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Cadmium Accumulation in Waikato Soils

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Disclaimer

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'New Zealand environmental and agricultural officials have to make a hard decision....'

- Dr Rufus Chaney, US Department of Agriculture

Executive Summary

Policy position and issue

A central objective of the Land and Soil section of the Waikato Regional Policy Statement is that the range of existing and foreseeable uses of the soil resource should not be reduced as a result of the contamination of soils. This rests alongside a complementary objective that versatility and productive capacity of the region's soil resources should be maintained.

An estimated 8.3 tonnes of the heavy metal cadmium is currently applied to Waikato soils each year, with the largest single source being superphosphate fertiliser. Cadmium is a naturally occurring, toxic, non-essential and biologically cumulative heavy metal. Concentrations of cadmium in Waikato soils have been gradually increasing since the advent of topdressing.

There are three means by which existing and foreseeable uses of the productive soil resource may be lost as a result of cadmium accumulation in soils. These are:

1. future inability to subdivide the land for residential or rural-residential purposes without some form of site assessment and/or remediation
2. possible market access restrictions for produce
3. non-compliance with food standards for crops grown on a property because of soil contamination.

Loss of soil resource capacity can be defined as points at which one or more of these outcomes are realised.

In terms of the first and second outcomes, the most readily quantifiable point for soil resource loss is 1 mg/kg for total soil cadmium. This is both the current recommended limit for cadmium in agricultural soils, and a default human health protection limit for Waikato properties being subdivided to residential or rural-residential land. The recommended agricultural soil cadmium limit is set partly with respect to current and anticipated expectations of New Zealand's international trading partners.

The third outcome, non-compliance with food standards, relates mainly to particular types of horticultural and arable crops. The exact point at which soil cadmium has become high enough to cause food standards to be exceeded can be difficult to predetermine, as it depends on crop and soil conditions. However, this outcome has been observed to occur at soil cadmium concentrations below the current recommended agricultural guideline of 1 mg/kg. For this reason, the agricultural soils guideline for cadmium can not be used as a proxy for food compliance.

Current status of Waikato's productive soils

Based on recent sampling, it is estimated that perhaps 11% of Waikato's pastoral soils and 17% of Waikato's horticultural soils already exceed 1 mg/kg soil cadmium. For horticultural soils, this would represent approximately 1775 hectares of land. For pastoral soils (sheep, beef and dairy land), this would represent about 157000 hectares. Within the pastoral soils sample set, all soil samples that have so far exceeded the 1 mg/kg agricultural guideline have been from dairy farms.

On **average**, Waikato's productive pastoral, horticultural and arable surface soils now contain five times more cadmium than they began with, and are two-thirds of the way to the 1 mg/kg threshold.

Loading calculations confirm that the dominant source of this cadmium is superphosphate fertiliser, which contains cadmium as an impurity.

Projections for pastoral and horticultural soils

At current cadmium loading rates, the next significant point at which the 1 mg/kg cadmium guideline will be reached over wide land areas is expected for dairy farms, which cover about 25% of the Waikato region (about 623000 hectares). Conservatively, the average cadmium concentration in Waikato dairy soils is projected to reach the recommended guideline in under 16 years.

In total, productive pastoral soils (mainly sheep, beef and dairy farms) comprise 57% of Waikato's land area (about 1,430,000 hectares). At current loading rates, the average cadmium concentration over all pastoral surface soils in the Waikato region is expected to reach the 1 mg/kg guideline in under 40 years.

In horticulture, the most rapid rate of accumulation occurs in soils under potato crops, where the estimated period before these soils average 1 mg/kg cadmium is 13 years. The Waikato is now New Zealand's second largest potato growing region.

It is important to note that these estimates are based on averages: on specific properties the guideline has been reached, or will be reached in a shorter time.

Implications for current and foreseeable uses of the soil resource

A current impact associated with the presence of cadmium in drystock farming is the rejection of offal meat. As a result of its high cadmium content, offal from animals older than 2.5 years is not permitted to be sold for human consumption. To the sheep and beef industries, this represents a significant lost income stream.

In recent years, the New Zealand food standard for cadmium in key crops has dropped by a factor of ten to 0.1 mg/kg, and recommended guidelines for cadmium in New Zealand agricultural and residential soils have dropped by a factor of three to 1 mg/kg.

In relation to the revised soil guidelines, two specific impacts associated with surface soils exceeding 1 mg/kg cadmium are the inability to subdivide land for residential (or rural residential) use without some form of assessment or remediation, and possible hindrances to market access. Although milk and muscle meat make a minimal contribution to human dietary intakes of cadmium, the agricultural soil guideline is set partly with reference to expectations of international trading partners. Such guidelines may take on a more significant trade role in the future.

As a result of the tightening of food standards, cadmium accumulation in agricultural surface soils is likely to be causing progressive loss of soil resource capacity through the food non-compliance mechanism. This loss of soil resource capacity relates to the proportion of soils that become unsuitable for (current or future) production of certain horticultural or arable crops at any point in time, based on whether crops grown in these soils could continue to meet the food standard for cadmium.

Overall, ongoing cadmium accumulation has the potential to reduce the range of foreseeable uses of approximately 58% of the Waikato region's total land area in the short-to-medium term (between 10-60 years depending on land use), covering pastoral agriculture (primarily dairy, beef and sheep farming), arable cropping and horticulture.

This proportion may further increase in response to land being converted from plantation forests to dairy farms. Dynamic changes to land use underscore a regulatory need to manage cadmium inputs in all areas. Land that is forested today may be pastoral tomorrow, and land that is pastoral today may be horticultural, or residential, tomorrow.

Comparison of estimates
Average projections estimated in this report for dairy soils, and soils under potatoes, are consistent with estimates reported by the New Zealand fertiliser industry, when differences in survey years and national versus regional coverage are accounted for.

The New Zealand fertiliser industry has also reported that preventing further accumulation in New Zealand soils would require an 80% reduction in the cadmium content of superphosphate fertiliser, to approximately 24 mg Cd/kg P_2O_5.

- This estimate is consistent with a recent opinion delivered by the European Commission's Scientific Committee on Toxicity, Ecotoxicity and the Environment (SCTEE), that cadmium accumulation in soil should not be significant at fertiliser concentrations less than 20 mg Cd/kg P_2O_5.

- A figure reported for US superphosphate fertiliser, where cadmium accumulation has not been significant, is 16 mg Cd/kg P_2O_5.

The current voluntary limit for cadmium in New Zealand phosphate fertilisers is 122 mg Cd/kg P_2O_5.

Human exposure
Exposure of the general population to cadmium is mainly through food. Of all contaminants in the diet, cadmium is the one that comes closest to its provisional tolerable weekly intake (PTWI). Evidence exists that the current food standard is routinely being exceeded in some New Zealand crops, particularly some varieties of wheat.

In order to provide a reliable benchmark for future work, a survey was carried out of cadmium concentrations in some key commercial produce sold in the Waikato region. The average cadmium concentration in potatoes purchased in the Waikato region in 2004 was 25.4 µg/kg, which is one quarter of the food standard, and analytically indistinguishable from the figure for potatoes from the latest New Zealand Total Diet Survey (25.8 µg/kg).

Based on an analysis of the sample distribution, it is estimated that approximately 1.5% of potatoes purchased in the Waikato region were likely to exceed the food standard in 2004.

Off-site effects
In terms of diffuse discharges to the wider environment, the main potential issue identified is the gradual accumulation of cadmium in stream, river, lake and coastal sediments of agricultural catchments. However, further work is required to assess whether cadmium accumulation in rural streams, rivers, and coastal receiving areas is sufficient to pose a risk to ecological receptors in the medium term.

Management approaches
The area of technical management and policy options that might be applied to avoid, remedy or mitigate cadmium accumulation in agricultural soils is substantial enough to require a separate investigation and report in its own right. Production of such a report (or reports) at national level is suggested as a recommendation of this work.

Further summary information
A more detailed summary can be found in **Section 9** of this report.

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1 Policy goals and anatomy of the problem

1.1 Waikato Regional Policy

A central objective of the **Land and Soil** section of the Waikato Regional Policy Statement (RPS, Section 3.3.8[1]) is that the range of existing and foreseeable uses of the soil resource should not be reduced as a result of the contamination of soils. This rests alongside the complementary objective that versatility and productive capacity of the Region's soil resources should be maintained (RPS, Section 3.3.9[1]).

An issue identified in the **Water Quality** section of the Regional Policy Statement is that water quality can be degraded as a result of the cumulative effect of the non-point source discharges of contaminants. The policy objective of this section is that (as a result of more appropriate management practices) there should be a net improvement in water quality across the Waikato region (RPS, Section 3.4.5[2]).

A number of agricultural treatments in current use have the potential to cause soil contamination that might compromise future use of the soil resource, and degradation of water quality.

1.2 Mechanisms of soil resource loss

1.2.1 General

Contaminants most likely to cause soil sustainability problems over the longer term are those which are capable of accumulating over the years, so that their total soil concentrations progressively increase. This can happen for any element or compound that is adsorbed by the soil, persistent, and routinely used. A number of trace metals used in agriculture fit all three of these criteria.

There are three means by which existing and foreseeable uses of the productive soil resource may be lost as a result of contaminant accumulation in soils. These are:

- Future inability to subdivide the land for residential or rural-residential purposes **Section 1.2.2**)

- Non-compliance with food standards because of soil contamination (**Section 1.2.3**)

- Possible market access restrictions (**Section 1.2.4**).

Loss of soil resource capacity can be defined as points at which one or more of these outcomes are realised. Once they occur, reversal or amelioration is difficult.

An overview of each of these soil resource loss mechanisms is given in the following sections.

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1 Waikato Regional Policy Statement, **2000**. Sections 3.3.8 and 3.3.9. Available from: http://www.ew.govt.nz/policyandplans/rpsintro/rps/RPS3.3.8.htm

2 Waikato Regional Policy Statement, **2000**. Section 3.4.5. Available from: http://www.ew.govt.nz/policyandplans/rpsintro/rps/RPS3.4.5.htm

1.2.2 Site contamination

One responsibility of Territorial Authorities, who operate partly with reference to the Health Act (1956)[3] as well as the Resource Management Act (1991), is to ensure that land is suitable for its intended purpose. Under the latest round of amendments to the Resource Management Act, the role of regional councils in investigation and management of contaminated land is also being explicitly defined for the first time. For the Waikato Regional Council, this comes in addition to regional policy objectives that already exist relating to contamination and the range of existing and foreseeable uses of the soil resource (**Section 1.1**).

Like food standards, soil acceptance criteria for human health are risk-based, and rest on models of potential exposure under different land-use regimes. Guideline values for residential and agricultural soils tend to be lower (more conservative) than those for commercial or industrial soils.

In cases where accumulation has been sufficient to cause contaminant levels to exceed guideline values for human health, a property technically becomes a contaminated site. Best practice guidelines for contaminated land recently produced by the Ministry for the Environment[4] indicate that such a site should be registered as contaminated.[5] The range of land uses to which the property might be put is then restricted because the site is deemed as not being suitable for certain activities.

Most diffuse contamination of this nature that Local Authorities have dealt with to date is due to historic practice, involving pesticides that are no longer in use. These include the insecticides lead arsenate and DDT. Old orchards are the most common example of this phenomenon to date; these are often situated on an urban fringe, and city boundaries tend to expand over them. In a number of cases, arsenic or DDT levels in old orchards have been found to exceed guideline values for residential soils, and residential redevelopment can not be allowed to proceed until soil remediation has taken place. In terms of Local Authority involvement, the main trigger point is when an owner applies to subdivide the land, and concurrently change the zoning from agricultural to residential. Arsenic (from the lead arsenate) is usually the limiting contaminant. Arsenic is a human carcinogen, and the risk-based guideline value for arsenic in residential soil is 30 mg/kg.[6] This is approximately six times the natural concentration of arsenic in New Zealand soils.[7]

Financial losses mediated through this mechanism can include:

- Costs of a preliminary site investigation to establish whether guideline values are likely to be met, and (if they are not)
- Costs of a second-tier investigation to identify remediation options
- Costs of remediation (usually involving soil treatment or removal)
- Costs of a site validation report
- Additional costs associated with a more involved resource consent assessment
- Influence on the market value of a property.

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3 Work is underway to replace the Health Act **1956** with a new Public Health Bill. This, if anything, will further clarify the law in this area. It is intended that the new Public Health Bill will *'allow for the management of a wide range of risks to public health, but will focus on communicable diseases and environmental health.'*

4 Ministry for the Environment, **2004**. Best practice guidelines for management of contaminated land are available from: http://www.mfe.govt.nz/publications/hazardous/

5 Providing that relevant information comes to the attention of the Local Authority. Local Authorities may collect such information through either active means (*e.g.* as a result of targeted surveying) or reactive means (*e.g.* as a result of a subdivision consent application).

6 Ministry for the Environment and Ministry of Health, **1997**. *Health and Environmental Guidelines for Selected Timber Treatment Chemicals.*

7 Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.

1.2.3 Soil and food

Contaminant levels in soils play a key part in determining residues in foods.[8] Legislation governing contaminant levels in New Zealand foods has been through a number of changes over recent years, the most significant of which is a move to a single New Zealand Food Safety Authority (formed July 2002) which administers a genuine risk-based regulatory model.[9] The relevant standard governing contaminants in food is now Section 1.4.1 of the Food Standards Code.[10] Under this Code,[11] acceptable levels of some heavy metal contaminants in food are now lower than previously. For example, the standard for the heavy metals cadmium and lead in most vegetables is now 0.1 mg/kg, whereas previous standards were 10 and 20 times higher, respectively.[12] For these two contaminants in particular, adoption of risk-based food standards means that, for most food groups, the margin between current and tolerable levels of contamination in agricultural soils has recently become narrower.

At the point where a soil of a given property accumulates sufficient contaminant for a food standard to be routinely broken, that property is no longer a suitable venue for food production, and the soil resource has lost one of its more significant uses. Recent changes to New Zealand legislation, and regulations derived from it, therefore have a direct impact on regional councils' need to more closely manage certain trace contaminant inputs in their agricultural soils.

DDT contamination of pastoral soils is the main prior example of contamination of the soil resource restricting a type of land use. Before being de-registered, the insecticide DDT was widely used on pastoral land, both in its own right, and as a fertiliser additive. Peak years of application were the 1950s through until the mid 1970s. DDT is strongly adsorbed by soil and accumulates with repeated application; it is also resistant to microbial degradation and takes some time (several decades) to break down.

Although it has been three decades since this compound was last widely used, levels in pastoral soils are still sufficient to place a limit on the proportion of Waikato properties that can carry dairy cows. This is because DDT is fat-soluble and accumulates in milk. The New Zealand dairy industry will not accept milk from properties where soil DDT levels exceed a certain threshold, because presence of DDT and its metabolites in milk constitute a market barrier. In the case of Fonterra, this soil limit is 0.2 mg/kg[13] for DDT and its metabolites (using a specific extraction method). From unpublished data assessed in-house it is evident that over two-fifths of the Waikato soil samples submitted for DDT analysis still fail to meet this threshold.

Although it could be argued that restriction of further intensification of dairy farming may be an environmental benefit, the general principle has already been established that trace contamination of soil has the capacity to restrict use of the soil resource. DDT contamination is not permanent: the source of contamination has been removed, and residues will gradually break down over the long time periods. Trace metals, by comparison, are still accumulating in agricultural soils, and do not break down.

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8 This topic is delineated further for cadmium in **Section 3**.
9 New Zealand Food Safety Authority, **2004**: http://www.nzfsa.govt.nz/about-us/questions-answers/index.htm
10 John Van den Beuken, New Zealand Food Safety Authority, **2003**. Personal communication, 20 October 2003.
11 Food Standards Code, **2004**. Available from: http://www.foodstandards.gov.au/foodstandardscode/index.cfm
12 Note that the old food standards were partly based on what was able to be measured at the time, as well as the need to protect against acute toxicity.
13 Global Dairy Company Limited [Fonterra] Supplying Shareholder Handbook, Section 7.15: *'The Company has a policy restricting new milk supply to properties with a weighted average soil level of less than 0.2 mg/kg for DDT and its metabolites.'*

1.2.4 Soil guidelines and market perception

In addition to the relationship between soil and food, there is an issue of market perception. When soil guideline values for contaminants are exceeded, a possible consequence is the restriction of international trade access.

With this in mind it is worth noting that the recommended upper limit for cadmium agricultural soils is partly set on the basis of expectations of international trading partners, and the European Community in particular (**Section 3.8.2**).

Recent discoveries relating to cadmium's ability to act as both a carcinogen and endocrine disruptor (**Section 2.3.2**), have generated new scientific interest in the role of dietary cadmium in hormone-related cancers that show a high incidence in Western populations (*e.g.* breast and testicular cancers).[14] As the results of such work become available, and regulatory developments in the European Community take effect (**Section 4.3**), there is a possibility that market preferences may develop from some of New Zealand's trading partners toward sourcing produce from countries with low soil cadmium.

An example of market perception causing a significant change in agricultural practice is the 1962 recall of the organochlorine dieldrin, which was triggered by a trading block raised by Canada in response to dieldrin residues in New Zealand butter.

1.2.5 Summary of soil resource loss mechanisms

Contaminant accumulation in soils can mediate the loss of soil resource through three distinct mechanisms, identified in **Sections 1.2.1–1.2.3**. These ideas are summarised using cadmium as the example in **Figure 1**.

[14] Johnson MD, Kenney N, Stoica A, Hilakivi-Clarke L, Singh B, Chepko G, Clarke R, Sholler PF, Lirio AA, Foss C, Reiter R, Trock B, Paik S and Martin M, **2003**. Cadmium mimics the in vivo effects of estrogen in the uterus and mammary gland. *Nature Medicine*, Vol. 9, No. 8, pp 1081-1084.

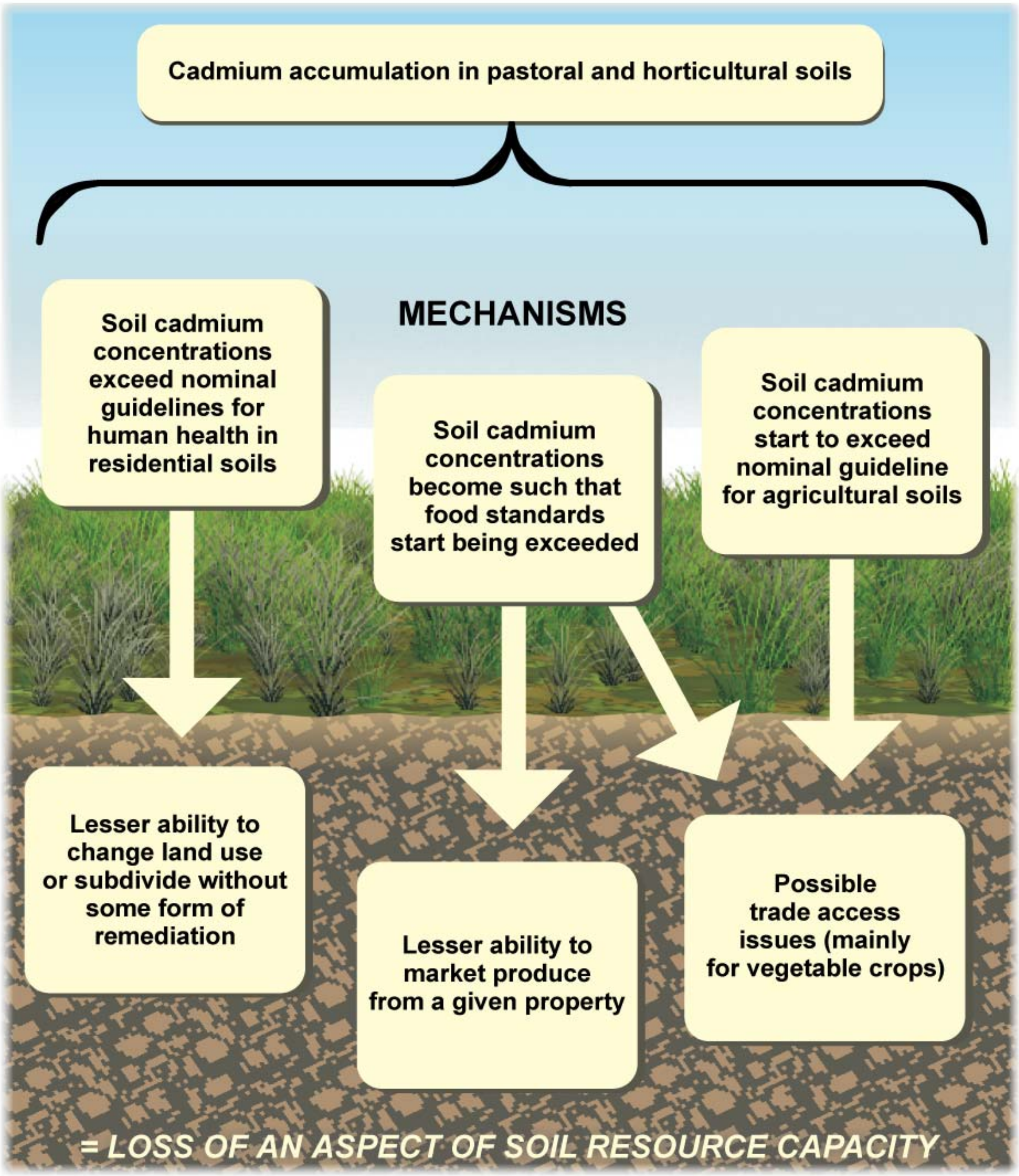

Figure 1 Mechanisms by which contaminant accumulation in productive soils can cause loss of soil resource capacity, with cadmium as the example.

The Waikato Regional Policy Statement objective (WRPS section 3.3.8) is that the range of existing and foreseeable uses of the soil resource should not be reduced as a result of the contamination of soils.

1.3 Off-site migration

Regional councils are also responsible for ensuring lack of significant adverse effects from discharges of contaminants that may enter water, either directly or indirectly. Like soils, freshwater and marine sediments act as cumulative sinks for metals, with the main difference being that sediments tend to integrate exposure over wider regions. For persistent contaminants, the main potential issue is accumulation in sediments to levels that start to cause toxicity to aquatic organisms.

As an example, preliminary evidence gathered by Environment Waikato suggests that freshwater lake sediments in Waikato agricultural catchments are steadily accumulating zinc. Currently, zinc is used in some 369 veterinary medicines and animal remedies[15] and 35 registered pesticides.[16] Although metals are not particularly mobile, zinc is at the upper end of the metal mobility range, and some of the compounds being used are relatively soluble. Zinc accumulation in sediments from agricultural catchments is therefore not entirely unexpected.

