposits of Narau Is. (588 mg Cd/kg P, calculated from Syers et al. 1986, McKelvey 1967) and considerable accumulation of Cd was observed (McIntosh et al 1997, Taylor 1997). As a result of raised concerns about Cd accumulating in soil, the fertiliser industry set an initial voluntary limit of 340 mg Cd/ kg P in phosphate fertiliser in 1995, which was lowered to 280 mg Cd/kg P in 1997. The fertiliser industry has kept well below this level with a long-term average of 184 mg /kg P over the period 2003 – 2015 (Figure 6).

Thus, the New Zealand fertiliser industry implemented voluntary limits on the Cd content of fertilisers and maintained monthly-averaged concentrations of Cd in phosphate fertiliser below the voluntary limits. During the period 2003 to 2015 of routine monitoring there have been 4 mild exceedances of the voluntary limit in phosphate fertiliser. Two of these occasions occurred when stockpiles of phosphate rock destined for further blending were inadvertently sampled and the remaining occasions of mild exceedance occurred during a period of limited access to low cadmium phosphate rock. This was reported to MPI at the time and product was used judiciously at lower application rates to soil typically known to have lower soil cadmium. Although monthly average has trended down below the long-term average in the last two years, the concentration of Cd in the final product is entirely dependent on the natural levels in the rock phosphate raw materials. Hence variability in available raw materials will inevitably give rise to fluctuation over time in final Cd levels in fertiliser products.

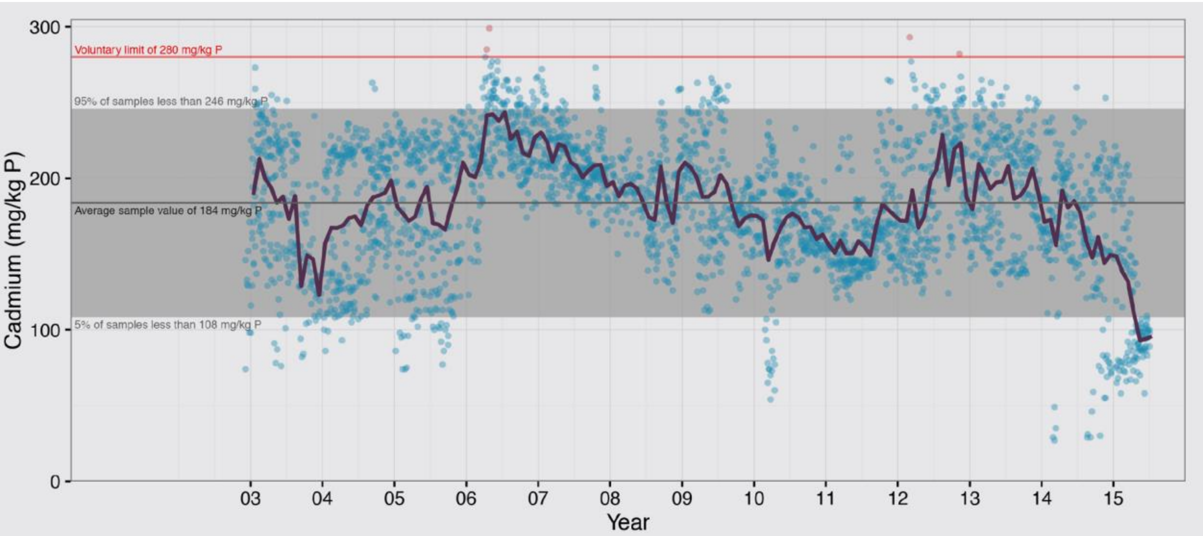

Figure 6. Cadmium in fertiliser samples manufactured at Ravensdown and Ballance processing plants in New Zealand. Solid line is the monthly average.

The industry has a commitment not to exceed the agreed limits for phosphate fertiliser and seeks to provide products with the lowest Cd possible. This initiative is built on with the implementation of the Tiered Fertiliser Management System which is designed to ensure soil cadmium remains within a recommended range of values over the 100 years at least.

The fertiliser industry continues to monitor international initiatives seeking to develop commercially viable decadmiation processes for manufacturing and development of recycled waste products. However, a review covering the recovery and reuse of P from wastewater concluded that despite the use of Ca and Mg/NH4 salts for P recovery from wastewaters, no process is presently able to compete with conventional sources of P supply to the market (Naidu et al 2012). In the meantime, Cd is still being applied to land in phosphate fertilisers and, if not accumulating in soil, it is transferred at trace levels into the food chain and/or the wider environment. As part of the state of environment monitoring and reporting, cadmium levels in the potential receiving environments of groundwater, surface water and sediment are monitored by Waikato Regional Council. The results of this monitoring, show only very low levels of cadmium in these environments and no evidence of any cause for concern. Continued monitoring is necessary to provide sufficient warning should the situation change.