Guidelines already exist for metal levels in sediments,[17] and in future years these will be replaced by various standards through setting of Environmental Exposure Levels (EELs) by the Environmental Risk Management Authority (ERMA), in their implementation of the Hazardous Substances and New Organisms (HSNO) Act. As the HSNO Act is progressively implemented, and Central Government policy further developed, indications are that regional councils will also take on an expanded role in management of sediment contamination within catchments, involving discharges from multiple users.

Although it seems likely that a proportion of the metals used in agriculture are finding their way to associated stream, river and lake, sediments, little is known about the rate and significance of this accumulation at present. However, such diffuse source contamination will require investigation, and may require more active management approaches in the future.

1.4 Cadmium compared with other contaminants

Urban, industrial and agricultural soils receive inputs from a wide range of chemical contaminants. The significance of such inputs depends on a number of factors. Some contaminants degrade readily, some are more persistent, and others are virtually permanent. Some contamination events are one-off, whereas others are repeated and ongoing. The nature of the soil being contaminated is also an important factor: contamination of some soils carries greater significance than contamination of others. In this respect, agricultural soils are of special value, because they underpin the New Zealand economy.

In terms of potential to cause losses of significant aspects of the soil resource (**Section 1.1**) over large areas, and proximity and permanence of the issue, the most significant contaminant in modern New Zealand agriculture appears to be the heavy metal cadmium. Cadmium accumulation in Waikato soils is the focus of this report.

2 Cadmium

2.1 Occurrence, production and use

Cadmium was discovered in 1817 by Strohmeyer in Germany, who isolated it from calamine (zinc carbonate). The name cadmium is derived from *cadmia*, the ancient Greek name for calamine.[18] Elemental cadmium is a lustrous, silvery-white metal with a bluish tinge. It is soft, malleable and easily worked. Due to its density of 8.65 g/cm^3, cadmium is classified as a heavy metal.[19] With melting and boiling points of 320.9 and 767 °C, respectively, cadmium is also considered to be a relatively volatile metal. Cadmium vapour reacts rapidly in air to form brown cadmium oxide (CdO). Cadmium dissolves in most inorganic acids but, in contrast to zinc, is insoluble in alkaline media. Cadmium halides, nitrate and sulphate are soluble whereas cadmium oxide, hydroxide, carbonate and sulphide are not.

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[15] For example, in facial eczema cures. Zinc containing medicines and animal remedies are used as antibiotics, antidotes, antifungals, anti-inflammatorys, antimicrobials, bactericides, coccidiostats, ectoparasiticides, endoparasiticides, fungicides, oral nutrient/electrolytes, parenteral nutrient/electrolytes, probiotics, and skin/coat conditioners (**Section 6.2.2**).

[16] For example, the zinc dithiocarbamate fungicides Propineb and Mancozeb. Zinc-based pesticides cover the range anti-fouling paint, bactericide, fungicide, and insecticide.

[17] ANZECC, **2000**. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*, Table 3.5.1.

[18] Nriagu JO, **1980**. Production, uses and properties of cadmium. **In** Nriagu JO (Ed.) *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.

[19] This designation is applied to metals of densities greater than 5 g/cm^3.

Geochemically, cadmium is associated with minerals of zinc, lead and copper. Association of cadmium with these metals has significance when estimating total inputs of cadmium from all sources, and these associations are explored where applicable as part of this report. Six cadmium minerals have been discovered: greenockite and hawleyite (the hexagonal and cubic forms of cadmium sulphide); otavite (cadmium carbonate); monteponite (cadmium oxide); cadmoselite (hexagonal cadmium selenide); and saukovite (cubic cadmium metacinnabar).[20] However, none of these deposits are of sufficient size to warrant commercial extraction of cadmium.[21]

Cadmium and its compounds are intentionally used in a number of industries, and a summary of these uses is provided in **Appendix 1**. World production of cadmium stands at approximately 17000 t/yr. Approximately nine-tenths of the cadmium utilised by industry is in the first four categories listed in **Appendix 1**: coating and plating, battery production, pigments and stabilizers.[22] Almost all cadmium produced commercially is recovered as a by-product during the smelting of zinc ores, in which it is a minor (about 0.2%) isomorphic component.[23] Small additional amounts of cadmium are recovered during the processing of zinc-lead, zinc-copper and complex ores.

Cadmium and its salts are non-essential and toxic to humans, animals and plants.[23,24,25] In natural soils, cadmium toxicity to plants (phytotoxicity) is rare because zinc toxicity intervenes before it can develop.[26]

Presence of cadmium in the wider environment is brought about both by natural and man-made (anthropogenic) means. Natural production and cycling of cadmium gives rise to an ubiquitous background level, which varies depending on local geological features. For example, sedimentary rocks, and soils derived from them, tend to have higher concentrations of cadmium than other rock and soil types.[27]

The mean natural concentration of cadmium in the earth's crust is estimated to be 0.15 mg/kg (150 µg/kg).[28] Other background estimates for the metal are: air[29,30] 0.01–1.0 ng/m^3; freshwater[31,32] 0.01–0.07 µg/L; seawater[28,33] 0.001–0.075 µg/L; rainwater[28] 0.0001–0.001 µg/L; and Antarctic ice[34] about 0.0001–0.0002 µg/kg.

It is onto this natural background level that any cadmium dispersed by anthropogenic means is added. Cadmium liberated to the atmosphere serves to illustrate this idea. Natural sources of cadmium to the atmosphere include forest fires, volcanoes, sea-salt

20 Bewers JM, Barry PJ and MacGregor DJ, **1987**. Distribution and cycling of cadmium in the environment. *Adv. Env. Sci. Tech.* Vol. 19, pp 1-18.

21 Schulte-Schrepping KH and Piscator M, **1985**. Cadmium and cadmium compounds. **In** Gerhartz W.(Ed.) *Ullman's Encyclopedia of Industrial Chemistry Vol. A4, 5th edn.* Verlagsgesellschaft mbH (VCH), Federal Republic of Germany.

22 Plunkert P, **1988**. Cadmium. **In** *Minerals Yearbook 1988 Vol.I; metals and minerals.* U.S. Department of the Interior, U.S. Govt. Printing Office, U.S.A.

23 Förstner U, **1980**. Cadmium. **In** Hutzinger O.(Ed.) *The handbook of environmental chemistry, Vol. 3, part A; anthropogenic compounds.* Springer-Verlag, New York.

24 Venugopal B and Luckey TD, **1978**. *Metal toxicity in mammals 2. Chemical toxicity of metals and metalloids.* Plenum Press, New York.

25 Kabata-Pendias A and Pendias H, **2001**. *Trace elements in soils and plants (3rd Ed.)* CRC Press, USA.

26 Chaney R, **2005**. US Department of Agriculture–Agricultural Research Service. Personal communication: response to review comment.

27 Gong H, Rose AW and Suhr NH, **1977**. The geochemistry of cadmium in some sedimentary rocks. *Geochim. Cosmochim. Acta* Vol. 41, pp 1687-1692.

28 CRC Handbook of Chemistry and Physics, 80tth Edition, **1999-2000**. 14-14. CRC Press.

29 Nriagu JO, 1980. Production, uses and properties of cadmium. **In** Nriagu JO (Ed.) *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.

30 Bewers JM, Barry PJ and MacGregor DJ, **1987**. Distribution and cycling of cadmium in the environment. *Adv. Env. Sci. Tech.* Vol. 19, pp 1-18.

31 Ahlers WW and Hunter KA, **1988**. Mass transport and natural distribution of some trace metals in the Manuherika River, Central Otago. **In** Trace elements in New Zealand: environmental, human and animal**.** *Proc. N.Z. Trace Element Group Conf.* 30 Nov.–2 Dec. 1988, Lincoln College, Canterbury. pp 37-46.

32 Förstner U, **1980**. Cadmium. **In** Hutzinger O.(Ed.) *The handbook of environmental chemistry, Vol. 3, Part A; Anthropogenic compounds.* Springer-Verlag, New York.

33 Hunter KA and Ho FWT, **1984**. Copper, nickel and cadmium in ocean waters. *Proc. of the Conf. of the N.Z. Trace Element Group* 7-8 Aug. 1984, Massey University, Palmerston North, pp 35-43.

34 Batifol F, Boutron C, and de Angelis M, **1989**. Changes in copper, zinc and cadmium concentration in Antarctic ice during the past 40 000 years. *Nature* Vol. 337, No. 9, pp 544-546.

spray, wind-borne soil particles, the sloughing of vegetation and possibly the degassing of crustal rocks.[35] Predominant anthropogenic sources to the atmosphere are non-ferrous metal production, waste incineration and fertiliser manufacture.[36] Globally, cadmium emissions to the atmosphere from anthropogenic sources now exceed those from natural sources by a factor of five.[35,36] After about one week, 70% of the cadmium released to the atmosphere during a given day is re-deposited on the land and the other 30% falls on the oceans.[37] Since cadmium settles on the land at a faster rate than natural or anthropogenic processes remove it, a net accumulation of the metal occurs in soil. This accumulation through atmospheric deposition is naturally the greatest in those parts of the world that have seen the highest density of industrialisation. For example, analysis of an archived soil collection in Britain revealed that the soil burden of cadmium attributable to atmospheric deposition alone had increased by between 27 and 55% since the year 1850.[38]

However, agricultural soils appear to be receiving significantly more cadmium than other soil types. Here the primary source is not the atmosphere, but cadmium impurities in specific soil treatments applied to productive land, in particular phosphate fertilisers and sewage sludges. Both of these can contain appreciable quantities of cadmium.[39,40,41] The enhanced accumulation of cadmium in agricultural soil has been identified as a legitimate cause for concern. Of all the common heavy metals, it is cadmium which shows the greatest tendency to accumulate in food plants under usual soil conditions, and so enter the food chain.[42] In New Zealand, where industrial inputs to soils are minimal[43] and application of biosolids to land have so far been limited, the main source of anthropogenic cadmium to agricultural soils is phosphate fertilisers. Sources of cadmium to New Zealand agricultural soil are further explored in **Section 3.2**, and quantified in **Section 6**.

2.2 Human exposure in general

2.2.1 Exposure routes

The two principal means by which cadmium is absorbed into the human body are ingestion and inhalation (eating and breathing).[44,45] It has been estimated that between 25 and 50% of inhaled cadmium is absorbed by the lungs whereas only about 6% of ingested cadmium is absorbed by the gastrointestinal tract.

Despite this, food accounts for over 90% of the individual body burden of cadmium in an 'uncontaminated' population, as the levels of cadmium in food are normally far higher than those ordinarily prevalent in ambient air. Air and drinking water supply an estimated 4–7% and 2–4%, respectively, of the average daily intake.[46,47] Non-food

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35 Nriagu JO, **1989**. A global assessment of natural sources of atmospheric trace metals. *Nature* Vol. 338, No. 6210, pp 48-49.

36 Nriagu JO and Pacyna JM, **1988**. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* Vol. 333, No. 6169, pp 134-139.

37 Nriagu JO, **1980**. Global cadmium cycle. **In** Nriagu J.O.(Ed.) *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.

38 Jones KC and Symon CJ, **1987**. Retrospective analysis of an archived soil collection II. Cadmium. *Sci. Total Env.* Vol. 67, pp 75-89.

39 Rothbaum HP, Goguel RL, Johnston AE and Mattingly GEG, **1986**. Cadmium accumulation in soils from long-continued applications of superphosphate. *J. Soil Sci.* Vol. 37, No. 1, pp 99-107.

40 Brown KW, Thomas JC and Slowey JF, **1983**. The movement of metals applied to soils in sewage effluent. *Water Air Soil Poll.* Vol. 19, pp 43-54.

41 Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of arsenic, cadmium, copper, lead and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol. 47, pp 23-32.

42 Sherlock JC and Smart GA, **1986**. Cadmium in soil and the diet. *Trace Subst. Env. Health* Vol. 20, pp 401-412.

43 Gray CW, McLaren RG and Roberts AHC, **2003**. Atmospheric accessions of heavy metals to some New Zealand pastoral soils. *Science of the Total Environment*, Vol. 305, pp 105-115.

44 Dermal absorption is insignificant for cadmium, due to its apparent capacity to bind to epidermal keratin. Guy RH, Hostynek JJ, Hinz RS and Lorence CR (Eds.) **1999**. *Metals and the skin: topical effects and systemic absorption.* Marcel Dekker, Inc., New York.

45 Förstner U, **1980**. Cadmium. **In** Hutzinger O (Ed.) *The handbook of environmental chemistry, Vol. 3, Part A; Anthropogenic compounds.* Springer-Verlag, New York.

46 Yasumura S, Vartsky D, Ellis KJ and Cohn SH, **1980**. Cadmium in human beings. **In** *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.

contributions in the New Zealand general population may be even lower than this. In a study in Christchurch,[48] food was found to account for 99.75% of the daily cadmium intake of the general non-smoking (and non-occupationally exposed) population, whereas air only contributed 0.25% of total exposure. For young children, a small amount of additional cadmium may also be attributable to ingestion of household dust, which can be moderately elevated in cadmium. This is quantified in **Appendix 2**.

An exception exists in the case of smokers, due both to the ability of the tobacco plant to accumulate cadmium from the soil and to the fact that a large part of the inhaled dose is absorbed.[49] Kidneys of smokers generally contain twice as much cadmium as those of non-smokers; indicating that in smokers, the intake of cadmium from cigarettes can equal or exceed the intake from food.[50]

In cases of occupational cadmium poisoning, inhalation is usually the main intake route responsible. This relates to the fact that the lungs are more efficient than the gastrointestinal tract at cadmium absorption, so that when concentrations in air do become elevated, absorption is rapid. Many cases of acute cadmium poisoning involve heating of cadmium containing welding rods or alloys in confined areas (**Appendix 1**); under these conditions, cadmium concentrations in air can quickly become elevated due to the metal's high volatility (**Section 2.1**).

2.2.2 Accumulation in the body

No homeostatic mechanism has been located by which the amount of cadmium in the human body may be regulated.[51] For this reason, the amount of cadmium in a person increases with that person's age, from an estimated 1 µg at birth to between 15000 and 80000 µg in the 50 year old (not occupationally or environmentally exposed to a significant degree) depending on geographic locality and personal history.[51] The mean residence time of cadmium in humans has been calculated to lie somewhere between 20 and 40 years.[52]
Of the cadmium absorbed by the body, 47% is sequestered in the liver and the cortex of the kidneys. Another 3% of the body burden is shared between the lungs and pancreas. The remaining 50% ends up more or less evenly distributed among the other tissues.[53,54]

2.3 Human toxicity

2.3.1 Chronic and acute poisoning

In general terms, non-essential heavy metals act as systemic poisons. *Acute* poisoning is that which occurs *via* exposure to a high concentration of a given metal over a relatively short time period. Cadmium is regarded as a highly toxic metal. The lethal dose to humans has been estimated to be only 0.35–9 g by ingestion and 1900 min.mg/m^3 (*e.g.* 190 mg/m^3 for 10 min) by inhalation.[53] Death occurs 24 hr to 2 weeks later. According to Yasumura *et al.* (1980)[53] *'In a large number of cases it is the naïve, careless, or untrained worker who is at greatest risk of acute poisoning.'*

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47 Fleisher M, Sarofim AF, Fassett DW, Hammond P, Shacklette HT, Nisbet ICT, and Epstein S, **1974**. Environmental impact of cadmium: a review by the panel on hazardous trace substances. *Env. Health Persp.* May 1974, pp 253-323.

48 Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury.

49 Brooks RR and Trow JM, **1979**. Lead and cadmium content of some New Zealand and overseas cigarettes. *N. Z. J. Sci.* Vol. 22, pp 289-291.

50 Schulte-Schrepping KH and Piscator M, **1985**. Cadmium and cadmium compounds. **In** Gerhartz W (Ed.) *Ullman's Encyclopedia of Industrial Chemistry Vol. A4, 5th edn.* Verlagsgesellschaft mbH (VCH), Federal Republic of Germany.

51 Venugopal B and Luckey TD, **1978**. *Metal toxicity in mammals 2. Chemical toxicity of metals and metalloids.* Plenum Press, New York.

52 Nriagu JO, **1980**. Global cadmium cycle. **In** Nriagu JO (Ed.) *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.

53 Yasumura S, Vartsky D, Ellis KJ and Cohn SH, **1980**. Cadmium in human beings. **In** *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.

54 Ivengar GV, Kollmer WE and Bowen HJM, **1978**. *The elemental composition of human tissues and body fluids.* Verlag Chemie GmbH, Weinheim, West Germany.

Chronic poisoning, by contrast, occurs as a result of exposure to a low concentration over an extended time period. There is more than one mechanism by which chronic toxicity can come about.

- Cadmium and lead have long residence-times in the body, and therefore accumulate with age and exposure. In the case of cumulative metals, overt organ damage will always occur once tissue concentrations pass certain thresholds. To date, in most members of the general population, these thresholds are never reached, before death from other causes intervenes.

- At lower levels, in its systemic action, cadmium can interfere with ordinary biochemical reactions across the whole organism. Like lead and mercury, cadmium has a particular binding affinity for functional groups across a range of biomolecules, and will inhibit the function of a wide range of proteins and enzymes, as well as nucleic acids. For example, recently it has been shown[55] that *in vitro*, cadmium inhibits the ability of the DNA molecule to repair itself. Intra-cellular ligands to which cadmium has a strong affinity include carboxyl, cysteinyl, hydroxyl, hystidyl, phosphatyl and sulphydryl groups. Enzymes containing these groups are inhibited by cadmium.[56] As pathways by which more serious illnesses may develop (depending on the body's ability to cope), such chronic mechanisms are better described by increased risk probabilities rather than thresholds. Cadmium is now classified[57] as a known human carcinogen (based on inhaled cadmium), and has also been confirmed as being strongly estrogenic.[58]

2.3.2 Effects and symptoms of cadmium poisoning

Effects and symptoms of cadmium poisoning are summarised in **Appendix 3**, and a full toxicological profile on cadmium is available from the US Agency for Toxic Substances and Disease Registry (ASTDR).[59] A summary of notable cases of acute and chronic cadmium poisoning in New Zealand and elsewhere is given in **Appendix 4**.

Effects of chronic cadmium toxicity cover a spectrum ranging all the way from molecular disruption (a small-scale sub-clinical effect) through cellular damage and organ damage, to death (large-scale effect).[60] Within this chronic progression, it is important to note that clinical symptoms of cadmium poisoning only become apparent when poisoning is already quite advanced, by the point that organs have been damaged. Unfortunately, reversal of toxicity is usually not possible at this stage. Under normal circumstances, none of the overt clinical effects would be expected to occur as a result of dietary cadmium, and food standards have been designed to prevent such outcomes from occurring.

The most common effects of cadmium poisoning are kidney damage, cirrhosis of the liver and lung disease (**Appendices 3** and **4**). Cadmium acts as a specific inducer of metallothionein, a small sulphydryl-rich and low molecular weight protein synthesised in the liver and kidneys. The resultant cadmium-thionein complex serves the purpose of temporarily inhibiting cadmium's toxic activity. Once the amount of metallothionein available is insufficient to complex all the cadmium, the toxicity of the metal is felt.[61,62]

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55 Jin YH, Clark AB, Slebos RJC, Al-Refai H, Taylor JA, Kunkel TA, Resnick MA and Gordenin DA, **2003**. Cadmium is a mutagen that acts by inhibiting mismatch repair. *Nature Genetics*, Vol. 34, No. 3, pp 326-329.

56 Berman E, **1980**. *Toxic metals and their analysis.* Heyden and Son Ltd., Great Britain.

57 U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, December **2002**. *Report on Carcinogens, Tenth Edition*: http://ehp.niehs.nih.gov/roc/toc10.html

58 Johnson MD, Kenney N, Stoica A, Hilakivi-Clarke L, Singh B, Chepko G, Clarke R, Sholler PF, Lirio AA, Foss C, Reiter R, Trock B, Paik S and Martin M, **2003**. Cadmium mimics the in vivo effects of estrogen in the uterus and mammary gland. *Nature Medicine*, Vol. 9, No. 8, pp 1081-1084.

59 Agency for Toxic Substances and Disease Registry: http://www.atsdr.cdc.gov/toxprofiles/tp5.html

60 Piotrowski JK and Coleman DO, **1980**. *Environmental hazards of heavy metals: summary evaluation of lead, cadmium and mercury. A general report.* Monitoring and Assessment Research Centre (MARC), University of London.

61 Mason R, **1984**. Function and behaviour of metallothionein in the absorption and distribution of trace elements in the neonate. **In** *Trace elements in the eighties. Proc. of the Conf. of the N.Z. Trace Element Group*, 7-8 Aug., Massey University, Palmerston North, pp 75-77.

In other words, a threshold level of cadmium must be exceeded before serious renal or hepatic damage begins (probable kidney value: 200 mg/kg).[60] Unfortunately, by the time that the symptoms of renal damage manifest, the kidneys have already been irreversibly damaged. In addition to this, the small amount of cadmium that is eliminated from the body must leave *via* the kidneys, further damaging them.

Acute oral cadmium intoxication has frequently been (initially) misdiagnosed. This is largely because the symptoms are similar to those caused by microbial food poisoning, although physicians' awareness has also been questioned.[63] It is also worth noting that many of the chronic effects listed in **Appendix 3** are not observed in acute cases because the subject dies before the effects have time to develop.

At the cellular level, dissolved cadmium (Cd^{2+}_{aq}) competes with calcium, copper, iron and zinc for binding sites.[64] It follows that absorption of excess cadmium can cause symptoms reminiscent of dietary deficiencies of these metals.[65] Conversely, dietary intakes of calcium, copper, selenium, zinc, ascorbic acid and/or vitamin D which exceed bodily requirements can ameliorate some effects of cadmium poisoning.[66,67] The absorption of cadmium by the body and its subsequent toxicity also depend to some extent on its speciation (exact chemical form).[68] For example, orally administered cadmium-thionein is not absorbed by rats to the same extent as cadmium chloride.[69]

Recently, it has been confirmed that cadmium is strongly estrogenic. Cadmium bears no structural similarity to human estrogen, but nonetheless acts like steroidal estrogens in breast cancer cells as a result of its ability to form a high-affinity complex with the hormone binding domain of the estrogen receptor.[70]

2.3.3 Potential effects of ordinary dietary cadmium

There are currently two opposing scientific opinions on the possible links between low level dietary cadmium and adverse health effects in the general population. One view argues that low level cadmium is likely to be detrimental to human health, based on biochemical considerations which include (but is not limited to) use of biomarkers of renal dysfunction. The other view argues that risks of cadmium in food are overstated for Western societies because they are based on a rice diet model, and do not take into account interactions between dietary cadmium and other trace elements in the Western diet such as zinc, iron and selenium.[71] In the latter respect it is worth noting that New Zealand intakes of zinc and selenium are actually marginal and deficient, respectively.[72]

Such differences will be resolved as more information becomes available, because potential adverse effects of low level cadmium exposure are an area of active research. For example, the recent discovery of cadmium's estrogenicity has generated renewed scientific interest in examining the role of dietary cadmium in the hormone-related

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62 Förstner U, **1980**. Cadmium. **In** Hutzinger O (Ed.) *The handbook of environmental chemistry, Vol. 3, Part A; Anthropogenic compounds.* Springer-Verlag, New York.

63 Berman E, **1980**. *Toxic metals and their analysis.* Heyden and Son Ltd., Great Britain.

64 Venugopal B and Luckey TD, **1978**. *Metal toxicity in mammals 2. Chemical toxicity of metals and metalloids.* Plenum Press, New York.

65 Yasumura S, Vartsky D, Ellis KJ and Cohn SH, **1980**. Cadmium in human beings. **In** *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.

66 Spivey-Fox MR, **1988**. Nutritional factors that may influence bioavailability of cadmium. *J. Env. Qual.* Vol. 17, No. 2, pp 175-180.

67 Sugawara N, Hirohata Y and Sugawara C, **1989**. Testicular dysfunction induced by cadmium and its improvement caused by selenium in the mouse. *J.Env. Pathol. Toxicol. Oncol.* Vol. 9, No. 1, pp 53-64.

68 Olidges H, Hochrainer D and Glaser U, **1989**. Long term inhalation study with Wistar rats and four cadmium compounds. *Toxicol. Env. Chem.* Vol. 19, No. 3-4, pp 217-222.

69 Klassen CD, Lehman LD and Maitani T, **1986**. Effect of dosage and form of cadmium on its adsorption and distribution. *Trace Subst. Env. Health* Vol. 20, pp 113-121.

70 Johnson MD, Kenney N, Stoica A, Hilakivi-Clarke L, Singh B, Chepko G, Clarke R, Sholler PF, Lirio AA, Foss C, Reiter R, Trock B, Paik S and Martin M, **2003**. Cadmium mimics the *in vivo* effects of estrogen in the uterus and mammary gland. *Nature Medicine*, Vol. 9, No. 8, pp 1081-1084.

71 McLaughlin M, **2005**. Centre for Environmental Contaminants Research CSIRO Land and Water. Personal communication: response to review comment.

72 Vannoort R, Cressey P and Silvers K, **2000**. 1997/98 *New Zealand Total Diet Survey Part 2 : Elements. Selected Contaminants & Nutrients.* ESR Client Report FW 99/47.

cancers that show a high incidence in Western populations (*e.g.* breast and testicular cancers).[73] Some recent New Zealand work in this area is currently *in press*.[74,75]

2.4 Dietary intakes in New Zealand and Australia

2.4.1 Tolerable intakes and food standards

As noted above (**Section 2.2.1**), food accounts for most cadmium exposure experienced by members of the general population. The current provisional tolerable weekly intake (PTWI) for cadmium recommended by JECFA (the Joint FAO/WHO Expert Committee on Food Additives) is 7 µg/kg body weight/week.[76] This limit defines tolerable risk, is essentially based around the need to ensure that cadmium does not accumulate to toxic levels in members of the general population over an extended period (see **Appendix 4**), while leaving a suitable margin for error.

- It is interesting to note that the previous New Zealand standard for cadmium in most food[77] (1 mg/kg) would have enabled the onset of chronic cadmium poisoning in some individuals, had most foods contained cadmium anywhere near this figure. 1 mg/kg was the mean concentration of cadmium in rice in the *itai itai* case (**Appendix 4**). Under the previous regime, genuine protection relied in the fact that most foods contained cadmium at levels well below 1 mg/kg.

The adopted PWTI defines New Zealand's level of tolerable risk for cadmium in food. Food standards are better considered as a regulatory compliance tool, and do not define risk in their own right. However, in the case of cadmium the two measures closely relate to each other. Current standards for cadmium (usually 0.1 mg/kg) in New Zealand food are in line with the international PTWI, in the sense that substitution of the relevant food standard in to known intakes of each food group results in a hypothetical daily intake commensurate with the PWTI.[78]

2.4.2 Results of food surveys

At least nine official and non-official surveys have been carried out over the years in which at least one of the objectives was to assess cadmium intakes of New Zealanders. These are as follows:

- 1977 Guthrie and Robinson, Dunedin (University of Otago)[79]
- 1978 Dick *et al* (DSIR)[80]
- 1982 New Zealand Total Diet Survey (commissioned by the Ministry of Health)[81]
- 1987/88 New Zealand Total Diet Survey (commissioned by the Ministry of Health)[82]

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73 Johnson MD, Kenney N, Stoica A, Hilakivi-Clarke L, Singh B, Chepko G, Clarke R, Sholler PF, Lirio AA, Foss C, Reiter R, Trock B, Paik S and Martin M, **2003**. Cadmium mimics the in vivo effects of estrogen in the uterus and mammary gland. *Nature Medicine*, Vol. 9, No. 8, pp 1081-1084.

74 Gray MA, Centeno J and Harris A (In Press). Cadmium, zinc, selenium and prostate cancer. In Moore T, Black A, Centeno J, Harding J and Trumm D (Eds.) *Metal contaminants in New Zealand: Sources and Effects on Health and Ecology*. Resolutionz Press, Christchurch.

75 Gray MA, Delahunt B, Fowles JR, Weinstein P, Cooke RR and Nacey JN (In Press). Demographic and clinical parameters as determinands of levels of total prostate specific antigen and its derivatives. *Anticancer Research*.

76 Vannoort R, Cressey P and Silvers K, **2000**. 1997/98 *New Zealand Total Diet Survey Part 2 : Elements. Selected Contaminants & Nutrients.* ESR Client Report FW 99/47.

77 New Zealand Food Regulations, **1984**.

78 Food standards are: cereal based products 0.1 mg/kg, meats 0.05 mg/kg and vegetables 0.1 mg/kg. Intake rates are: cereal based products 0.208 kg/day, meat, poultry, fish and eggs 0.225 kg/day, and vegetables 0.377 kg/day. With other food groups, the hypothetical intake reaches µg/kg body weight/week, or 107% of the PWTI.

79 Guthrie BE and Robinson MF, **1977**. Daily intakes of manganese, copper, zinc and cadmium by New Zealand women. *Br. J. Nutr.* Vol. 38, pp 55-63; Guthrie BE and Robinson MF, **1978**. The nutritional status of New Zealanders with respect to manganese, copper, zinc and cadmium—a review. *N.Z. Med. J.* Vol. 87, No. 603, pp 3-8.

80 Dick GL, Hughes JT, Mitchell JW and Davidson F, **1978**. Survey of trace elements and pesticide residues in the New Zealand diet I. Trace element content. *N.Z.J. Sci.* Vol. 21, No. 1, pp 57-69.

81 Pickston L, Brewerton HV, Drysdale JM, Hughes JT, Smith JM, Love JL, Sutcliffe ER and Davidson F, **1985**. The New Zealand diet: a survey of elements, pesticides, colours and preservatives. *N.Z.J. Tech.* Vol. 1, No. 2, pp 81-89.

- 1989 Kim, Christchurch (University of Canterbury)[83]

- 1990/91 New Zealand Total Diet Survey (commissioned by the Ministry of Health)[84]

- 1997/98 New Zealand Total Diet Survey (commissioned by the Ministry of Health)[85]

- 2000 Timilsina, Hamilton (University of Waikato)[86]

- 2003/04 New Zealand Total Diet Survey (commissioned by the New Zealand Food Safety Authority)[87]

The latest of these, commissioned by the New Zealand Food Safety Authority, is underway at time of writing, with analytical results having been released [e.g.88] The current provisional tolerable weekly intake (PTWI) for cadmium is 7 µg/kg body weight/week.[89] Estimates of average intakes in 'young male' New Zealanders[90] are listed in **Table 1**. These figures represent intakes in the absence of shellfish consumption, which can augment estimates significantly due to high levels of cadmium in oysters.

Table 1 Dietary intake estimates for cadmium in young male New Zealanders.

Date	Estimated dietary cadmium intake[89] µg/kg body weight/week	Instrumental method
1977	(2.1)[a]	Flame AAS
1978	1.1	Flame AAS
1982	3.3	Flame AAS
1987/88	4.0	Flame AAS
1989	2.0	Graphite Furnace AAS
1990/91	2.3	ICP-MS
1997/98	1.7	ICP-MS
2000	2.5	ICP-OES
2003/04	not yet available	ICP-MS
Geometric Mean[b]	**2.2**	

[a] Adjustment for young male intakes is not possible from this report, as food weights were reported on a dry weight basis.

[b] Geometric mean used to dampen effects of high and low estimates, discussed in **Section 2.5.3** (value stays the same with or without Guthrie and Robinson's 1977 estimate.)

[82] ESR (Institute of Environmental Science and Research Ltd) / Ministry of Health, **1994**. *The 1987/88 New Zealand Total Diet Survey.* Wellington.

[83] Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury, Ch. 6.

[84] Vannoort RW, Hannah ML, Pickston L, Fry JM., **1995**. 1990/91 *New Zealand Total Diet Survey, Part 2 : Contaminant Elements*. ESR Client Report FW 95/7.

[85] Vannoort R, Cressey P, Silvers K, **2000**. 1997/98 *New Zealand Total Diet Survey Part 2 : Elements. Selected Contaminants & Nutrients.* ESR Client Report FW 99/47.

[86] Timilsina A, **2001**. *Assessment of trace element exposure from cosmetics and herbal supplements in relation to exposure from food.* MSc thesis in Chemistry, University of Waikato.

[87] New Zealand Food Safety Authority, **2004**. 2003/04 New Zealand Total Diet Survey: http://www.nzfsa.govt.nz/science-technology/research-projects/total-diet-survey/

[88] Shaw IW, Vannoort RW, Thomson BM, **2003**. 2003/04 *New Zealand Total Diet Survey Analytical Results – Q1.* ESR Client Report FW 03/77.

[89] Vannoort R, Cressey P, Silvers K, **2000**. 1997/98 *New Zealand Total Diet Survey Part 2 : Elements. Selected Contaminants & Nutrients.* ESR Client Report FW 99/47.

[90] By NZTDS convention, a young male is defined as 19-24 years of age, weighing 70 kg, and ingesting 11.5 MJ/day. Figures have been adjusted to reflect these assumptions.

Key findings of recent food surveys in both New Zealand and Australia are as follows:

1. Of all contaminant elements in the diet, cadmium is the one closest to its provisional tolerable weekly intake (PTWI). The same is the case in Australia.

   - The geometric mean of all survey listed is 2.2 µg/kg body weight/week (**Table 1**). The arithmetic mean of the most recent four surveys is very similar, at 2.1 µg/kg body weight/week. Average cadmium intakes (in young men) are therefore about 30% of the PTWI. For adult males and females, and vegetarian females, estimates are 18%, 16% and 25% of the PTWI, respectively.[89] As a point of comparison, for the heavy metal lead, intakes over these groups are only 4% to 6% of the PTWI.[89]

   - In children and young children, cadmium intakes are proportionately higher than this. In the 1997/98 total diet survey, these were estimated as 43% and 46% of the PTWI, respectively.[89] However, there is some question over whether such comparisons for young children should be made, because the PWTI is averaged over a 50 year exposure period.[91]

   - Both of these estimates are actually averages, based on 50th percentile food (energy) consumption patterns. Recommended international practice is moving toward protection of the majority of the population, represented by 95th percentile energy intakes. As noted by Vannoort *et al.*,[89] a rule of thumb is that the upper bounds of these will be about three times the population average. It is therefore probable that about one in twenty (5% of) New Zealanders already ingest cadmium near at somewhere near four-fifths (80%) of the PTWI.

2. Intakes of cadmium in New Zealand and Australia appear to be higher than those in a number of other countries. New Zealand and Australia were second and third highest cadmium intakes of seven countries for which comparisons could be made.[92] This could be partly due to historic use by both countries of phosphate fertilisers from Nauru which were very high in cadmium, but may actually relate more strongly to the natural acidity of New Zealand and Australian soils (**Section 3.5** and **Appendix 6**). Crop uptake of cadmium is markedly greater in more acidic soils (see for example, **Figure 6**).

3. In general, cereals and vegetables contribute the most to total dietary cadmium. This has relevance to the current and future status of cadmium in horticultural and arable soils (**Sections 5** and **6**). After oysters—consumption of which is idiosyncratic—potatoes, breads, silverbeet and carrots are foods which make the greatest individual contributions to dietary cadmium intakes in adults.

On the basis of these findings, Recommendation 7 of the 1997/98 NZTDS report[92] was as follows:

'Given the estimated dietary exposure to cadmium for the six age-sex groups of the 1997/98 NZTDS, that there is only a relatively small safety margin between exposure in the normal diet and exposure that produces harmful effects, it is imperative that dietary cadmium continue to be monitored on an on-going basis in future NZTDSs.'

At present, internationally recognised PTWI gives adequate margins for 50 years of exposure of the renal cortex.[92] The present PWTI does not take into account cadmium's recently discovered ability to disrupt mammalian hormonal signalling at serum levels concomitant with dietary exposures (**Section 2.4**). It is therefore possible that the internationally endorsed PTWI, with which food standards are consistent, may drop further in the future. It is not likely to increase.

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91 Chaney R, **2005**. US Department of Agriculture–Agricultural Research Service. Personal communication: response to review comment.

92 Vannoort R, Cressey P, Silvers K, **2000**. 1997/98 *New Zealand Total Diet Survey Part 2 : Elements. Selected Contaminants & Nutrients.* ESR Client Report FW 99/47.

2.4.3 Trends over time

Given the loadings of cadmium to New Zealand's agricultural soils over the last 65 years (**Sections 5** and **6**), the high acidity of these soils (**Section 3.5**), and our experience with other dietary trace contaminants such as lead,[92] it is probable that cadmium intakes in the New Zealand diet have been increasing over the decades.

However, there is not yet any firm evidence for (or against) this from direct analysis of foods—no particular trend over time in dietary cadmium intakes is apparent from the data in **Table 1**.

This is not particularly surprising given the amount of sampling and analytical uncertainty that would be expected, particularly in the earlier surveys.

1. Analytical instrumental methods in use up to and including the 1987/88 food survey may have been insufficiently sensitive to allow precise estimates of dietary cadmium intakes (although some come close to current estimates fortuitously). This is because cadmium is a minor trace element, and levels in food digests are such that measurements were being carried out at the lowest end of the detection range for Flame Atomic Absorption Spectroscopy (FAAS).
   - Cadmium was not actually detected in the majority of foods in at least one of the earlier studies, that of Dick *et al.*[93] The apparently low cadmium intake estimate reported from this study is likely to partly come about as a result of the authors selecting to set 'non-detect' values to zero when estimating dietary intakes. Deciding how to treat non-detected values has always been a problem, but current and recommended practice is to use numerical values equal to half the reported detection limit.[94]
   - Part of the apparently high estimate in the 1987/88 total diet survey (relative to later estimates) is likely to be due to instrumental detection limits being about 10 times higher than those of subsequent total diet surveys.[95] Use of half the value of the FAAS detection limit will result in higher intake estimates than use of half the value of the ICP-MS, ICP-OES or GFAAS detection limits. (This is compounded by the fact that there are fewer detections in FAAS in the first place.)
   - Some apparently positive detections by FAAS are unlikely to have been genuine where complex sample matrices were involved, whether or not appropriate background correction was in place.[96]

2. Some longer term trends can also be masked by shorter term variation in eating habits with time, or assumptions made about these. Changes in eating habits were one subject of the 1997 National Nutrition Survey.[97]

3. Variation in cadmium content of cultivars for crops that account for a significant fraction of dietary cadmium (*e.g.* potatoes[98] and wheat[99]) is also expected to play some part in variation seen between some of the larger and smaller studies.

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93 Dick GL, Hughes JT, Mitchell JW and Davidson F, **1978**. Survey of trace elements and pesticide residues in the New Zealand diet I. Trace element content. *N.Z.J. Sci.* Vol. 21, No. 1, pp 57-69.

94 Vannoort R, Cressey P, and Silvers K, **2000**. 1997/98 *New Zealand Total Diet Survey Part 2 : Elements. Selected Contaminants & Nutrients.* ESR Client Report FW 99/47.

95 This was noted to be the case for lead by Vannoort *et al.* (footnote 94).

96 Where the background signal is significant, accurate subtraction of the background becomes more tenuous as the analyte signal approaches the instrumental detection limit. Under these conditions, the measured signal represents one large number (the background) subtracted from another (background plus analyte) to yield a small residual.

97 Russell D, Parnell W, Wilson N, Faed J, Ferguson E, Herbison P, Horwath C, Nye T, Reid P, Walker R, Wilson B, and Tukuitonga C, **1999**. *NZ Food: NZ People : Key results of the 1997 National Nutrition Survey, 1999*. Produced by the LINZ Activity & Health Research Unit, University of Otago for the Ministry of Health.

98 McLaughlin MJ, Williams, CMJ, McKay A, Gunton J, Jackson K, Dowling B, Kirkham R, Partington D, Smart MS and Tiller KG, **1994**. Effect of potato variety on cadmium accumulation in potato tubers. *Aust. J. Agric. Res.*, Vol. 45, pp 1483-1495.

99 Gray CW, McLaren RG and Roberts AHC, **2001**. Cadmium concentrations in some New Zealand wheat grain. *N. Z. J. Crop Hort. Sci.*, Vol. 29, pp 125-136.

Confirmation that dietary cadmium intakes are gradually increasing or remaining static will require better benchmarking of cadmium concentrations key food crops than has been attempted in the past. Acquisition of good baseline data for selected crops is the purpose of work presented in **Section 7** of this report.

2.4.4 Evidence of food standards being exceeded

The PWTI defines tolerable risk from exposure to dietary contaminants, whereas food standards are a regulatory compliance tool. However, it was noted in **Section 2.4.1** that New Zealand's current food standards are consistent with the PWTI for cadmium. With this in mind it is worth noting that in addition to cadmium's proximity to the PWTI, published evidence exists that food standards for cadmium are routinely exceeded in a small but significant proportion of crops, particularly some varieties of wheat. This evidence is reviewed in **Section 3.5.2**.

3 Soil and food

3.1 Scientific research

Scientific recognition of the cadmium problem in agriculture has resulted in a substantial amount of high quality research into accumulation and chemistry of cadmium in New Zealand agricultural soils. Most of this research (36 of 40 identified papers with an agricultural focus) has been published in the last decade, with the bulk also emanating from three regional agricultural centres: Canterbury (Lincoln), Palmerston North, and Hamilton. Key organisations have been as follows:

- *AgResearch*, Ruakura Agriculture Centre, Hamilton and NZ Pastoral Agriculture Research Institute, Palmerston North

- *HortResearch* (Environment and Risk Management Group), Palmerston North

- *Landcare Research*, Hamilton

- *Lincoln University* (Soil, Plant and Ecological Sciences Division), Canterbury

- *Massey University* (mainly the Soil and Earth Sciences Group; also the Fertiliser and Lime Research Centre), Palmerston North

- *Waikato University* (Department of Chemistry and Department of Earth Sciences), Hamilton.

Related contributions have also been made by researchers at the (former) DSIR, ESR Limited (Porirua), the Christchurch Polytechnic Institute of Technology, Otago University (Medical School), and CSIRO Soil Division (Australia). The value of this scientific research should not be under-estimated. As a general record for future reference, and to assist future researchers in not duplicating work already covered, citations of research papers relating to cadmium in New Zealand agricultural soils are provided in **Appendix 5**. Many of these are also referred to in the text.

Further recent data has become available as an adjunct to work commissioned by two regional councils and one Unitary Authority, focusing specifically on residual contaminants in horticultural soils. These reports are available from the Auckland Regional Council[100], Environment Waikato[101] and Tasman District Council.[102] This

[100] Gaw SK, **2002**. Pesticide Residues in Horticultural Soils in the Auckland Region. Auckland Regional Council Working Report No. 96.

[101] Gaw SK, **2003**. Historic pesticide residues in horticultural and grazing soils in the Waikato Region. Environment Waikato Document **835071**.

work was carried out as part of a PhD research project relating to horticultural contaminants, being undertaken at the University of Waikato (Hamilton).

A sizeable body of Australian work also exists on the same issues.

The New Zealand Fertiliser Manufacturers' Research Association Inc. (*Fert Research*) has also commissioned research in this area, particularly through AgResearch, Ruakura. Some of this has been published in the wider scientific literature (and appears in **Appendix 5**).

Fertiliser industry management initiatives designed to address the cadmium problem are outlined in **Section 4.2**.

3.2 Sources of cadmium in agricultural soils

3.2.1 Natural cadmium

The natural abundance of cadmium in the earth's crust is 0.15 mg/kg,[103] and most soils tend to contain background cadmium at about this concentration. In a national benchmark survey, the average cadmium concentrations of the topsoil (0-7.5 cm) of 86 non-farmed New Zealand sites was found to be 0.2 mg/kg.[104,105]

Most of this will be natural cadmium. ('True' background sites can actually be hard to locate, given the multiplicity of minor anthropogenic sources that can add to the natural level by such pathways as atmospheric deposition. In one study, soil from underneath old houses (built 1852-1900) and from an elevated reserve area were found to contain cadmium ranging from 0.07 to 0.16 mg/kg.[106])

Generally, natural cadmium tends to be less available for plant uptake than anthropogenic cadmium, because proportionately more of it is held inside the matrices of resistant minerals. Further comments on cadmium availability are provided in **Section 3.4**.

3.2.2 Additional cadmium

In New Zealand, phosphate fertilisers are regarded as the dominant source of anthropogenic cadmium on farmed land, and the main reason for accumulation of this metal. This is because:

- Phosphate fertilisers contain relatively high concentrations of cadmium;[107]
- Loading estimates match observed soil enrichments;[108]
- The cadmium and phosphorus contents of farmed soil are strongly correlated with each other;[109]
- Other sources that can be significant overseas are relatively minor in New Zealand.