***Groundwater monitoring*:** Results from Waikato Regional Council's groundwater monitoring over the period 2008–2012 showed that Cd was detected in only 16% of the samples and these samples tended to be from high intensity farming areas. Nevertheless, the highest Cd concentrations were still only half of the drinking water standard limit value of 4 μg/L. A further round of monitoring is being carried out this year (2017).

***Waikato River water monitoring*:** Results from 1995 to present from the Waikato Regional Council surface water monitoring show that Cd concentrations are below the detection limit of 0.01 μg/L (Table 3). The *Australian New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC) for cadmium in water is 0.2 μg/L, so there is currently no evidence to suggest that cadmium is an issue in the Waikato River.

Table 3. Results of monitoring for cadmium in the Waikato River, 1995-2015 (Source: Waikato Regional Council).

Waikato River site	Narrows Br	Ohakuri Tailrace Br	Taupo Control Gates	Tuakau Br	Narrows Boat Ramp	ANZECC guideline
Cd (μg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	0.2

***Sediment monitoring*:** Monitoring of sediment by Waikato Regional Council showed Cd concentrations were below the ANZECC sediment guidelines for protection of aquatic ecosystems. However, in some cases, enrichment of Cd has been identified when compared with background soil concentrations, especially in the peat lakes (Table 4) where increased soil acidity can result in increased mobility of Cd, e.g. the highest sediment concentration has been identified in the peat lake, Mangakaware, at 1.37 mg/kg, which is close to the ANZECC trigger limit of 1.5 mg/kg (over which further investigation is recommended) but still well below the high ANZECC trigger limit of 10 mg/kg (above which significant adverse effects are likely).

Concentrations of Cd have also been found to be higher in the estuarine sediments within the Lower Firth of Thames compared with the west coast estuaries (Table 4). However, sediment levels are below the values which would trigger further detailed investigation, and below limits which might indicate significant adverse effects. Where enrichment has been identified, the main source is expected to be from the use of phosphate fertilisers although historic mining activities are also expected to be a significant contributor within the Firth of Thames. The enrichment of Cd in sediment and its loss from soil suggests soil is acting as a source and sediment a sink.

Table 4. Concentrations of Cd in lake, river and estaurine sediments from the Waikato Region (Source: Waikato Regional Council).

Cd (mg/kg)	Waikato lake sediments (22 lakes)			Coromandel Estuarine sediments				West coast estuarine sediments			Ohinemuri River sediments
	Dune	Peat	Riverine	FoT (Thames to Coromandel Harbour)	Eastern Coast (Tairua & Whitianga)	Piako River mouth	Waihou River mouth	Raglan	Aotea	Kawhia	
	0.09	0.64	0.28	0.17	0.04	0.23	0.11	0.02	0.02	0.03	0.23

Note: Low ANZECC trigger limit is 1.5 mg/kg and high ANZECC trigger limit is 10 mg/kg.

Take Home Messages

Since the mid 1990's, the New Zealand fertiliser industry has maintained concentrations of Cd in phosphate fertiliser below the voluntary limits resulting in a reduction of Cd being applied to the New Zealand environment.

The industry has reaffirmed its commitment that phosphate fertiliser products will remain below the industry limit and the industry monitors international initiatives for reducing Cd content in phosphate fertilisers.

Monitoring of soil Cd by Waikato Regional Council, aggregated soil sampling by the fertiliser industry and soil sampling at the long-term trial site at Winchmore research station all indicate there has been no appreciable increase in soil Cd over recent years.

Monitoring of the Waikato River water show that Cd concentrations were below the detection limits. There is currently no evidence to suggest that Cd is an issue in the waters of the Waikato River.

Cadmium was detected in a relatively small number of groundwater samples. These were under intensive production land but were well within guideline values.

Enrichment of Cd in peat lake sediments and estuarine sediments within the Lower Firth of Thames suggests some Cd is moving through the soil profile into the wider environment. This is expected to be from agricultural land and other sources, such as historic mining.

Although current evidence indicates that Cd is not accumulating in New Zealand soils and that cadmium levels within surface water, groundwater and sediments within the Waikato region are not likely to be resulting in an adverse effect on the environment, continued monitoring, including more targeted and integrated monitoring, is necessary to provide sufficient warning should the situation change.

Ongoing implementation of the Cadmium Management Strategy is likely to ensure that there remains minimal risk to human health and the environment over the foreseeable future.

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