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102 Gaw SK, **2003**. Historic pesticide residues in horticultural and grazing soils in the Tasman District. Tasman District Council.
103 CRC Handbook of Chemistry and Physics, 80th Edition, **1999-2000**. 14-14. CRC Press.
104 Roberts AHC, Longhurst RD and Brown MW, **1994**. Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research*, Vol. 37, No. 1, pp 119-29.
105 Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.
106 Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury, Ch. 3.
107 Syers JK, MacKay AD, Brown MW and Currie LD, **1986**. Chemical and physical characteristics of phosphate rock materials of varying reactivity. *J. of the Sci. of Food and Agriculture* Vol. 37, No. 11, pp 1057-1064.
108 Taylor MD, **1997**. Accumulation of cadmium derived from fertilisers in New Zealand soils. *Science of the Total Environment*, Vol. 208, No. 1,2, pp 123-126.
109 Roberts AHC, Longhurst RD, Brown MW, **1997**. Cadmium accumulation in New Zealand pastoral agriculture. *Biogeochemistry of Trace Metals*, pp 1-41. Science Reviews, Northwood, UK.

Cadmium is enriched in phosphate fertilisers throughout the world; however, New Zealand, Australia and the United Kingdom got off to a particularly bad start compared with other countries due to historic use of phosphate rock from Nauru, that contained up to 100 mg/kg cadmium. This was not appreciated until the mid 1970s. In 1973 Williams and David, two Australian researchers, found high concentrations of cadmium in Australian phosphate fertilisers. Superphosphate, of the type commonly used for aerial top-dressing in New Zealand, contained 38–48 mg/kg cadmium, generating some concern.[110,111]
Syers *et al.*[112] characterized ten types of phosphate rock, and found concentrations which ranged from 2 mg/kg in Chatham Island phosphorite to 100 mg/kg in Nauru Island phosphate rock. By 1986 the latter variety constituted 40% of the phosphate rock used for fertiliser manufacture in New Zealand and Australia.

Use of superphosphate in New Zealand began in 1867 but did not become widespread until after WWI.[113] Top-dressing (not aerial) became widespread in the inter-war period, and by 1939, nearly a quarter of the pastures were being top-dressed annually. In 1938, superphosphate fertiliser usage was estimated at approximately 400,000 tonnes per annum.[114] Aerial top-dressing started in earnest after 1949, enabled by a surplus of aircraft and pilots from WWII (1939-45). More recently, fertiliser use was recorded as part of the last Agricultural Census carried out by *Statistics New Zealand*. Total use of phosphate fertilisers in New Zealand in 2002 was estimated at 1,232,196 t/yr, with 17.3% of New Zealand's total use being in the Waikato region.[115] However, the fertiliser industry report that these figures are an underestimate (**Section 6.3.2**): current use of superphosphate in New Zealand is likely to be closer to 2 million t/yr. Assuming 17.3% of this is used in the Waikato region, regional use would be in the order of 346,000 t/yr.

Other potential sources of cadmium to agricultural land include:

- Atmospheric deposition (probably mainly from urban areas);[116,117]

- Land application of sewage sludge or biosolids (processed human sewage sludge);[118]

- Land application of other agricultural soil treatments;[119]

- Use of zinc or copper based products (containing a cadmium component) for plants or livestock.

These sources have been generally been regarded as relatively minor when compared with phosphate fertilisers; however, on some crops, this is not always the case. Relative contributions from each of these sources are discussed further in **Section 6**.

110 Nielsen SA and Nathan A, **1975**. Heavy metal levels in New Zealand molluscs. *N.Z.J. Marine Freshwater Res.* Vol. 19, No. 4, pp 467-481.
111 Dick GL, Hughes JT, Mitchell JW and Davidson F, **1978**. Survey of trace elements and pesticide residues in the New Zealand diet I. Trace element content. *N.Z.J. Sci.* Vol. 21, No. 1, pp 57-69.
112 Syers JK, MacKay AD, Brown MW and Currie LD, **1986**. Chemical and physical characteristics of phosphate rock materials of varying reactivity. *J. of the Sci. of Food and Agriculture* Vol. 37, No. 11, pp 1057-1064.
113 Waitangi Tribunal Wai 262 Report, **2004**. *Crown laws, policies, and practices in relation to flora and fauna, 1840-1912; Chapter 2. Phases of ecological change*. Available from: http://www.waitangi-tribunal.govt.nz/doclibrary/wai262/crownlawspolicies/Chapt02.pdf
114 New Zealand Electronic Text Centre, **2004**. http://www.nzetc.org/etexts/WH2Econ/c8-10.html
115 Statistics New Zealand, **2004**. 2002 Agricultural Production Census (Final Results): June 2002: Fertiliser tables are available from: http://www.stats.govt.nz/domino/external/web/prod_serv.nsf/Response/Fertiliser+tables
116 Fergusson JE and Stewart C, **1992**. The transport of airborne trace elements copper, lead, cadmium, zinc and manganese from a city into rural areas. *Science of the Total Environment*, Vol. 121, pp 247-69.
117 Gray CW, McLaren RG and Roberts AHC, **2003.** Atmospheric accessions of heavy metals to some New Zealand pastoral soils. *Science of the Total Environment*, Vol. 305(1-3), pp 105-115.
118 New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand*.
119 Kabata-Pendias A and Pendias H, **2001**. *Trace elements in soils and plants (3rd Ed.)* CRC Press, U.S.A., Table 5.

3.2.3 Sampling depth and soil guidelines

In cases where a trace contaminant is applied to the soil surface, and is adsorbed reasonably strongly, soil sampling depth can have a significant influence on measured contaminant concentrations. Cadmium is such a trace contaminant (**Sections 3.2.2** and **3.4**). Generally, cadmium accumulates in the topsoil.[120] Concentrations of cadmium in agricultural soils are higher in surface than deeper layers, with the rate of leaching and depth of penetration being dependent on soil type and rainfall. This being the case, it is important to specify sampling depth when making comparisons to soil guideline values. It would also be important to take sampling depth in to account if attempting to make comparisons of soil cadmium concentrations between New Zealand and other countries. Guidelines for soil cadmium are reviewed in **Section 3.8**. An outline of relevant sampling depths in relation to soil guidelines is provided in **Section 3.9**.

3.3 Evidence and rates of accumulation

Evidence that cadmium is progressively accumulating in New Zealand soils comes from three complementary experimental approaches. These are:

1. Analysis of archived soil collections;[*e.g.* 121]

2. Results from experimental trial plots with controlled application rates;[*e.g.* 122,123]

3. Results from field surveys.[*e.g.* 124]

These approaches all involve direct measurement of cadmium in agricultural soils of one form or another, rather than being loading estimates. Cadmium concentrations measured in treated soils represent the background level plus the net amount which has accumulated in the soil over time (*i.e.* loss processes such as leaching, topsoil erosion, and plant uptake are accounted for).

A substantial proportion of applied cadmium is retained in the crop root zone. For example, Rothbaum *et al.*[125] determined that over a 30 years period, about half the cadmium applied to a Papatoetoe clay loam was retained in the top 22.5 cm of soil. Uptake of cadmium by clover pasture was estimated to be about 2% of that applied.

Some estimates can be made about net rates of accumulation of cadmium in pastoral and horticultural soils, based on these direct measurements. This can be done by making the following assumptions:

- 1939 is nominated as a suitable ‘time zero’ year where most (three-quarters of) New Zealand agricultural land was likely to have contained very little cadmium above background, but also when superphosphate application should have been reaching reasonable amounts (with one quarter of pastures being top-dressed);

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[120] Gray, C. W.; McLaren, R. G.; Roberts, A. H. C., **2003**. Cadmium leaching from some New Zealand pasture soils. *European Journal of Soil Science*, Vol. 54(1), pp 159-166.

[121] Taylor MD, **1997**. Accumulation of cadmium derived from fertilizers in New Zealand soils. *Science of the Total Environment*, Vol. 208(1,2), pp 123-126.

[122] Gray CW, McLaren RG, Roberts AHC and Condron LM, **1999**. The effect of long-term phosphate fertiliser applications on the amount and forms of cadmium in soils under pasture in New Zealand. *Nutrient Cycling in Agroecosystems*, Vol. 54, pp 267-277.

[123] Loganathan P, Hedley MJ, Gregg PEH and Currie LD, **1997**. Effect of phosphate fertilizer type on the accumulation and plant availability of cadmium in grassland soils. *Nutrient Cycling in Agroecosystems*, Volume Date 1996-1997, Vol. 46, No. 3, pp 169-178.

[124] Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.

[125] Rothbaum HP, Goguel RL, Johnston AE and Mattingly GEG, **1986**. Cadmium accumulation in soils from long-continued applications of superphosphate. *Journal of Soil Science*, Vol. 37(1), pp 99-107.

- Cadmium concentrations in New Zealand soil in 1939 would have been close to the background value for non-farmed soils, identified by Roberts *et al.* as 0.2 mg/kg.[126]

Net accumulation rate estimates based on these assumptions are provided in **Table 2. Figure 2** is a conceptual illustration of cadmium accumulation based on overall averages of average and upper accumulation rates from each study. For convenience it is useful to refer to cadmium accumulation rates in units of µg/kg/year (parts-per-billion per year); where this is done, accumulation rates in units of mg/kg/yr (parts-per-million per year) are also provided in brackets.

The mean cadmium accumulation rate ranges from 1.6-11.8 µg/kg/year (0.0016 to 0.0118 mg/kg/yr) between studies, and averages **6.6 µg/kg/year** (0.007 mg/kg/yr) over all studies (**Table 2**).

Table 2 Estimates of net cadmium accumulation rates in soils over various survey regions between 1939 and the time of each survey. Assumptions are as outlined in the text.

Survey scope	Apparent net cadmium accumulation rate in soil (µg/kg/year)		Soil sampling depth	Date of survey
	Mean	Maximum		
NZ wide: pastoral soils[a]	4.5	25.1	0–7.5 cm	1992
NZ wide: pastoral and horticultural soils[b]	11.8	30.0	0–15 cm (mostly)[c]	1990
Waikato: horticultural soils[d]	8.1	21.1	0–7.5 cm	2003
Waikato: pastoral soils[d]	9.0	18.3	0–10 cm	2002
Auckland: horticultural soils[e]	4.8	14.3	0–7.5 cm	2002
Tasman: horticultural soils[f]	1.6	12.5	0–7.5 cm	2003
Overall averages	6.6	20.2		1999

[a] Derived from data in Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.

[b] Derived from data in Taylor MD, **1997**. Accumulation of cadmium derived from fertilizers in New Zealand soils. *Science of the Total Environment*, Vol. 208, No. 1,2, pp 123-126., augmented with personal communication with the author regarding appropriate mid-years for means, and individual maximum observations, April 2004.

[c] See **Sections 3.2.3** and **3.9**. From reference [b]: *'Archived soil samples were either single pit samples or composite core samples usually 0-6 inches (0-15 cm) in depth. Present day samples were a composite of 20 cores taken at the same depth as the corresponding archived soil.'*

[d] See **Section 5** of this report.

[e] Derived from Gaw SK, **2002**. Pesticide Residues in Horticultural Soils in the Auckland Region. Auckland Regional Council Working Report No. 96.

[f] Derived from Gaw SK, **2003**. Historic pesticide residues in horticultural and grazing soils in the Tasman District.

[126] Roberts AHC, Longhurst RD, and Brown MW, **1994**. Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research*, Vol. 37, No. 1, pp 119-29.

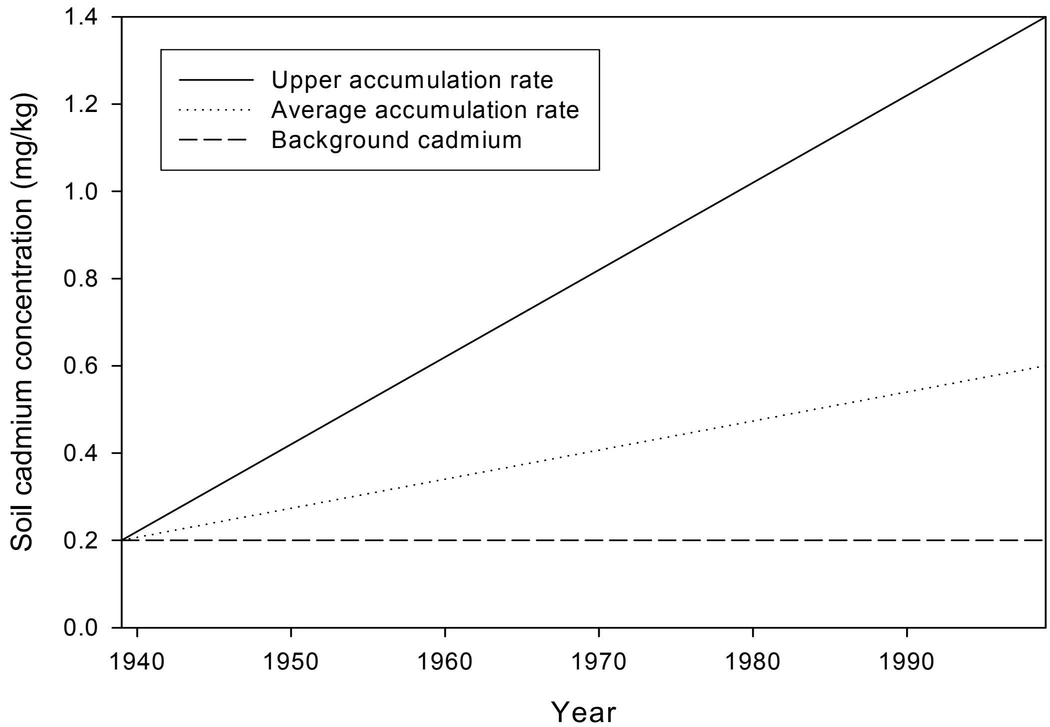

Figure 2 Illustration of cadmium accumulation in New Zealand agricultural soils based on overall averages provided in Table 2.

Note that individual properties will accumulate more or less cadmium than indicated by these mean lines, depending on soil type, topography, climate, and land history.

In relation to the highest and lowest mean accumulation rates (**Table 2**), it is worth noting that the low result for horticultural soils of Tasman District is likely to be related to the fact that these soils are sandy, and will have a lower cadmium retention capacity than most other New Zealand soils. At the other end of the scale, the high mean value of 11.8 µg/kg/year (~0.012 mg/kg/yr) probably contains some bias towards properties on 'easy and accessible' land that were settled early, and dairy farms.[127] These low and high results tend to balance each other, and the mean value remains the same whether they are included or excluded from the data set.

Upper accumulation rates are generally more consistent with each other in the first instance, and average about **20 µg/kg/year** (0.02 mg/kg/yr) (**Table 2**). It can be seen that the upper accumulation rate is about three times the average accumulation rate. From a regulatory perspective, upper rates of accumulation are of greatest immediate interest because they represent those properties which will be first to lose soil resource capacity (*e.g.* by falling out of production) as a result of soil contamination. Relevant Regional Policy goals are outlined in **Section 1**. The current soil status of Waikato horticultural and pastoral soils are discussed further in **Section 5.2.2** and **Section 5.2.3**, respectively.

3.4 Behaviour of cadmium in soils and limitations of availability estimates

The chemistry of cadmium, and interactions between cadmium and its immediate environment, determine its toxicity and mobility patterns.

[127] Taylor M, Landcare Research, **2004**. Personal communication. The former is because the samples were archived soils, and sample collection partly relied on ease of access in the early days.

When phosphate fertiliser is applied, the cadmium it supplies to the soil is in forms that provide reasonable proportions for plant uptake.[e.g.128] Over time, with no further fertiliser inputs (and reasonably moist soil), natural equilibrium processes work to redistribute a significant amount of this cadmium to soil phases for which it has a progressively higher affinity, making it less available for plant uptake.[e.g.129] Soil phases responsible for cadmium fixation, in order of probable importance, include organic matter, hydrated metal oxides, clay minerals, carbonates, and sulphides.[130,131,132,133]

Notwithstanding this process, under typical field conditions, with ongoing fertiliser input, the total amount of plant available cadmium increases steadily with time.[134] In terms of the environmental chemistry, this is because:

1. The total cadmium concentration is increasing (**Figure 2**);
2. New readily available cadmium is being added at a faster rate that soil sorptive phases can partially immobilize it (kinetic limitations);
3. The proportional availability of high affinity sorption sites on appropriate soil phases decreases as the total cadmium concentration increases (thermodynamic limitations);
4. This type of fixation on soil phases is almost always partially reversible over the longer term, being susceptible to dynamic soil processes (**Table 3**).

Consideration of availability can have an important part to play in contaminated site risk assessments. This is particularly the case when the contaminant metal is in a form that is robust enough to retain its integrity over the medium to longer term. For example, bio-availability of natural soil lead to children is much lower when it is present as a form of lead phosphate,[135] which is relatively robust to many physicochemical soil processes. In other cases, a site management plan is put in place which ensures that conditions remain such that contaminant release is not favoured in the future. Two examples of post-closure site management plans are those covering inspection and maintenance of landfill caps, and treatment of residual leachate from closed mining operations.

Table 3 Significant immobilization and remobilization processes for applied soil cadmium. In general terms, the strength of cadmium fixation increases with each entry down the Table.

Immobilization process	Remobilization processes	Example
Adsorption to exchange sites (these can be over a range of soil phase types including those listed below)	Decrease in soil pH; increase in alternative exchangeable cations; increase in natural or synthetic complexation agents in soil solution	Use of zinc-based dithiocarbamate fungicide (*e.g.* Mancozeb, Propineb) on crops. These supply both an exchangeable metal (zinc) and a strong cadmium complexing agent (dithiocarbamate).
Adsorption to clay minerals	As above	Progressive soil acidification through nitrification

128 Loganathan P and Hedley MJ, **1997**. Downward movement of cadmium and phosphorus from phosphatic fertilizers in a pasture soil in New Zealand. *Environmental Pollution*, Vol. 95(3), pp 319-324.

129 Gray CW, McLaren RG, Roberts AHC and Condron LM, **1999**. The effect of long-term phosphatic fertilizer applications on the amounts and forms of cadmium in soils under pasture in New Zealand. *Nutrient Cycling in Agroecosystems*, Vol. 54, No. 3, pp 267-277.

130 Gray CW, Mclaren RG, Roberts AHC and Condron LM, **1998**. Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. *Australian Journal of Soil Research*, Vol. 36, No 2, pp 199-216.

131 Gray CW, McLaren RG, Roberts AHC and Condron LM, **2000**. Fractionation of soil cadmium from some New Zealand soils. *Communications in Soil Science and Plant Analysis*, Vol. 31, No. 9-10, pp 1261-1273.

132 Kim ND and Fergusson JE, **1991**. Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soil. *Science of the Total Environment*, Vol. 105, pp 191–209.

133 Kim ND and Fergusson JE, **1992**. Adsorption of cadmium by an aquent New Zealand soil and its components. *Australian Journal of Soil Research*, Vol. 30, No. 2, pp 159-67.

134 Taylor MD, **1997**. Accumulation of cadmium derived from fertilizers in New Zealand soils. *Science of the Total Environment*, Vol. 208, No. 1-2, pp 123-126.

135 Davis A, Ruby MV and Bergstrom PD, **1992**. Bioavailability of arsenic and lead in soils from the Butte, Montana, mining district. *Environmental Science and Technology*, Vol. 26, pp 461-468. Note, for example, that the solubility product of the mineralogical phase $Pb_5(PO_4)_3(OH,Cl)$ is 3×10^{-77}.

Adsorption to carbonate minerals (however, the carbonate content of New Zealand soil is low to begin with.)	1. As above; 2. Carbonates themselves dissolve more readily below pH 5.	Soil acidification through biosolids addition (addition of humic acids)
Adsorption to, and encapsulation within, hydrated soil iron and manganese oxides	1. Decrease in soil pH; 2. Amorphous iron and manganese oxides dissolve under reducing conditions, releasing their retained metal	Seasonal shift to reducing conditions in the subsoil; reducing conditions in the rhizosphere (zone around the plant root containing dead cells: an area of intense biological activity accompanied by significant pH and redox changes)
Adsorption and chelation by organic matter	1. Decrease in soil pH; 2. Loss of soil organic matter; 3. Progressive degradation of humic acids, a process which becomes more rapid as conditions become more oxidising.	Loss of soil organic matter through cropping; soil shift to more oxygen rich environment through plowing; oxidising conditions in the rhizosphere; smaller fragments of organic matter (the fulvic acid fraction) can act in the opposite direction, extracting the soil metal.
Fixation as a sulphide	Shift to oxidising conditions	Turning the soil over

It has been suggested that availability should also be taken into account when applying fertilisers and other soil amendments to agricultural land. In relation to cadmium in productive agricultural soils, however, it would be short-sighted to attempt to make use of availability in this way. Reasons are as follows:

1. Short term cadmium immobilization represents temporary amelioration, but at the same time it is actually the main process responsible for the underlying problem, which is accumulation;

2. Laboratory availability measurements usually represent point-in-time snapshots. In cases where a substantial portion of the metal is anthropogenic, most immobilization processes responsible for the current picture are at least partially reversible in the longer term (**Table 3**).

3. As noted above, empirical evidence demonstrates that the proportion of available cadmium is increasing as the concentration of total cadmium increases, showing that whatever net immobilization has taken place, it has been insufficient to cope with input rates.

At least two longer term processes are known to be operating in agricultural soils are likely to partially remobilise parts of the pool of cadmium which is already present, regardless of future inputs. These are progressive acidification, and loss of soil organic matter in cropping soils.

- The most important factor governing cadmium adsorption and desorption, and crop uptake, is pH.[136] As the soil becomes more acidic, more cadmium is remobilised.[137] This is understandable given the range of cadmium remobilisation processes which are influenced by pH (**Table 3**, coupled with the fact that the mobile species of cadmium in soils (Cd^{2+}_{aq}) is favoured over a wide redox and pH range (*viz.* positive redox potentials and any pH value less than 8).[138] Soils in the Waikato region are naturally acidic. Pressure on the soil resource caused by the natural acidity and possible further acidification of Waikato soils is discussed further in **Appendix 6**.

[136] McBride, MB, **2002**. Cadmium uptake by crops estimated from soil total Cd and pH. *Soil Science*, Vol. 167, No. 1, pp 62-67.
[137] Gray CW, Mclaren RG, Roberts AHC and Condron LM, **1998**. Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. *Australian Journal of Soil Research*, Vol. 36, No. 2, pp 199-216.
[138] Hermann R and Neumann-Mahlkau P, **1985**. The mobility of zinc, cadmium, copper, lead, iron and arsenic in ground water as a function of redox potential and pH. *Science of the Total Environment,* Vol. 43, pp 1-12.

- The most important solid phase responsible for cadmium fixation is organic matter. When more (insoluble) organic matter is present, fixation increases.[139,140] Conversely, when soil organic matter is removed, the amount of cadmium adsorbed decreases, leaving more in soil solution and potentially available for plant uptake.[141] Significant losses of soil organic matter are the norm in horticultural cropping soils, the type of soil of most significance in relation to dietary cadmium intakes. Soil resource pressure caused by loss of organic matter in cropping soils is discussed further in **Appendix 6**.

- The nature of organic matter is also important. Small soluble forms of organic matter (mainly fulvic acids) work to increase cadmium mobility through formation of organocadmium bonds, and other interactions between cadmium and organic ligands.[142] Enhanced microbial degradation of insoluble soil organic matter which accompanies cultivation and fertiliser use is expected to increase the proportion of soluble to insoluble organic matter, and may also increase cadmium mobilisation.

The capacity of cadmium to re-associate with less available soil pools is therefore moderately good news in the short term, because it means that dietary intakes are lower today than they would be otherwise. However, it also increases the size of the total soil cadmium reservoir, creating a progressively growing deferral to the future. As reviewed in **Section 2.4.2**, the margin between current and tolerable intakes is already slim under present conditions, where the impact of all applied cadmium is not being felt. Overall, cadmium sorption by soil constituents is sufficiently strong to ensure the element's accumulation in soils, but not strong enough to prevent significant crop uptake. Bio-availability measurements are of scientific interest, but natural cadmium fixation is not a solution to the problem of ongoing cadmium accumulation. Under certain circumstances, changes in soil conditions are likely to result in remobilisation of a fraction of the cadmium that has previously been immobilised.

3.5 Crop uptake

3.5.1 Theory and predicted uptake

As noted above, the mobile species of cadmium in soils is the divalent ion (Cd^{2+}_{aq}), formation of which is favoured at positive values of the redox potential and pH values less than 8.[143] Specific insoluble soil phases (particularly organic matter and hydrated metal oxides) work to decrease cadmium's mobility, through reactions which are at least partially reversible. Conversely, some soluble organic compounds can work in the opposite direction, increasing cadmium's mobility by extracting it from surfaces.[144] These interactions and other physical and plant factors—such as rainfall, soil density, porosity and sorption characteristics, and variety of cultivar—determine the amount of cadmium taken up in crops, the fraction retained by the soil, and the amount which leaches from the soil to the water table.[145,146,147,148]

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139 Gray CW, McLaren RG, Roberts AHC and Condron LM, **2000**. Fractionation of soil cadmium from some New Zealand soils. *Communications in Soil Science and Plant Analysis*, Vol. 31, No. 9-10, pp 1261-1273.

140 Gray CW, McLaren RG, Roberts AHC and Condron LM, **1999**. Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. *European Journal of Soil Science*, Vol. 50, No. 1, pp 127-137.

141 Kim ND and Fergusson JE, **1992**. Adsorption of cadmium by an aquent New Zealand soil and its components. *Australian Journal of Soil Research*, Vol. 30, No. 2, pp 159-67.

142 Ram N and Verloo M, **1985**. Effect of various organic materials on the mobility of heavy metals in soil. *Environmental Pollution,* Vol. 10, pp 241-248.

143 Hermann R and Neumann-Mahlkau P, **1985**. The mobility of zinc, cadmium, copper, lead, iron and arsenic in ground water as a function of redox potential and pH. *Science of the Total Environment,* Vol. 43, pp 1-12.

144 Ram N and Verloo M, **1985**. Effect of various organic materials on the mobility of heavy metals in soil. *Environmental Pollution,* Vol. 10, pp 241-248.

145 Amacher MC, Selim HM and Iskandar IK, **1988**. Kinetics of chromium(VI) and cadmium retention in soils: a nonlinear multireaction model. *Soil Science Society of America Journal* Vol. 52, pp 398-408.

146 Baes CF and Sharp RD, **1983**. A proposal for estimation of soil leaching and leaching constants for use in assessment models. *Journal of Environmental Quality*, Vol. 12, No. 1, pp 17-28.

147 Christensen TH, **1985**. Cadmium soil sorption at low concentrations: III prediction and observation of mobility. *Water Air and Soil Pollution,* Vol. 26, pp 255-264.

148 McLaughlin MJ, Williams CMJ, McKay A, Gunton J, Jackson K, Dowling B, Kirkham R, Partington D, Smart MS and Tiller KG, **1994**. Effect of potato variety on cadmium accumulation in potato tubers. *Australian Journal of Agricultural Research*, Vol. 45, pp 1483-1495.

Within a given soil, with all other factors remaining constant, the most important soil factors controlling crop uptake of cadmium are the total cadmium concentration in the soil, and the soil pH.[149,150]

Acidity works to increase a number of remobilisation processes indicated in **Table 3**. The effect of pH on cadmium mobilisation is more pronounced than for most other common heavy metals, such as copper, lead and mercury. This is because, on average, cadmium forms weaker bonding interactions with significant soil solid phases than these other metals. For example, when cadmium and copper are adsorbed to calcite, the former can be released by use of a simple ion-exchange reagent (Mg^{2+}),[151] whereas the latter is not released until the calcite is dissolved.[152] Similarly, in sequential extraction tests on model systems, cadmium bound to humic acid is mainly released in the exchangeable, mildly acidic ('carbonate') and reducing/acidic ('Fe/Mn oxide') fractions, whereas release of the majority of the copper requires destruction of the organic matter (**Figure 3**).

This relative lack of complexity in terms of the dominant control mechanism governing cadmium in soil solution means that for a given soil and crop, empirical equations based on only two parameters, total cadmium and the pH, are relatively successful at predicting crop uptake. Such equations have the form:[149]

$$\log[Cd]_{crop} = a + b \log [Cd]_{soil} - c\,(pH_{soil}), \text{ where:}$$

a, b and c are constants related to the specific soil, and
[Cd] is the dry weight concentration of cadmium

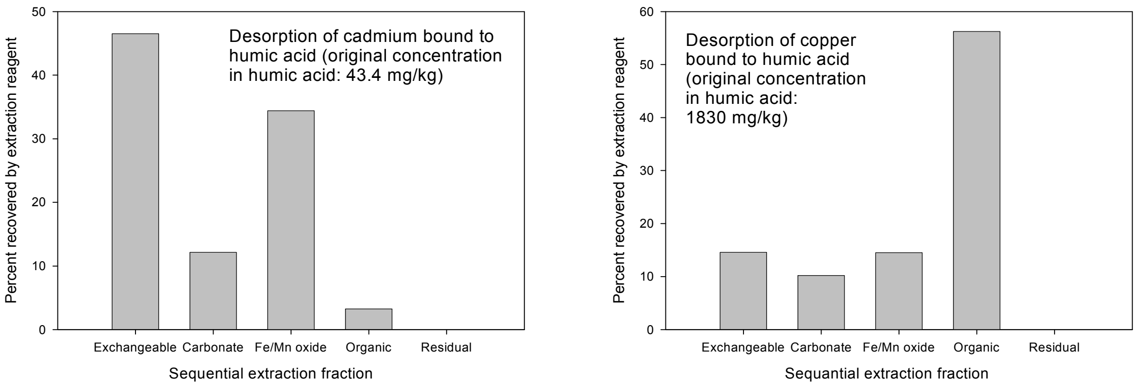

Figure 3 Release of cadmium[153] and copper[154] from humic acid (essentially insoluble soil organic matter) using the sequential extraction scheme of Tessier *et al*.[155]

In general terms, the 'strength' of chemical extraction reagents increase in sequence from left to right. Note that more copper is retained on organic matter despite the fact that total copper concentrations are higher (implying that higher energy exchange sites are less likely to be saturated in the cadmium case).

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149 McBride MB, **2002**. Cadmium uptake by crops estimated from soil total Cd and pH. *Soil Science*, Vol. 167, No. 1, pp 62-67.

150 Gray CW, Mclaren RG, Roberts AHC and Condron LM, **1999**. Effect of soil pH on cadmium phytoavailability in some New Zealand soils. *New Zealand Journal of Crop and Horticultural Science*, Vol. 27, No. 2, pp 169-179.

151 Kim ND and Fergusson JE, **1991**. Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soil. *Science of the Total Environment*, Vol. 105, pp 191–209.

152 Schriner R, **1994.** *Aspects of the solid-phase speciation of copper in the marine environment.* MSc thesis in Chemistry, University of Waikato, Ch 5.

153 Kim ND and Fergusson JE, **1991**. Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soil. *Science of the Total Environment*, Vol. 105, pp 191–209.

154 Schriner R. **1994.** *Aspects of the solid-phase speciation of copper in the marine environment.* MSc thesis in Chemistry, University of Waikato, Ch 5.

155 Tessier A, Campbell PGC and Bisson M, **1979**. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry,* Vol. 51, No. 7, pp 844-851.

McBride[156] provides best fit equations for cadmium uptake in lettuce and silverbeet (Swiss chard) grown on three different sewage sludge amended soils. Predicted cadmium uptakes based on these equations are shown in **Figure 4**.

These estimates are made at the mid-pH range recommended for each crop. Recommended soil pH ranges are 6.3–7.3 for lettuce,[157] and 5.6–6.8 for silverbeet.[158] Mid-points used in the calculation are therefore pH 6.2 for silverbeet, and pH 6.8 for lettuce.

Cadmium uptake from such amended soils might be expected to under-estimate uptake in an active Waikato horticultural area, for two reasons:

1. Sewage sludge provides more soil organic matter than might be regarded as typical;
2. Waikato horticultural soils are likely to be more toward the lower end of the suitable pH ranges for these crops. The pH range for 37 Waikato pastoral and horticultural properties, many of which already receive lime, is 4.6–6.6, with an average of pH 5.6.[159] Soils at the low end of this range are likely to be peat soils, in which a lower pH can be tolerated, compared with mineral soils. **Figure 5** shows indicative cadmium uptake (based on the same equations), recalculated for the lowest suitable pH for lettuce and silverbeet growing.

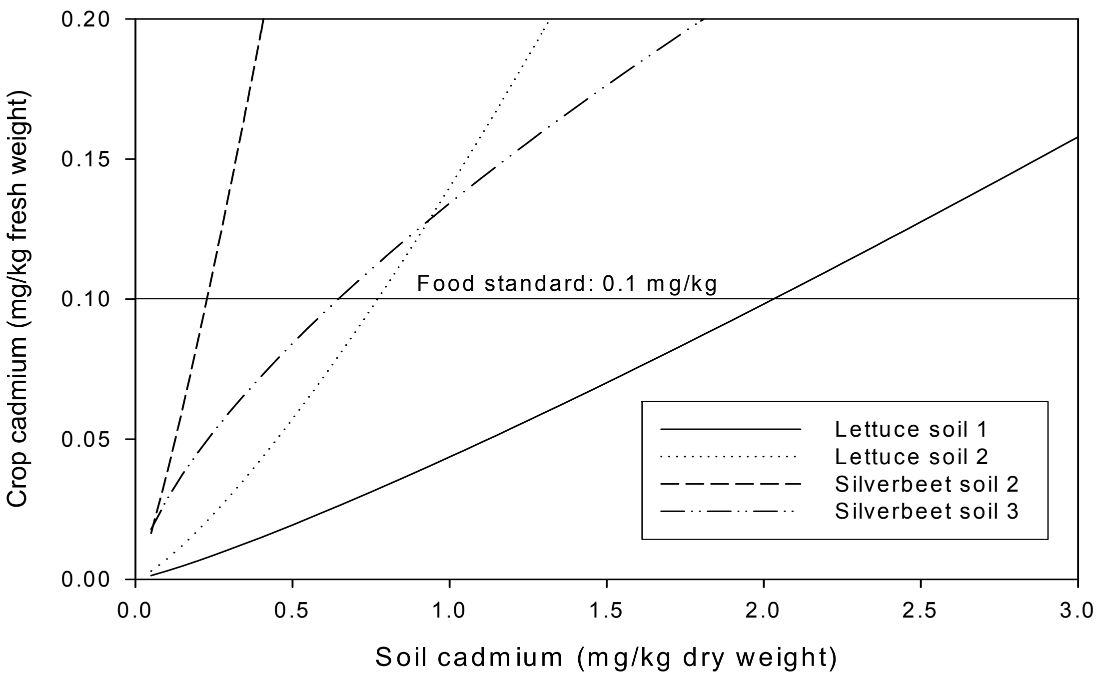

Figure 4 Predicted cadmium uptake in lettuce and silverbeet grown on three sewage sludge amended soils based on equations provided by McBride,[160] calculated at the pH mid-point for lettuce and silverbeet growing.

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[156] McBride MB, **2002**. Cadmium uptake by crops estimated from soil total Cd and pH. *Soil Science*, Vol. 167, No. 1, pp 62-67.
[157] Cornforth IC, **1998**. *Practical soil management.* Lincoln University Press, Canterbury, New Zealand.
[158] Kay T and Hill R, **1998**. *Field consultants guide to soil & plant analysis.* Soil and Plant Division, Hill Laboratories, Hamilton.
[159] Samples submitted for multi-element analysis in the Waikato Regional Soil Quality Monitoring programme: Environment Waikato Document **844227**.
[160] McBride MB, **2002**. Cadmium uptake by crops estimated from soil total Cd and pH. *Soil Science*, Vol. 167, No. 1, pp 62-67.

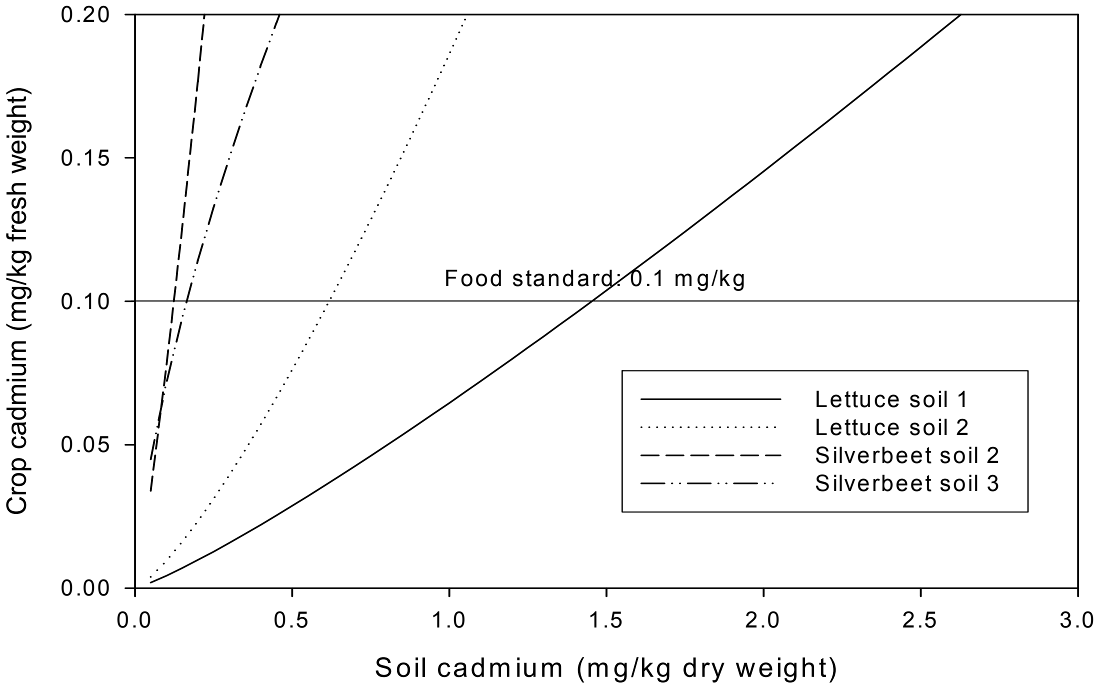

Figure 5 Predicted cadmium uptake in lettuce and silverbeet grown on three sewage sludge amended soils, calculated at the lowest suitable pH values for lettuce and silverbeet growing (pH 6.3 and 5.6, respectively).

In the Waikato horticultural soils, 23% of samples were found to equal or exceed 1.0 mg/kg cadmium (**Section 5.2.2**). By comparison with indicative (order-of-magnitude) cadmium uptakes shown in **Figures 4** and **5**, it is apparent that on theoretical grounds, the food standard for some types of lettuce and silverbeet on some Waikato soils may well be closely approached or exceeded at current soil cadmium concentrations.

In more general terms, the UK Environment Agency Department for Environmental, Food and Rural Affairs (DEFRA) make use of two generic uptake equations for leafy and root vegetables in their Contaminated Land Exposure Assessment (CLEA) module for cadmium, used in deriving human health guideline values for residential soils.[161] These cadmium uptake equations are based on a literature review of garden vegetables of interest, and are as follows:

$$\text{Leafy vegetables: } \ln(CF) = 11.174 - 1.6461(pH)$$

$$\text{Root vegetables: } \ln(CF) = 11.206 - 1.6340(pH)$$

where CF is the soil-to-plant concentration factor (with both being on a dry weight basis)

In calculating potential concentrations in leafy and root vegetables, the equations therefore require three variables: soil cadmium, pH, and plant moisture content. **Figure 6** shows predicted uptake for leafy vegetables over a soil cadmium range of 0–3 mg/kg, a pH range of 5–8.5, and an assumed moisture content of 94% (halfway between that of lettuce and silverbeet).

[161] UK Environment Agency, **2002.** *Soil guideline values for cadmium contamination.* Department for Environmental, Food and Rural Affairs (DEFRA): Available from: http://www.environment-agency.gov.uk/commondata/acrobat/sgv3_cadmium_676065.pdf

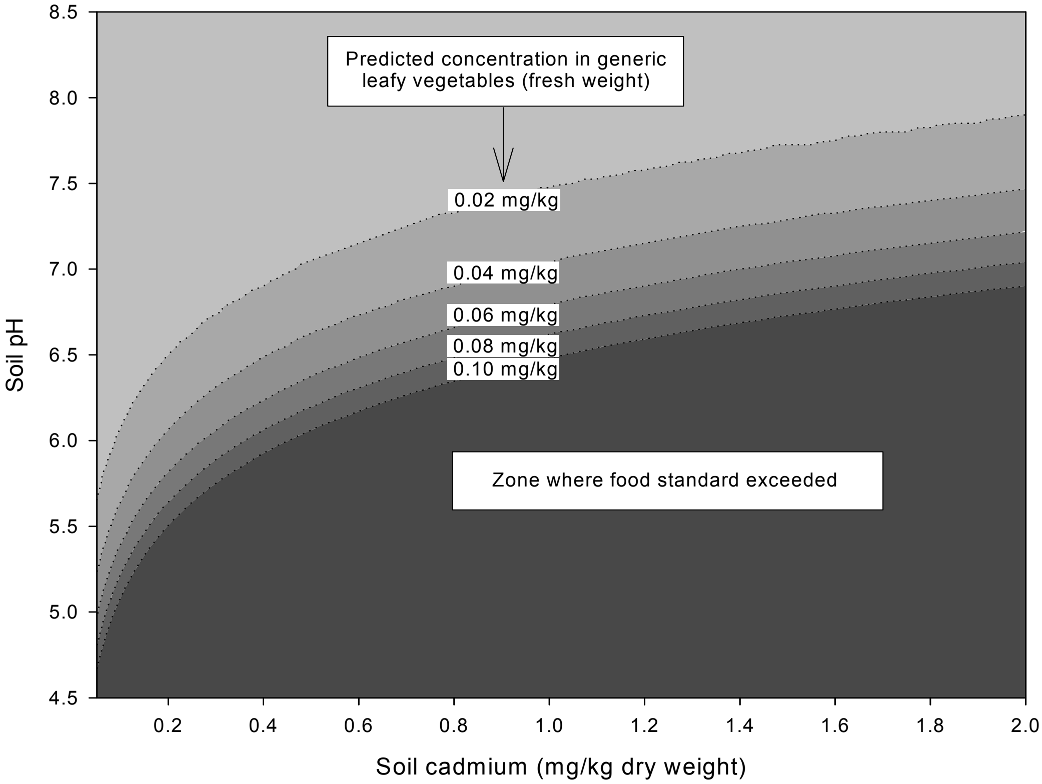

Figure 6 **Contour diagram of estimated uptake of cadmium by generic leafy home garden vegetables (assumed moisture content 94%) as predicted by the UK Environment Agency (DEFRA) CLEA model.**

The relevant New Zealand food standard in leafy vegetables is 0.1 mg/kg.

It should be noted that making exact predictions about the uptake of cadmium in specific crops is more difficult than may be indicated by generic uptake equations of the types illustrated above, which relate more to average uptake over a range of crops and soil types. Exact uptake is crop, soil and climate specific. However, orders of magnitude for cadmium uptake over different soil types that are indicated in these equations (Figures 4–6) suggest that there may already be an issue with cadmium exceeding food standard in some New Zealand food crops.

3.5.2 Evidence of food standard exceedances

Theory is one thing but empirical evidence is preferable. Confirmation that soil cadmium levels are already sufficient to cause food standards to be exceeded in some New Zealand crops (and soils) has in fact already been provided in previously published material. This is reviewed below.

1. **Fertiliser industry/CRI research (Roberts *et al.* 1995)**
   A decade ago, the New Zealand Fertiliser Manufacturer's Research Association (*Fert Research*) commissioned an *AgResearch* survey of cadmium in soil and produce of South Auckland market gardens (90 sites) and mid-Canterbury wheat farms (70 sites).[162]

   At the time, the food standard was 1 mg/kg, being partly based on what was measurable with analytical instruments in use when the standards were gazetted (1986) (**Section 1.2.3**). This figure was always over an order-of-magnitude above average cadmium concentrations in food, and actual protection relied on the fact that most foods never came anywhere close to 1 mg/kg (exceptions being oysters,

[162] Roberts AHC, Longhurst RD and Brown MW, **1995**. *Cadmium Survey of South Auckland Market Gardens and Mid Canterbury Wheat Farms.* Report prepared for the New Zealand Fertiliser Manufacturers Research Association. AgResearch: Hamilton.

liver and kidney).[163] Unsurprisingly, fresh weight cadmium concentrations in all foods tested (lettuce, potatoes, onions, and wheat) were found to be in compliance with the 1 mg/kg figure.

Interpreted retrospectively in the light of the current risk-based food standard for cadmium in these foods (0.1 mg/kg), the results of this work are less reassuring. Results of the report show that in 1995, cadmium in 4% of the South Auckland market garden crops already equalled or exceeded the current food standard. The exceedance rate for mid-Canterbury wheat was higher, at 23%. In comparing the results with foods from other countries, the authors noted:[162]

"…on average, New Zealand wheat grain is at the upper end of reported values."

2. **University research (Grey *et al.* 2001)**
Gray *et al.*[164] examined cadmium in cultivars of wheat (*Triticum aestivum L*). Ability to accumulate cadmium in the wheat grain differed by up to fourfold between cultivars. Overall, 10% of grain samples were found to exceed 0.1 mg/kg cadmium, with 50% of these coming from a single property.

Strictly speaking, the food standards relate to foods 'as consumed'; it is unclear whether these exceedances would necessarily extend to foods made from the grain. Trace element concentrations are higher in the outer layers of grains. Guthrie[165] noted that refined cereals contained lower trace metal concentrations, due to the metal-rich outer layers (and germinal epithelia) of the grain being removed during the refining process. For this reason, wholemeal flour and bread contain more cadmium than white flour and bread.[166]

3. **Biosolids Guidelines (NZWWA, 2003)**
The work of Roberts et al (1995) and Grey et al (2001) is also reiterated in Section 5.2.2 of the *Guidelines for the Safe Application of Biosolids to Land in New Zealand*, published in 2003 (see **Section 3.8.2**). This entry also emphasises the problems that these food standard exceedances are occurring at soil concentrations well below even the new recommended agricultural guideline for soil cadmium:

'Cd is regarded as one of the most bio-available of the heavy metals, and at relatively low concentrations in the soil can accumulate in the edible part of crop plants, while having no detrimental effects on crops themselves (Smith, 1996). Even with current New Zealand pasture soil Cd levels (mean 0.4 mg/kg), a substantial percentage of ovine and bovine kidneys exceed the maximum residue level of 1 mg/kg for the Cd content of meat and offal for human consumption. As a result, the New Zealand meat industry now automatically condemns kidneys of slaughtered sheep over 2.5 years of age (Roberts et al., 1994). In addition, a survey of wheat crops in Mid Canterbury (Roberts et al., 1995) revealed that 15% of grain samples had Cd concentrations above the current maximum permissible concentration (MPC) of 0.1 mg/kg fresh weight (Australia New Zealand Food Authority Standards). A more recent investigation by Gray et al. (2001) found 10% of the wheat grain samples examined were non-compliant with the MPC. The Cd concentrations of the soils on which these wheat crops were grown were all below 0.45 mg/kg (Gray et al., 2001).'

163 As noted in **Appendix 4**, 1 mg/kg was the mean level of cadmium in rice in the Japanese *itai itai* poisoning event. It is likely that 1 mg/kg was partly selected to protect against instances of acute cadmium poisoning that had historically arisen from cadmium-plated items that came into contact with food, such as ice-cube trays, coffee-urns and cooking utensils. Regulatory understanding of chronic toxicity took longer to develop.

164 Gray CW, McLaren RG and Roberts AHC, **2001**. Cadmium concentrations in some New Zealand wheat grain. *New Zealand Journal of Crop and Horticultural Science*, Vol. 29, No. 2, pp 125-136.

165 Guthrie BE, **1975**. Chromium, manganese, copper, zinc and cadmium content of New Zealand foods. *New Zealand Medical Journal*, Vol. 82, No. 554, pp 418-424.

166 Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury, Ch. 6.

4. **Fertiliser industry fact sheet (Ballance Agri-Nutrients, 2005)**
Ballance Agri-Nutrients provide an online fact sheet for cadmium,[167] in which the following is noted:

'A potential problem for wheat may arise as a result of proposed food standards being proposed by the Australia New Zealand Food Authority (ANZFA). The current standard for wheat is 1 mg Cd/kg. The proposed ANZFA standard is 0.1 mg Cd/kg. A particular wheat cultivar consistently exceeds the proposed 0.1 mg Cd/kg standard.'

The food standard has been 0.1 mg/kg for over three years. It can therefore be presumed that the particular wheat cultivar mentioned by *Ballance Agri-Nutrients* now routinely exceeds the food standard.

Based on results of the 1995 *Fert Research* study,[168] it would appear that this cultivar is *Monad* (mean value 0.11 mg/kg on a fresh weight basis over 13 samples). However, cadmium in another wheat cultivar (of the five tested) also exceeded the current food standard in at least one sample: this was *Domino*.

Cadmium levels in a baseline survey of selected produce purchased in the Waikato region in 2004 are discussed in **Section 7**.

Presence of cadmium concentrations in produce which exceed risk-based food standards is not likely to be a problem that is unique to New Zealand. Jinadasa *et al.*[169] report the same issue is appearing in Australia.

3.5.3 Liming and its limits

To an extent, cadmium uptake in crops can be counteracted by raising the soil pH through liming. However, there are financial and practical limits to this:

- Liming brings an associated cost, which will increase with the more lime that is required. As soil cadmium concentrations increase, the pH (and amount of lime) required to maintain the same level of crop uptake also increases.

- Use of pH for amelioration of cadmium uptake can only be taken so far, because there is an upper limit for each crop in terms of tolerated alkalinity. For lettuce the recommended upper soil pH limit 7.3,[170] and for silverbeet it is 6.8.[171] This concept is illustrated for lettuce in **Figure 7** (based on equations used for **Figures 4** and **5**).

For lettuces grown on these different soils, the upper soil pH limit corresponds to soil cadmium concentrations of 2.85 mg/kg (soil 1) and 0.95 mg/kg (soil 2) (**Figure 7**). For silverbeet, the upper soil pH limit corresponds to soil cadmium concentrations of 0.40 mg/kg (soil 1) and 2.55 mg/kg (soil 2).

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[167] Ballance Agri-Nutrients, **2005**. Fact sheet for cadmium.; accessed 10 August 2005. Available from: http://www.ballance.co.nz/fscadmium.html
[168] Roberts AHC, Longhurst RD and Brown MW, **1995**. *Cadmium Survey of South Auckland Market Gardens and Mid Canterbury Wheat Farms.* Report prepared for the New Zealand Fertiliser Manufacturers Research Association. AgResearch: Hamilton.
[169] Jinadasa KBPN, Milham PJ, Hawkins CA, Cornish PS, Williams PA, Kaldor CJ, Conroy JP, **1997**. Heavy metals in the environment. *Journal of Environmental Quality*, Vol. 26, No. 4, pp 924-933.
[170] Cornforth IC, **1998**. *Practical soil management.* Lincoln University Press, Canterbury, New Zealand.
[171] Kay T and Hill R, **1998**. *Field and consultants' guide to soil and plant analysis.* Soil and Plant Division, Hill Laboratories, Hamilton.

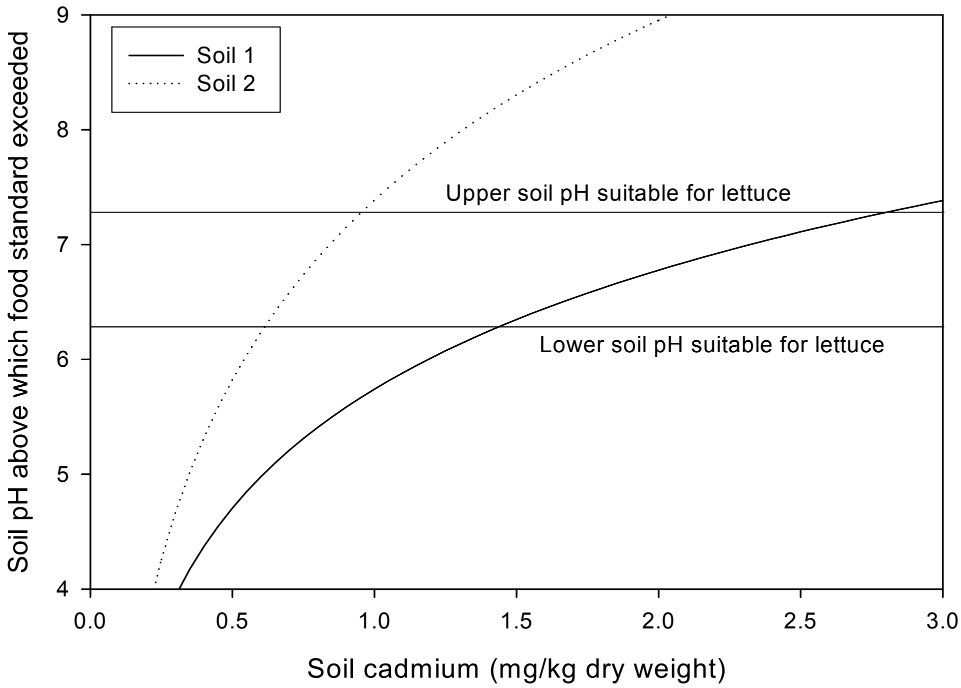

Figure 7 Illustration of soil pH values above which the 0.1 mg/kg food standard is likely to be broken for lettuce grown on two example soils, along with lines indicating soil pH ranges suitable for growing these crops.

(Based on equations provided by McBride.[172])

3.6 Livestock and pastoral soils

A reasonable amount of research attention has been directed at cadmium uptake by livestock. Concentrations of cadmium in milk and muscle meat are always low. The main human food issue with stock exposure relates to cadmium residues in liver and kidney meat.[173] Over 1988-1991, 22-28% of sheep and 14-20% of cattle kidneys sampled exceeded the NZ maximum residue level of the time, which was 1 mg/kg.[174]

Presence of elevated cadmium in liver and kidney meat is not surprising, being partly a consequence of mammals retaining about half of the absorbed dose in these organs (**Section 2.2.2**). Cadmium accumulates steadily with age, so the issue becomes worse with older animals: as at 2002, offal from animals older than 2.5 years was not permitted to be sold for human consumption for this reason.[175] To the sheep and beef industries, this already represents a significant lost income stream.

Cadmium can be taken in by grazing animals from three ingestion sources: phosphate fertiliser, soil, and pasture. Loganathan *et al.*[176] have developed a model to predict kidney and liver cadmium concentrations in grazing animals. These authors suggest

172 McBride MB, **2002**. Cadmium uptake by crops estimated from soil total Cd and pH. *Soil Science*, Vol. 167, No. 1, pp 62-67.

173 Loganathan P, Hedley MJ, Grace ND, Lee J, Cronin SJ, Bolan NS and Zanders JM, **2003**. Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine: a review. *Australian Journal of Soil Research*, Vol. 41, No. 3, pp 501-532.

174 Roberts AHC, Longhurst RD and Brown MW, **1994**. Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research*, Vol. 37, No. 1, pp 119-29.

175 *Fert Research*, **2002**. *Cadmium in New Zealand—Its Presence and Management.* Addendum 8 to the Code of Practice (COP) for Fertiliser Use: http://www.fertresearch.org.nz/attachments/document/UpdatedCodeAddenda.pdf

176 Loganathan P, Louie K, Lee J, Hedley MJ, Roberts AHC and Longhurst RD, **1999**. A model to predict kidney and liver cadmium concentrations in grazing animals. *New Zealand Journal of Agricultural Research*, Vol. 42, No. 4, pp 423-432.

that cadmium concentrations in sheep liver and kidneys are most sensitive to fertiliser cadmium concentrations, moderately sensitive to the pasture ingestion rate, and least sensitive to the soil ingestion rate. This suggests that a decrease in the cadmium content of phosphate fertilisers would be likely to result in a fairly direct reduction of cadmium in offal meat.

Roberts and Longhurst[177] also examined cadmium uptake in sheep (Romney ewes) in a hill-country farming system. Comparing pasture ingestion with soil ingestion, the authors found that of the two, the former was the most significant source of cadmium to sheep. Annual increases in cadmium concentrations in livers and kidneys of ewes (aged between 18-66 months) were estimated at 19% and 43%, respectively. The authors emphasized the need to reduce further cadmium inputs to soils in order to minimise the uptake by plants of cadmium already present.

Uptake and status of cadmium in herbage has also been examined. Longhurst *et al*[178] have recently summarised their (early 1990s) survey of cadmium in New Zealand pastoral topsoils and herbage. Over farmed and non-farmed properties, cadmium concentration ranges (on a dry weight basis) were as follows:

- Grasses: 0.03–0.30 mg/kg (with a significant variation between species);
- Legumes: 0.03–0.10 mg/kg;
- Weeds: 0.07–0.23 mg/kg.

In another New Zealand study, Loganathan *et al*[179] examined the effect of phosphate fertiliser type on accumulation and pasture availability of cadmium. Four types of phosphate fertiliser containing different cadmium concentrations were examined: North Carolina phosphate rock, single superphosphate, diammonium phosphate and Jordan phosphate rock. Over a ten year period, about 90% of the applied cadmium was still present in the soil, with 93% of this being in the top 12 cm. Over the same period, plants grown in the treated plots were found to take up between 1.5–4.5% of the applied cadmium.

Loganathan *et al*[180] and Roberts and Longhurst[181] have also studied cadmium cycling in hill pastures (the latter is discussed above). In the study of Loganathan *et al,* soil cadmium accumulation was found to be highest on low slopes (0-12°) and lowest on high slopes; this tallies with information from Taylor[182] from Landcare Research, that the highest pastoral soil cadmium concentration observed in his previous work (3 mg/kg) was in a (formerly swampy) grassed natural depression which received local surface runoff. As part of this work Loganathan *et al*[180] also developed a model which predicts the amount of cadmium accumulation in pastoral soil on the basis of cadmium inputs, and animal grazing and camping behaviour. The model is reported to predict well, with (as might be expected) slight over-estimates on high slope sites and slight underestimates on low slope sites.

One direct consequence of increased levels of cadmium in pastoral soils and herbage will be an increased rate of rejection of liver and kidney meats, over current rates. The

[177] Roberts, A.H.C. and Longhurst R.D., **2002**. Cadmium cycling in sheep-grazed hill-country pastures. *New Zealand Journal of Agricultural Research*, Vol. 45, pp 103–112.
[178] Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.
[179] Loganathan P, Hedley MJ, Gregg PEH and Currie LD, **1997**. Effect of phosphate fertilizer type on the accumulation and plant availability of cadmium in grassland soils. *Nutrient Cycling in Agroecosystems*, Volume Date 1996-1997, Vol. 46, No. 3, pp 169-178.
[180] Loganathan P, Mackay AD, Lee J and Hedley MJ, **1995**. Cadmium distribution in hill pastures as influenced by 20 years of phosphate fertilizer application and sheep grazing. *Australian Journal of Soil Research*, Vol. 33, No. 5, pp 859-71.
[181] Roberts, A.H.C. and Longhurst R.D., **2002**. Cadmium cycling in sheep-grazed hill-country pastures. *New Zealand Journal of Agricultural Research*, Vol. 45, pp 103–112.
[182] Taylor MD, Landcare Research, **2004**. Personal communication.

food standards for cadmium in kidney (sheep, cattle and pig) is now 2.5 mg/kg, and for liver the standard is 1.25 mg/kg.[183]

There may be secondary issues with stock exposure, but these are less well characterised. Generally, it is likely that stock do not live sufficiently long for a clinical toxicity issue to emerge: however, horses live a reasonable length of time and are likely to accumulate more cadmium than other animals;[184] horses are also known to be about five times more susceptible to cadmium exposure than humans. For mammalian exposure, the kidney is generally regarded as the critical organ, in that it tends to be the first organ in which damage is observed. For humans, the kidney concentration associated with overt tubular dysfunction and morphological changes has been given as 200 mg/kg (wet weight)[185] (**Section 2.3.2**). For small mammals, a wet weight critical kidney concentration of 100 mg/kg has been suggested.[186] To the extent that offal rejected for human consumption may reappear in pet-foods, there are possible implications for rates of liver and kidney disease in household animals.

In relation to cadmium's ability to cause liver damage, an additional implication may follow from the timing of fertiliser application in relation to the peak production of sporodesmin, the fungal toxin responsible or facial eczema. This is discussed further at the end of **Appendix 6**.

In terms of human intakes, cadmium levels in pastoral soils may appear less important than those in horticultural soils, because grain and selected vegetable crops make the greatest individual contributions to dietary cadmium intakes (**Section 2.4.2**).

However, although milk and muscle meat make a minimal contribution to human dietary intakes of cadmium, the soil guideline is set partly with reference to expectations of international trading partners (**Section 3.8**). Such guidelines may take on a more significant trade role in the future, as a result of renewed scientific interest in the role of dietary cadmium in hormone-related cancers that show a high incidence in Western populations (*e.g.* breast and testicular cancers).[187] As the results of such work become available, and regulatory developments in the European Community take effect (**Section 4.3**), there is a possibility that market preferences may develop from some of New Zealand's trading partners toward sourcing produce from countries with low soil cadmium.

Additionally, from a regulatory perspective, pastoral soils are as important as horticultural soils, because land-uses change with time. Pastoral properties can be (are being) converted to horticulture in some areas (*e.g.* the Hauraki Plains), and are progressively replaced by residential housing in areas bordering the urban centres. Subdivision brings with it a regulatory requirement that the property should be suitable for its intended purpose, which in the case of residential soils means that suitable guideline values for contaminants in residential soil should not be exceeded. Such guidelines are based on potential exposure through ingestion of soil and crop uptake in home gardens.[*e.g.* 188]

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[183] Section 1.4.1 of the Food Standards Code: http://www.foodstandards.gov.au/foodstandardscode/index.cfm. These increases over the older value (1 mg/kg) partly reflect the proportionately low amounts that these foods comprise in an average diet.

[184] Janiszewska J and Cieśla A, **2002**. Concentration of cadmium and lead in horse blood serum and hair in relation to season and environment. *Electronic Journal of Polish Agricultural Universities*, *Animal Husbandry*, Vol. 5, Issue 1: http://www.ejpau.media.pl/series/volume5/issue1/animal/art-06.html

[185] Friberg L, Piscator M, Nordberg GF and Kjellström T, **1974**. *Cadmium in the environment, 2nd edn.* CRC Press Inc. USA.

[186] Cooke JA and Johnson MS, **1996**. *Cadmium in small mammals.* **In** Beyer, WN, Heinz GH, and Redmon-Norwood AW (Eds.) *Environmental contaminants in wildlife*. SETAC Special Publications Series, Lewis Publishers, CRC Press.

[187] Johnson MD, Kenney N, Stoica A, Hilakivi-Clarke L, Singh B, Chepko G, Clarke R, Sholler PF, Lirio AA, Foss C, Reiter R, Trock B, Paik S and Martin M, **2003**. Cadmium mimics the in vivo effects of estrogen in the uterus and mammary gland. *Nature Medicine*, Vol. 9, No. 8, pp 1081-1084.

[188] Ministry for the Environment and Ministry of Health, **1997**. *Health and Environmental Guidelines for Selected Timber Treatment Chemicals.*

Relevant soil guideline values are discussed in **Section 3.8** (and sampling depths to which these generally apply are outlined in **Section 3.9**). Losses of current and future soil resource caused by cadmium accumulation in pastoral soils are quantified and outlined in more depth in **Sections 5.3 and 6.4**.

3.7 Soil resource pressures

3.7.1 Factors relating to the soil chemistry of cadmium

The soil resource is subject to a wide range of pressures, many of which can have their own impact on the chemistry and rate of cadmium fixation and release. Such processes have the potential to exert various influences on the mobility, bioavailability, plant uptake and toxicity of cadmium, and are reviewed in **Appendix 6**.

3.7.2 Land use factors

A summary of land use by area in the Waikato region is provided in **Appendix 7**. Of the areas listed, cadmium accumulation is likely to be occurring at a reasonably rapid rate in soils under pastoral use (dairy, sheep and beef), arable crops, and horticulture (**Section 6**). Together these soil constitute about **58%** of Waikato region's total land area.

In the eight years from 1994 to 2002, horticultural land use increased by 6 percent across New Zealand, standing at 110,000 hectares in June 2002. Waikato now contains over 10,000 hectares of horticultural land, and has become North Island's third largest horticultural region (after Hawkes Bay and Bay of Plenty).

Over the same period, the area of land in potatoes in the Waikato increased by 28%, from 1,800 to 2,300 hectares. Waikato is now represents the second largest potato growing area of New Zealand, after Canterbury. The substantial increase in potato growing in the Waikato region is significant, because potatoes are the crop which receive the highest cadmium loadings (**Sections 6.3.1** and **6.3.2**).

Soil used for commercial forestry is also accumulating cadmium, but the accumulation rate under this land use tends to be less than one-tenth of the rate for pastoral land uses (**Table 18**). With the addition of production forests, the overall area of land in the Waikato currently accumulating cadmium is about 78%.

At time of writing, work is underway to convert approximately 40000 ha of forested land in the Waikato region to dairy farms. Dynamic changes to land use of this nature underscore the regulatory need to manage cadmium inputs in all areas, not only to horticultural land. Land which is production forest today may be pastoral tomorrow. Land which is pastoral today may be horticultural, or residential, tomorrow.

3.7.3 Summary of soil resource pressures

A summary of identified soil resource pressures and wildcards relating to cadmium accumulation in Waikato surface soils is provided in **Table 4.**

Table 4 **Summary of identified[189] pressures, constraining factors, and wildcards (italics) relating to cadmium accumulation in Waikato soils.**

Category	Pressure or wildcard
Baseline factors (**Appendix 6**)	- Prior history of contamination raising the baseline - Ongoing cadmium accumulation
Soil and plant factors (**Appendix 6**)	- Need for high phosphorus inputs - Natural acidity of Waikato soils - Further acidification of soils through nitrification or natural processes - Upper limit on pH suitable for growing each crop - Loss of soil organic matter under cropping - *Use of dithiocarbamate fungicides* - *Use of facial eczema remedies*
Land use factors (**Section 3.7.2**)	- Amount of Waikato land accumulating cadmium at a reasonably rapid rate (58%) - Need to consider future changes in land use

3.8 Soil guidelines

The recommended upper limit for total cadmium in New Zealand agricultural soil is **1 mg/kg**. The limit above which agricultural soils are considered contaminated is **1.4 mg/kg**. The provenance of these figures is as follows.

3.8.1 Guidelines from 1992 to 2003

Sewage sludge/biosolids disposal

In 1973, the Department of Health (DoH) published a circular entitled *Disposal of Sewage Effluent and Sewage Sludge on Land*.[190] In 1984, a follow-up memorandum was issued, entitled *Disposal of Sewage Sludge on Land*.[191] Further developments ensued, and in 1992, the Department of Health published a more formalised guideline document entitled *Public Health Guidelines for the Safe Use of Sewage Effluent and Sewage Sludge on Land*. This document recommended an upper limit for total soil cadmium of **3 mg/kg**.

Contaminated land

Contemporaneously with this, the Australia and New Zealand Environment and Conservation Council and the National Health and Medical Research Council (ANZECC/NHMRC) developed a list of threshold values for identification of potentially contaminated sites.[192] This is still in fact a draft document even now, but a figure of **3 mg/kg** was nominated as a suitable 'environmental investigation' value for soil cadmium. This was not a risk-based number, but a threshold value taken to be indicative of potential gross site contamination, usually on industrially contaminated sites. It was intended as an indicative value for samples collected from potentially contaminated sites, above which further site-specific investigation was likely to be necessary. However, in the absence of better information, in the ensuing decade, consultancies and regulatory agencies involved in the management of contaminated

[189] Note that this list is not intended to be comprehensive, and that other significant factors may also exist.
[190] New Zealand Department of Health, **1973**. Circular Memorandum No. 1973/132
[191] New Zealand Department of Health, **1984**. Circular Memorandum No. 1984/93
[192] ANZECC/NHMRC, **1992**. *Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites.* Australia and New Zealand Environment and Conservation Council and the National Health and Medical Research Council.

land tended to make use of the ANZECC/NHMRC (1992) environmental investigation value as both a trigger value for further investigation, and a *de facto* 'clean down to' goal for cadmium contaminated land.

3.8.2 Current guidelines

Sewage sludge/biosolids disposal

In late 2003, the New Zealand Water and Wastes Association (NZWWA) released the *Guidelines for the Safe Application of Biosolids to Land in New Zealand* (hereafter, the Biosolids Guidelines).[193] These were developed under the umbrella of a Minister for the Environment's Sustainable Management Fund (SMF) project and represented a substantial updating and revision of the *Public Health Guidelines for the Safe Use of Sewage Effluent and Sewage Sludge on Land*. Guideline development also involved an extended period of public, regulatory and industry consultation. Although these are an industry guideline, and not government policy, they are regarded as an improvement over older documents by the Ministries of Health, Environment, Agriculture and Forestry:

'The Ministries of Environment, Health, and Agriculture and Forestry were represented on the Steering Committee overseeing the development of the Guidelines, but the Guidelines are not published by these Ministries and are not government policy. However, the Ministries consider that the Guidelines improve and expand on the best practice set out in existing guidelines and, in supporting a nationally consistent approach to biosolids management, see value in their adoption and use in New Zealand.'[194]

The Biosolids Guidelines recommend an upper limit for total cadmium in New Zealand agricultural soil of **1 mg/kg**. The rationale for this is set out in Section 5.2.2. (of the Guidelines), which in part reads as follows:

"The soil limit of 1 mg Cd/kg soil is set primarily to minimise Cd concentrations in animal and crop products and to avoid barriers to international trade (failure to meet maximum residue levels and MPCs in food products set by importing countries). It should also be noted that although the current European Community maximum soil limit is 3 mg/kg (CEC, 1986), this value is under review (EC, 1999), and several European countries are already using much lower limits. The most recent European Community draft directive proposes cadmium levels between 0.5 and 1.5 mg/kg depending on soil pH (EC, 2000). It is seen as important that our limits for Cd, in particular, are not substantially higher than that of the European Community, which is an important export market for New Zealand produce."[194]

In other words, the key drivers for recommending a lower limit for soil cadmium were uptake in crops and animals, international best practice, and potential issues over trade barriers.

Unhelpfully, the Biosolids Guidelines do not specify a single soil depth to which this limit should be applied. However, in sampling biosolids (sewage sludge) amended soils, the Biosolids Guidelines do suggest a minimum sampling depth of 10 cm, and a maximum depth of 20 cm. This minimum depth is in keeping with the minimum suggested depth for biosolids incorporation:

> *'Soil incorporation should take place on the same day the biosolids are applied, and biosolids should be incorporated to a depth of at least 100 mm, and preferably 200 mm. (It is acknowledged that a full 200 mm incorporation depth may not be practical unless the land is ploughed). Soil samples for analysis should be taken to the depth of incorporation up to a maximum of 200mm.'*[194]

[193] New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand*.

[194] New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand*.

Sampling depth is therefore related to land use—the activity that has been, is being, or will be carried out. Suggested default sampling depths for soil cadmium on pastoral, horticultural and residential land are outlined in **Section 3.9**.

Contaminated land
Also in late 2003, the Ministry for the Environment released a guideline document[195] which sets out recommended procedures to be followed in selecting guideline values for management of contaminated land, entitled *Hierarchy and Application in New Zealand of Environmental Guideline Values*. This was necessary because New Zealand risk-based values are not available for many contaminants.

A guideline hierarchy is set out in this document. This hierarchy, in order from most to least preferred, is as follows:

1. New Zealand derived risk-based guideline values;

2. Rest of the world derived risk-based guideline values, with preference given to those that employ risk assessment methodologies and exposure parameters consistent with those already used in New Zealand;

3. New Zealand derived threshold values;

4. Rest of the world derived threshold values.

Risk-based human health guidelines are those where the tolerable soil limit is derived on the basis of a scientific methodology which begins with tolerable daily intakes, and takes various exposure routes and sources into account. For soil guidelines, exposure routes include ingestion, inhalation, dermal absorption; sources include soil, and food grown in it. Risk-based guidelines to protect ecological health are derived on the basis of a slightly different methodology involving levels at which adverse environmental endpoints are observed. A review of guideline derivation methodologies by different jurisdictions has been provided by Cavanagh and O'Halloran.[196]

As noted in **Section 3.8.1**, the ANZECC/NHMRC (1992) value of 3 mg/kg was not a risk-based guideline, but a threshold value for environmental investigation. It fits into the third category of the MfE guideline hierarchy.

Other principles of application set out in Section 5.1 of the Hierarchy and Application Guideline include:[195]

- When selecting from a range of overseas guideline values, and in the absence of any site-specific argument, the lowest (most conservative) appropriate guideline value is used;

- Under the Resource Management Act, it is important to consider all receptors (human and ecological) on and near a site.

In relation to procedures adopted in deriving guideline values, it is also seen as important to note that New Zealand takes produce consumption into account as an exposure pathway. This means that in selecting a guideline to use, preference is given to those which also take this pathway into account. UK, Canadian and Dutch criteria are the only ones that include produce consumption as a pathway of exposure.

Relevant UK, Canadian and Dutch criteria for cadmium in residential, agricultural and commercial/industrial soil are provided in **Table 5**.

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195 Ministry for the Environment, **2003**. *Contaminated Land Management Guidelines No.2. Hierarchy and Application in New Zealand of Environmental Guideline Values*.

196 Cavanagh JE and O'Halloran K, **2002**. Overview of international soil criteria and derivation of numeric values. **In**: *Conference Proceedings for the 14th Annual WASTMINZ Conference*, 6–8 November.

Table 5 UK,[197] Canadian[198] and Dutch[199] risk-based guideline values for cadmium in residential, agricultural and commercial/industrial soil.

Jurisdiction	Receptor protected	Residential: normal (with home produce consumption)	Residential: high density (limited or no home produce consumption)	Agricultural	Commercial or Industrial
United Kingdom	Human health	1, 2, 8[a]	30	-	1400
Canada	Human and ecological health	10	-	1.4	22
Netherlands	Human and ecological health	0.8, 12[b]	-	-	-

[a] Figures for sandy soils at pH values of 6, 7, and 8, respectively. Waikato soils are not generally sandy; however, pH natural values average less than 6 and pH is a key control parameter, so the most conservative figure (1 mg/kg) would be applicable for residential soil.

[b] Target value and intervention value, respectively.

In applying the preferred hierarchy,[200] the Canadian CCME value of **1.4 mg/kg** is the lowest applicable value for agricultural soil covering both human and environmental health from a relevant jurisdiction, and emerges as the default value above which New Zealand agricultural soil is currently considered to be contaminated. (This may change in the future as a result of the development of national soil standards by the Ministry for the Environment, but is the figure that applies at time of writing.)

For residential soil in the Waikato region (which is of low soil pH), the default figure is **1 mg/kg** (**Table 5**), the same as the recommended upper limit for agricultural soil. In a regulatory policy context (**Section 1.2.2**), this residential human health protection figure becomes relevant at the point where agricultural land is subdivided for residential use.

Suggested sampling depths appropriate for these guidelines in the New Zealand regulatory context are outlined in **Section 3.9**.

Contaminated land threshold values for a given land use should not be seen as recommended values for soil cadmium, but 'clean down to' targets. For example, an agricultural contaminated land figure of 1.4 mg/kg is not meant to imply that soil can or should be contaminated up to this level. This aspect is also emphasised in the Canadian (CCME) guideline derivation documents.

3.8.3 Limitations of current guidelines

Crop uptake

It is evident on theoretical grounds that neither the applicable contaminated land guideline for agricultural soil (**1.4 mg/kg**), nor the recommended upper limit of **1 mg/kg**, would be sufficiently low to protect against cadmium concentrations in at least a proportion of crops exceeding new food standards, under typical soil pH conditions (Figures **4–7**).

[197] DEFRA and EA (Department of Environment, Food and Rural Affairs and Environment Agency), **2002**. *Assessment of Risks to Human Health from Land Contamination: An overview of the development of soil guideline values and related research*. Report CLR 7. Bristol, UK: Environment Agency.

[198] CCME (Canadian Councils for Ministers for the Environment), **2002**. *Canadian Environmental Quality Guidelines*. Available from: http://www.ccme.ca/publications/can_guidelines.html

[199] Ministry of Housing, Spatial Planning and the Environment, **2000**. *Circular on Target Values and Intervention Values for Soil Remediation*. Bilthoven, The Netherlands: Ministry of Housing, Spatial Planning and the Environment. Available from: http:www.vrom.nl/international

[200] Ministry for the Environment, **2003**. *Contaminated Land Management Guidelines No.2. Hierarchy and Application in New Zealand of Environmental Guideline Values*.

In work previously cited[201] (**Section 3.5.2**), it was found that current cadmium food standards were exceeded (in 1995) in a small but significant proportion of lettuce, onion, and potato crops grown in South Auckland market gardens, and a substantial proportion of wheat samples grown in mid-Canterbury arable farms. A notable aspect of this previous work was the fact that soil cadmium concentrations associated with these exceedances were all below 1 mg/kg. The highest soil cadmium level observed in the 90 market garden samples was 0.85 mg/kg; and the highest over 70 wheat farms sampled in 1995 was 0.69 mg/kg.

Land use change

It is also evident that remaining below the contaminated land limit for agricultural soil of 1.4 mg/kg will not necessarily protect a property owner against the need to remediate land prior to subdivision. During subdivision application, Territorial Authorities have the responsibility for ensuring that land is suited to its new intended purpose (**Section 1.2.2**), and (for contaminants) this assessment is made with respect to human health guideline values. For agricultural-to-residential land use changes, the applicable risk-based guideline values for residential soil will usually default to 1 mg/kg at a pH value of below 6 (**Table 5**).

The need to safeguard the agricultural soil resource to enable its future use for non-agricultural activities[202] reiterates the general point that some reasons for needing to limit soil cadmium are extrinsic to agriculture.

3.8.4 Summary

A summary of regulatory control needs and applicable soil cadmium guideline values relating to each need is provided in **Table 6**.

Table 6 Soil cadmium guideline values (mg/kg dry weight) based on desired control need.

Control need	Residential soil	Pastoral soil	Horticultural soil
Protection of human and ecological health (human part with home produce consumption)	1.0 (pH 6)[a]	1.4[b]	1.4[b]
Safeguarding future land uses (conversion of horticultural or pastoral to residential, or conversion of pastoral to horticultural)[b]	1.0 (pH 6)[a]	1.0 (pH 6)[a]	1.0 (pH 6)[a]
Possible requirements of trading partners[c]	none	1.0[d]	1.0[d]
Protection against breaking of food standards	undefined	undefined	undefined

[a] DEFRA and EA (Department of Environment, Food and Rural Affairs and Environment Agency), **2002**. *Assessment of Risks to Human Health from Land Contamination: An overview of the development of soil guideline values and related research*. Report CLR 7. Bristol, UK: Environment Agency. Selected from applicable international values by following recommended best practice approach as outlined in Ministry for the Environment, **2003**. Contaminated Land Management Guidelines No.2. Hierarchy and Application in New Zealand of Environmental Guideline Values.

[b] CCME (Canadian) Environmental Quality Guideline for protection of human and ecological health. Selected from applicable international values by following recommended best practice approach as outlined in Ministry for the Environment, **2003**. Contaminated Land Management Guidelines No.2. Hierarchy and Application in New Zealand of Environmental Guideline Values.

[c] In this case all land-uses would take on the guideline value for the most sensitive use.

[d] New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand*, Section 5.2.2.

[201] Roberts AHC, Longhurst RD and Brown MW, **1995**. *Cadmium Survey of South Auckland Market Gardens and Mid Canterbury Wheat Farms.* Report prepared for the New Zealand Fertiliser Manufacturers Research Association. AgResearch: Hamilton.

[202] Consistent with Environment Waikato operative policy goals: see **Section 1.1**

3.9 Sampling depth in relation to soil guidelines

3.9.1 Overview

As noted in **Section 3.2.3** and elsewhere, concentrations of cadmium in agricultural soils tend to decrease with depth, with the rate of leaching and depth of penetration being dependent on soil type and rainfall. This being the case, it is important to specify sampling depth when making comparisons to soil guideline values. Guidelines for soil cadmium are reviewed in **Section 3.8**. An outline of relevant sampling depths in relation to soil guidelines is provided in this section.

Some common depths for soil sampling are as follows:

- Common (though not exclusive) sampling depths for pastoral and horticultural soils in New Zealand are 0-7.5 cm and 0-15 cm, respectively. In pastoral soils, the depth of 0-7.5 cm is said to incorporate the bulk of the grass root-zone.[203] In horticultural soils, the zone of significant root mass is deeper. With the exception of orchards and vineyards, most horticultural soils are also ploughed routinely, causing regular mixing to a depth of at least 15 cm.[203]

- In the Waikato Regional Soil Quality Monitoring Programme, a sampling depth of 0-10 cm was adopted as a compromise between pastoral and horticultural sampling depths. For Waikato soils, the soil A horizon (the topsoil) also tends to extend further than 10 cm, so that soil sampled to a depth of 10 cm is always topsoil.[203]

- Common sampling depths for assessing contamination of residential soils are 0-7.5 cm for lawns, and 0-15 cm for vegetable gardens.[204]

Most regulatory soil guidelines for contaminants are not accompanied by information about the sampling depth to which they should apply.[205] However, some general guidance on sampling depth for investigation of contaminated land is provided in a best practice document recently released by the Ministry for the Environment.[204] One excerpt (which relates most closely to guidelines designed to protect human health in residential soils) reads:

> *'The collection of surface soil samples deeper than 15 cm increases the possibility of dilution of the surface soil sample by mixing with less contaminated subsurface soils. Depths of surface soil samples will be dependent on the DQOs [Data Quality Objectives], and 0-7.5 cm is commonly used to represent the direct human exposure pathway, whereas 0-15 cm is commonly used to represent the home produce exposure pathway, because the latter covers the significant root zone.'*[204]

When assessing soil contamination, the common approach of regulatory agencies has been to select a sampling depth that makes sense in relation to type of guideline being specified, given the current or proposed land use. The two most common types of soil guideline are those designed to protect ecological health and productive capacity of the soil itself (*e.g.* prevention of toxicity to plants), and those designed to protect human health.[206] Appropriate sampling depths for each type of guideline essentially depend on assumptions that were made about exposure pathways (for the contaminant concerned) in guideline derivation, also allowing for expected soil mixing practices.

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203 Hill R, Environment Waikato, **2004**. Personal communication.

204 Ministry for the Environment, **2004**. *Contaminated Land Management Guidelines No. 5: Site Investigation and Analysis of Soils,* Section 3.6.2. Available from: http://www.mfe.govt.nz/publications/hazardous/#guides2

205 Guidelines covering gasworks and petroleum hydrocarbon contamination is soils are a notable exception: in this case, guideline values are specific for different soil types and depths *e.g.* Ministry for the Environment, **2004**. *Guidelines for assessing and managing petroleum hydrocarbon contaminated sites in New Zealand*. Available from: http://www.mfe.govt.nz/publications/hazardous/#guides2

206 Ecological guidelines are usually employed prospectively, as values that should not be exceeded. By contrast, human health guidelines are often employed retrospectively, as remediation ('clean down to') standards on properties being subdivided.

For human health guidelines, standard exposure pathways include a surface-contact component (direct soil ingestion, normally represented by the 0-7.5 cm soil depth) and a component representing ingestion of home-grown produce (normally represented by the 0-15 cm depth). In the case of ecological guidelines, the applicable sampling depth will generally be the zone which encompasses the majority of productive soil activity.

3.9.2 Pastoral soils

The standard sampling depth used in pastoral soil fertility testing[207] is 0-7.5 cm. This range was also employed as the main reporting depth in the most extensive previous survey of cadmium in New Zealand pastoral soils, carried out by Roberts and Longhurst *et al* in 1992.[208]

By contrast, in a separate New Zealand survey involving comparison of archived (pastoral and horticultural) soils with their modern counterparts (**Section 3.3**),[209] most of the modern samples were collected to a depth of 15 cm. However, this was an unusual case where the design of the research precluded shallower samples. This was because the old archived soils had generally been collected to a depth of 6 inches, and new samples had to be collected to the same depth for purposes of comparison.

Interestingly, although it is likely that cadmium concentrations are significantly lower in 7.5-15 cm soils than the surface 0-7.5 cm, comparison of the results of the two New Zealand surveys outlined above provides no positive evidence of this. For farmed soils, the average result for 58 deeper (mainly 0-15 cm) samples in one survey (0.85 mg/kg) was twice the average reported for 312 shallower (0-7.5 cm) samples in the other (0.44 mg/kg). Both surveys were New Zealand-wide and undertaken across a range of major soil groups. However, direct comparison between the two surveys may not be valid, because the work involving archived soils probably contains some inherent bias towards properties on 'easy and accessible' land that were settled early, and dairy farms[210] (**Section 3.3**). In part of this work (**Section 6.4.3**), when assessing the suitability of pastoral land (sampled to 10 cm) for future horticultural use (relevant depth usually 15 cm), a conservative correction is made for depth, by assuming that cadmium is present only at natural background concentrations in the 10-15 cm layer.

On the other hand, there is evidence that in pastoral soil, cadmium concentrations tend to be higher in the immediate surface soil zone of 0-2.5 cm than deeper soils. As part of their extensive New Zealand-wide survey of 1992, Roberts *et al.*[208] noted that:

> *'Total soil Cd showed the same pattern for the two sampling depths 0-2.5 and 2.5-7.5 cm, although Cd contents were generally lower in the deeper samples.'*

As an ongoing default position, it is suggested that for pastoral soils, **0-7.5 cm** is an appropriate sampling depth for soil cadmium. This sampling depth best fits soil cadmium guidelines that might be applied to both the current land use (pastoral farming) and the most sensitive of future land uses (subdivision of the land for rural-residential use) (see below).

3.9.3 Residential soils

Residential soils can be assessed from two directions, before and after subdivision. Where contamination is suspected, recognised best practice is to assess soils to ensure lack of contamination (or remediation to a residential standard) before a subdivision is allowed to proceed. In these cases, sampling depth is partly in relation

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207 Chapman R, Soil and Land Evaluation, **2004**. Personal communication.

208 Roberts, A.H.C.; Longhurst, R.D.; Brown, M.W., **1994**. Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research*, Vol. 37(1), pp 119-29; also Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.

209 Taylor MD, **1997**. Accumulation of cadmium derived from fertilizers in New Zealand soils. *Science of the Total Environment*, Vol. 208, No. 1,2, pp 123-126

210 Taylor M, Landcare Research, **2004**. Personal communication. The former is because the samples were archived soils, and sample collection partly relied on ease of access in the early days.

to the past land use: in well-mixed horticultural soils, a depth of 15 cm might be applicable, whereas in pastoral soils, a depth of 7.5 cm might be more appropriate. These two sampling depths are also generally employed in cases where contamination is suspected after subdivision: 0-7.5 cm for lawns, and 0-15 cm for vegetable gardens.[211]

When assessing the suitability of unmixed soils for residential subdivision, or compliance with guidelines after subdivision, a case might be made that a more shallow soil depth than 7.5 cm (or 10 cm) could apply, based on the finding of Roberts *et al.*[212] that cadmium concentrations are higher in the immediate 0-2.5 cm surface soil. However, in acidic soils, exposure through ingestion of home-grown produce becomes the dominant factor in determining the acceptable soil guideline value (see **Section 3.5.1**), and this exposure pathway relates mostly to the plant root zone. Under such conditions, the direct soil ingestion pathway has lesser significance. In addition, once the source of cadmium (phosphate fertiliser) is discontinued at point of subdivision, the concentration gradient of cadmium down the soil profile is likely to become less marked over time, due to gradual leaching. This is relevant because residential soil guidelines generally assume an exposure period of 30 years.

For these reasons, it is suggested that a sampling depth of **0-7.5 cm** (rather than 0-2.5 cm) should generally remain an appropriate screening depth for assessing cadmium contamination in residential lawns, or possible conversion of pastoral or unmixed horticultural land for residential use. This approach is adopted in this work. However, it is recognised that there will be some residual uncertainty on this point, given a finding of higher cadmium concentrations at 0-2.5 cm than 0-7.5 cm. Regulators would be within their rights to request more shallow samples in relation to cadmium in residential lawns.

3.9.4 Horticultural soils

In working horticultural soils, a sampling depth of 0-15 cm is common.[213] The shallower depth range of 0-7.5 cm has also been employed in sampling horticultural soils, particularly where the purpose of surveying was to assess the suitability of the land for residential subdivision (**Table 2**).[214] In ploughed horticultural soils, a sampling depth of 0-7.5 cm is expected to yield reasonably equivalent results to a sampling depth of 0-15 cm. As a default position for screening purposes, it is suggested that for horticultural soils:

1. Where the horticultural soil is well-mixed by routine ploughing, sampling depths of **0-7.5 cm**, **0-10 cm**, or **0-15 cm** would all be appropriate for assessing compliance of horticultural soils with agricultural and residential guideline values for soil cadmium.

2. In other cases where mixing is limited (for example, most orchards and vineyards):

   - A sampling depth of **0-15 cm** would be appropriate for assessing soil quality against agricultural guidelines;

   - A sampling depth of **0-7.5 cm** would probably be more appropriate when assessing future uses of the soil resource.

[211] Ministry for the Environment, **2004**. *Contaminated Land Management Guidelines No. 5: Site Investigation and Analysis of Soils,* Section 3.6.2. Available from: http://www.mfe.govt.nz/publications/hazardous/#guides2

[212] Roberts, A.H.C.; Longhurst, R.D.; Brown, M.W., **1994**. Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research*, Vol. 37(1), pp 119-29.

[213] Roberts AHC, Longhurst RD and Brown MW, **1995**. *Cadmium Survey of South Auckland Market Gardens and Mid Canterbury Wheat Farms.* Report prepared for the New Zealand Fertiliser Manufacturers Research Association. AgResearch: Hamilton.

[214] *e.g.* Gaw SK, **2002**. Pesticide Residues in Horticultural Soils in the Auckland Region. Auckland Regional Council Working Report No. 96; Gaw SK, **2003**. Historic pesticide residues in horticultural and grazing soils in the Tasman District; Gaw SK, **2003**. *Historic pesticide residues in horticultural and grazing soils in the Waikato Region*. Environment Waikato Document **835071**

3.9.5 Treatment of sampling depth in this work

In making comparisons in this work, between recent survey data for soil cadmium and soil guidelines for cadmium (**Sections 5**), care has been taken to ensure that the sampling depths are directly applicable, or conservative, in relation to the guideline values used.

In this work, one limited but growing dataset referred to involves pastoral and horticultural samples collected to 10 cm depth, as part of the Waikato Regional Soil Quality Monitoring Programme (**Section 5**). It is recognised that this comparison may err toward being slightly conservative for some pastoral soils and unmixed horticultural soils, where it could be argued that the guideline might more closely apply to a sampling depth of 0-7.5 cm. This implies that the real rate of cadmium accumulation in Waikato surface soils as estimated in this report may be slightly understated in some cases.

Further, for assessing the future land use option of subdivision to residential land, it might be suggested that information about current cadmium concentrations in the near-surface (*e.g.* 0-2.5 cm) may have relevance. An assumption made in this work is that 0-7.5 cm is a suitable depth for screening purposes, for the reasons outlined in **Section 3.9.3**.

4 Previous management initiatives

4.1 General

The problem of cadmium accumulation in New Zealand agricultural soils was first identified three decades ago, in the early 1970s (**Section 3.2.2**). Until recently, it would appear that the underlying sustainability issue may have been under-estimated,[215] partly as a result of a high food standard, itself probably designed to protect against acute cadmium poisoning of the type observed in the 1920s and 1930s (**Section 2.4.1**). It has been noted that the previous standard of 1 mg/kg in most food[216] was the mean concentration of cadmium in rice in the *itai itai* case, and genuine protection for susceptible individuals always relied upon the fact that actual cadmium levels in most foods were at least an order of magnitude below this value. Results of previous surveys which confirmed compliance with the food standard[217] therefore carried no information about chronic risk.

With the move to risk-based food standards[218] and lowered soil guideline values (**Section 3.8.2**), the results of previous research now look less encouraging (**Section 3.5.2**).

It would be fair to say that the non-sustainability of the cadmium accumulation issue has been emphasised by scientific researchers in the last decade (**Section 3.1**; **Appendix 5**). However, policymakers and regulatory agencies have been slow to appreciate the largely irreversible nature of soil resource depletion that is occurring. A need to strengthen the relationship between science and environmental policy has recently been identified by the Parliamentary Commissioner for the Environment.[219] With the exception of scientific research to define the problem, initiatives to address the cadmium accumulation issue have been modest. To date, policymakers have been

[215] Furness H, **1996**. New Zealand in danger of over-reacting to cadmium issue. *Fertiliser Matters.* Issue 2 (March), pp 2-3.
[216] New Zealand Food Regulations, **1984**.
[217] Roberts AHC, Longhurst RD and Brown MW, **1995**. *Cadmium Survey of South Auckland Market Gardens and Mid Canterbury Wheat Farms.* Report prepared for the New Zealand Fertiliser Manufacturers Research Association. AgResearch: Hamilton.
[218] Section 1.4.1 of the Food Standards Code: http://www.foodstandards.gov.au/foodstandardscode/index.cfm
[219] Parliamentary Commissioner for the Environment, **2004**. *Missing Links: Connecting science with environmental policy* (September 2004). Available from: http://www.pce.govt.nz/reports/allreports/1_877274_52_6.shtml.

willing to accept an industry-led assurance that the issue can be appropriately managed through a voluntary accord supplemented by further research.[220,221]

4.2 Voluntary industry accords

4.2.1 Fertiliser industry

The New Zealand Fertiliser Manufacturers' Research Association Inc (*Fert Research*) represents the two main New Zealand manufacturers of superphosphate fertiliser, Ballance Agri-Nutrients Ltd and Ravensdown Fertiliser Co-operative Ltd. The two member companies manufacture, distribute and market around 90% of all fertiliser sold in New Zealand.[222]

These manufacturers have adopted a voluntary limit for cadmium in New Zealand superphosphate of 280 mg/kgP.
Three different interchangeable units are in use to describe the trace element content of phosphate fertilisers: mg/kg, mg/kgP, and mg/kgP_2O_5. Conversions between the three as they apply to the voluntary limit for cadmium in superphosphate of 280 mg/kgP are indicated in **Table 7**.

Table 7 Phosphate content and the voluntary industry limit for cadmium in New Zealand phosphate fertilisers, expressed in various units.

Variable	Single/double superphosphate	Triple superphosphate
Phosphate content as %P_2O_5	18 to 21 (20 assumed)	45
Phosphate content as %P	8.73	19.6
Voluntary cadmium limit: expressed as mgCd/kgP	280	280
Voluntary cadmium limit: expressed as mgCd/kgP_2O_5	122	122
Voluntary cadmium limit: expressed as mgCd/kg fertiliser	24.4	55.0

The voluntary limit is said to represent a reduction in the cadmium content of phosphate fertilisers by one-third. Progressive reduction to this new level was initiated in 1997.[223] Adherence to the voluntary limit for cadmium in superphosphate is monitored by audit under the Fertiliser Quality Council's *Fertmark* scheme.[224]

It is unclear based on empirical surveying whether the reduction in concentration has translated to a net decrease in the accumulation rate of cadmium in soils. Use of phosphate fertilisers follows economic trends: during some years prior to the reduction in cadmium content, use of fertilisers were depressed due to economic downturn. The situation in recent years has reversed, with a significant proportion of dairy and cropping farms routinely receiving more annual phosphorus than is required to maintain productivity.[225]

Despite this, loading estimates suggest that current cadmium accumulation rates are lower than the previous average rate for the period 1939-2002 (**Section 6.4.6**).

[220] Ministry for the Environment, **1997**. *The State of New Zealand's Environment 1997. Chapter 8 – the State of our Land.*
[221] Furness H, **1996**. *Cadmium in New Zealand: Its Presence and Management.* New Zealand Fertiliser Manufacturers Research Association, Auckland.
[222] Fert Research, **2004**. http://www.fertresearch.org.nz/
[223] Ministry for the Environment, **1997**. *The State of New Zealand's Environment 1997. Chapter 8 – the State of our Land.*
[224] Fert Research, **2002**. Addenda to the Code of Practice for Fertiliser Use. Available from: http://www.fertresearch.org.nz/attachments/document/UpdatedCodeAddenda.pdf
[225] Singleton P, Environment Waikato, **2004**. Personal communication.

The fertiliser industry are to be commended for taking a proactive approach to the sustainability issue associated with cadmium. However, retrospectively, the one-third reduction in fertiliser cadmium has not translated to much of an improvement in terms of regulatory compliance in 2005, and in fact the reverse has occurred. This is mainly because international and New Zealand developments have seen a reduction in cadmium limits deemed to be acceptable for both soil and food (**Sections 3.8** and **4.3**).

According to the Ballance Agri-Nutrient fact sheet for cadmium,[226] it will take an estimated 27 years before soil of average New Zealand dairy pasture exceeds 1 mg/kg. An estimate for Waikato dairy soils, made in this work, is 17 years (**Section 6.4.3**). Implications of pastoral soils exceeding this guideline are outlined in **Sections 3.6** and **6.4.3**: these include possible hindrances to international market access, and inability to subdivide a property for residential or rural-residential use.

In 1998, *Fert Research* released a Code of Practice for Fertiliser Use. In 2002, eight Addenda were added to this Code of Practice, the last of which[227] is entitled *'Cadmium in New Zealand—Its Presence and Management.'* This document is similar to the Ballance Agri-Nutrients online fact-sheet for cadmium.[228] Both documents contain useful information, but at time of writing, are out of date in relation to a number of central points.[229]

Addendum 8 to the Code of Practice states that farmers have an obligation to develop their own *Cadmium Management Plans*. Yet, it is doubtful that many farmers are even aware of the issue. One use of Addendum 8 may be to provide protection against industry liability for land which does become contaminated with cadmium as a result of fertiliser use.[230]

4.2.2 NZWWA

As outlined in **Section 3.8.2**, the New Zealand Water and Wastes Association (NZWWA) are the industry body responsible for release of the Biosolids Guidelines in late 2003.[231] These represent a substantial revision and updating of the *Public Health Guidelines for the Safe use of Sewage Effluent and Sewage Sludge on Land*.

NZWWA are involved in this issue as a result of a desire to find alternative options to landfill disposal of sludges produced from sewage treatment. The Ministries of Environment, Health, and Agriculture and Forestry consider that the Biosolids Guidelines improve on the best practice set out in previous documents.[231]

In developing the Biosolids Guidelines, reviews were carried out on recommended upper limits for metals in soils. As part of this process, a limit of **1 mg/kg** for soil cadmium was adopted on the basis of uptake in crops and animals, international best practice, and potential issues over trade access. (Suggested default soil depths to which this guideline would apply are given in **Section 3.9**.)

4.3 Recent initiatives

4.3.1 Recent European assessments

The European Community is one of New Zealand's market access areas. Detailed risk assessment reports on cadmium in fertilisers have recently been produced by all EC

226 Ballance Agri-Nutrients, **2005**. Fact sheet for cadmium.; accessed 10 August 2005. Available from: http://www.ballance.co.nz/fscadmium.html
227 Fert Research, **2002**. Addenda to the Code of Practice for Fertiliser Use. Available from: http://www.fertresearch.org.nz/attachments/document/UpdatedCodeAddenda.pdf
228 Ballance Agri-Nutrients, **2005**. Fact sheet for cadmium.; accessed 10 August 2005. Available from: http://www.ballance.co.nz/fscadmium.html
229 Including reference to the former food standard, and use of the former guideline for soil cadmium.
230 Applicable guidelines are outlined in **Section 3.8**.
231 New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand*.

member states (Austria, Belgium, Denmark, France, Finland, Germany, Greece, Ireland, Sweden and the United Kingdom) and also Iceland and Norway.[232] The European Commission's Scientific Committee on Toxicity, Ecotoxicity and the Environment (SCTEE) was asked to review these reports and prepare an opinion on the need for regulation in relation to this issue. This opinion was delivered in September 2002.[233] In this opinion, the European Commission's SCTEE has determined that:

'Despite the differences in assumption made by Member States for values of input variables, it is scientifically justified to conclude that the modelling of cadmium accumulation in agricultural soils in the various assessments suggests the following consistent trends:

- *For low fertilizer cadmium concentrations (between 1 to 20 mg Cd/kg P_2O_5), cadmium in soil tends to accumulate relatively slowly, or decreases after 100 years of application due to net removal rates (leaching, crop uptake) exceeding inputs;*

- *For fertilizer with Cd concentrations of 60 mg/kg P_2O_5 and above, accumulation in agricultural soils over 100 years is relatively high.'*

4.3.2 Fertiliser cadmium content required to prevent further accumulation in soils

Based on the evidence presented in the member state reports and some additional calculations, the European Commission's SCTEE determined that long-term cadmium accumulation in soils is expected where fertilisers contain 60 mg/kg P_2O_5 or above. Due to the combined effect of minor losses, soil accumulation was not expected to occur where fertilisers contain 20 mg Cd/kg P_2O_5 (4 mg/kg as superphosphate) or less.

The New Zealand fertiliser industry has also carried out work in this area, and reports that preventing further accumulation in New Zealand soils would require an 80% reduction in the cadmium content of superphosphate fertiliser.[234]

'To prevent cadmium accumulation in soil, phosphate fertiliser would need to contain about 50 mg Cd/kg P i.e. *an approximate 80% reduction of the current voluntary standard of 280 mg Cd/kg P.'*

European and New Zealand estimates are compared in **Table 8**. The US experience is that long-term application of low-cadmium phosphates has seen very little accumulation in US soils, and data for US superphosphate is also given in **Table 8**.

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232 Citations to these report are too extensive to list individually in footnote form. All reports from individual EC member states and EEA member states on the issue of cadmium in fertilisers are available in PDF from the European Commission website: http://europa.eu.int/comm/enterprise/chemicals/legislation/fertilizers/cadmium/reports.htm

233 European Commission Scientific Committee On Toxicity, Ecotoxicity And The Environment (CSTEE), **2002**. *Opinion on Member State assessments of the risk to health and the environment from cadmium in fertilizers*. 33rd CSTEE plenary meeting, Brussels, 24 September 2002. European Commission Directorate-General Health And Consumer Protection Directorate C - Scientific Opinions, Unit C2. Scientific Committee on Toxicity, Ecotoxicity and the Environment. Available at: http://europa.eu.int/comm/enterprise/chemicals/legislation/fertilizers/cadmium/sctee.pdf

234 Ballance Agri-Nutrients, **2005**. Fact sheet for cadmium. Available from: http://www.ballance.co.nz/fscadmium.html

Table 8 **Estimates of the amount of cadmium fertiliser would need to reach a point of no further cadmium accumulation in soils, expressed in various units.**

	Cadmium content in phosphate fertiliser		
	In mgCd/kgP	In mgCd/kgP_2O_5	In mg/kg (ppm) as superphosphate fertiliser
Current voluntary limit for New Zealand	280	122	24
No accumulation threshold: European Commission's SCTEE estimate[a]	46	20	4
No accumulation threshold: New Zealand fertiliser industry estimate	56	24	5
Reported content in US superphosphate (where accumulation not an issue)[b]	36	16	3

Notes:
a. Reference: see footnote 233
b. McBride MB and Spiers G, **2001**. Trace element content of selected fertilizers and dairy manures as determined by ICP–MS. *Communications in Soil Science and Plant Analysis*, Vol. 32, Nos. 1-2, pp 139-156.

The New Zealand fertiliser industry estimate that an 80% reduction in cadmium content would be required to prevent further accumulation in soils is therefore in good agreement with external data from the EC and US.

5 Current soil status

5.1 Observed soil cadmium concentrations

Recent cadmium concentrations measured in Waikato soils, and summary statistics, are provided in **Tables 9** and **10**. Data in **Table 9** is mainly taken from a 32 element ICP-MS assay of soil samples undertaken as part of the Waikato Regional Soil Quality Monitoring Programme,[235] with 15 additional samples coming from a separate survey of mainly pastoral soils.[236] Data in **Table 10** is taken from a survey of contaminants on Waikato horticultural properties, carried out by the University of Waikato in work commissioned by Environment Waikato.[237] In the few cases where cadmium was not detected to a detection limit of 0.1 mg/kg, concentrations were set to equal half the detection limit for purposes of calculation of summary statistics.

235 Environment Waikato Document **844227**.
236 Environment Waikato Documents **988316, 927529 and 983201**.
237 Gaw SK, **2003**. *Historic pesticide residues in horticultural and grazing soils in the Waikato Region*. Environment Waikato Document **835071**.

Table 9 Cadmium concentrations in soil samples collected from throughout the Waikato region in 2001–2003, mainly as part of Environment Waikato's Regional Soil Quality Monitoring Programme.

Sampling depths: 0-10 cm for 46 samples and 0-7.5 cm for 15 samples (see **Section 3.9**).

	Soil cadmium concentrations by land use (mg/kg dry weight)					
	Arable	Horticultural	Pastoral	Pastoral (continued)	Forest	Reserve or equivalent
	<0.1	0.20	0.11	0.76	<0.1	0.19
	0.50	0.20	0.17	0.79	<0.1	0.20
	0.60	0.40	0.20	0.80	0.20	0.20
	0.60	0.50	0.30	0.80	0.60	0.23
	0.70	0.50	0.37	0.80		
	0.80	0.60	0.40	0.80		
	0.80	0.80	0.47	0.80		
	0.80	0.80	0.59	0.80		
	0.90	0.80	0.59	0.80		
		0.80	0.60	0.80		
		1.00	0.60	0.81		
		1.30	0.60	0.90		
			0.60	0.90		
			0.62	1.00		
			0.69	1.00		
			0.70	1.01		
			0.70	1.20		
			0.70	1.50		
Summary statistics						
N	9	12		36	4	4
Mean (mg/kg)	0.64	0.66		0.70	0.23	0.21
Median (mg/kg)	0.70	0.70		0.70	0.13	0.20
Standard deviation (mg/kg)	0.25	0.32		0.28	0.26	0.02
Maximum (mg/kg)	0.90	1.30		1.50	0.60	0.23
Percent equal to or exceeding 1.0 mg/kg	0	17		14	0	0

Table 10 Cadmium concentrations in soil samples collected in 2003 as part of a survey of contaminants in Waikato horticultural areas.[238]

Sampling depth: 0-7.5 cm (see Section 3.9).

	Soil cadmium concentrations by land use (mg/kg dry weight)			
	Horticultural	Horticultural (continued)	Pastoral	Reserve
	0.2	0.6	0.5	<0.1
	0.2	0.6	0.6	<0.1
	0.2	0.7	0.6	<0.1
	0.3	0.7	0.6	<0.1
	0.3	0.8	0.7	0.2
	0.3	0.9	0.7	0.2
	0.3	0.9	1.5	0.3
	0.4	1.0		
	0.5	1.0		
	0.5	1.0		
	0.5	1.0		
	0.5	1.2		
	0.5	1.2		
	0.5	1.2		
	0.6	1.5		
	0.6			
Summary statistics				
N		31	7	7
Mean (mg/kg)		0.67	0.74	0.14
Median (mg/kg)		0.60	0.60	0.10
Standard deviation (mg/kg)		0.34	0.34	0.09
Maximum (mg/kg)		1.50	1.50	0.30
Percent equal to or exceeding 1.0 mg/kg		26	14	0

Results of the two recent surveys are remarkably similar (**Tables 9** and **10**).

- Pastoral soils: the average cadmium concentration in recent Waikato pastoral soils was **0.70 mg/kg** from one survey (sampling depth mainly 10 cm) and also **0.74 mg/kg** from the other (sampling depth 7.5 cm);

- Horticultural soils: the average cadmium concentration in recently sampled Waikato horticultural soils is **0.66 mg/kg** from one survey (sampling depth mainly 10 cm) and **0.67 mg/kg** from the other (sampling depth 7.5 cm);

- The highest value found in both surveys was **1.5 mg/kg**.

Some of the properties sampled in the horticultural soils survey (which was carried out under a condition of owner anonymity) may have also been sampled as part of the Regional Soil Quality Monitoring Programme. However, properties that were sampled in both surveys are likely to comprise a small proportion of the overall data set, and results from the two pieces of work are very similar. For this reason, data from the two surveys will be merged for comparison to relevant guideline values (see also comments in **Section 3.9** on sampling depths). The mid-point sample collection date for this merged data is the year 2003. A table of merged data (N=110 samples) is given in **Appendix 8**.

[238] Gaw SK, **2003**. *Historic pesticide residues in horticultural and grazing soils in the Waikato Region*. Environment Waikato Document **835071**. Raw data also supplied by Gaw SK, University of Waikato, **2004**. Personal communication.

In terms of overlapping confidence intervals, the means for arable, pastoral, and horticultural land are actually statistically indistinguishable from each other. Overall summary statistics for 95 samples covering all three of these land uses are provided in **Table 11**.

Table 11 **Summary statistics for cadmium concentrations in pastoral, horticultural and arable soils of the Waikato region, 2003.**

Sample depths relate to surface soil (0-7.5 cm and 0-10 cm): and represent data sets that were merged on the basis that cadmium results are statistically indistinguishable (see text and Appendix 9).

Variable	Value
N	95
Mean (mg/kg)	0.68
Standard deviation (mg/kg)	0.30
Geometric mean (mg/kg)	0.60
Median (mg/kg)	0.70
Maximum (mg/kg)	1.50

As has been observed and reported previously, cadmium concentrations in Waikato soils are strongly correlated with those of total phosphorus, in samples where both variables were measured ($N=66$, $R=0.758$, $p<0.0001$). The high correlation means that where the total concentration of soil phosphorus is known, an *approximate* estimate of the cadmium concentration can be made by using the linear regression equation:

$$\ln[Cd]\ (\mu g/kg) = 0.9892\ln[P]\ (mg/kg) - 1.0306$$

Soil cadmium concentrations should start to exceed 1 mg/kg once the **total** (not Olsen) phosphorus content exceeds approximately 3050 mg/kg.

5.2 Soil quality in relation to guideline values

5.2.1 Overall picture

Guideline values for soil cadmium were reviewed in **Section 3.8** and summarised in **Tables 5-6.** These are a contaminated land threshold for agricultural land of 1.4 mg/kg, and a recommended limit for agricultural soils (and human health protection value for residential soils) of 1.0 mg/kg. Percentages of samples exceeding each of these guidelines are given in **Table 12**.

Table 12 **Percentages of samples exceeding relevant guidelines for soil cadmium in Waikato arable, horticultural, and pastoral soils.**

Source data is provided in Appendix 8.

Guideline type	Numeric value	Percentage of samples exceeding relevant guideline			
		Arable	Horticultural	Pastoral	Reserve
Contaminated agricultural land threshold	1.4 mg/kg	0	2.3	4.7	0
Recommended guideline for agricultural and residential soils	1.0 mg/kg	0	23.3	14.0	0

5.2.2 Horticultural soils

Only one of the horticultural properties sampled triggered the regulatory threshold for contaminated land (1.4 mg/kg). However, about one-quarter (23%) of sampled horticultural properties exceeded the recommended upper limit for agricultural soil of 1 mg/kg. **Figure 8** is a histogram of soil cadmium levels found for Waikato horticultural properties.

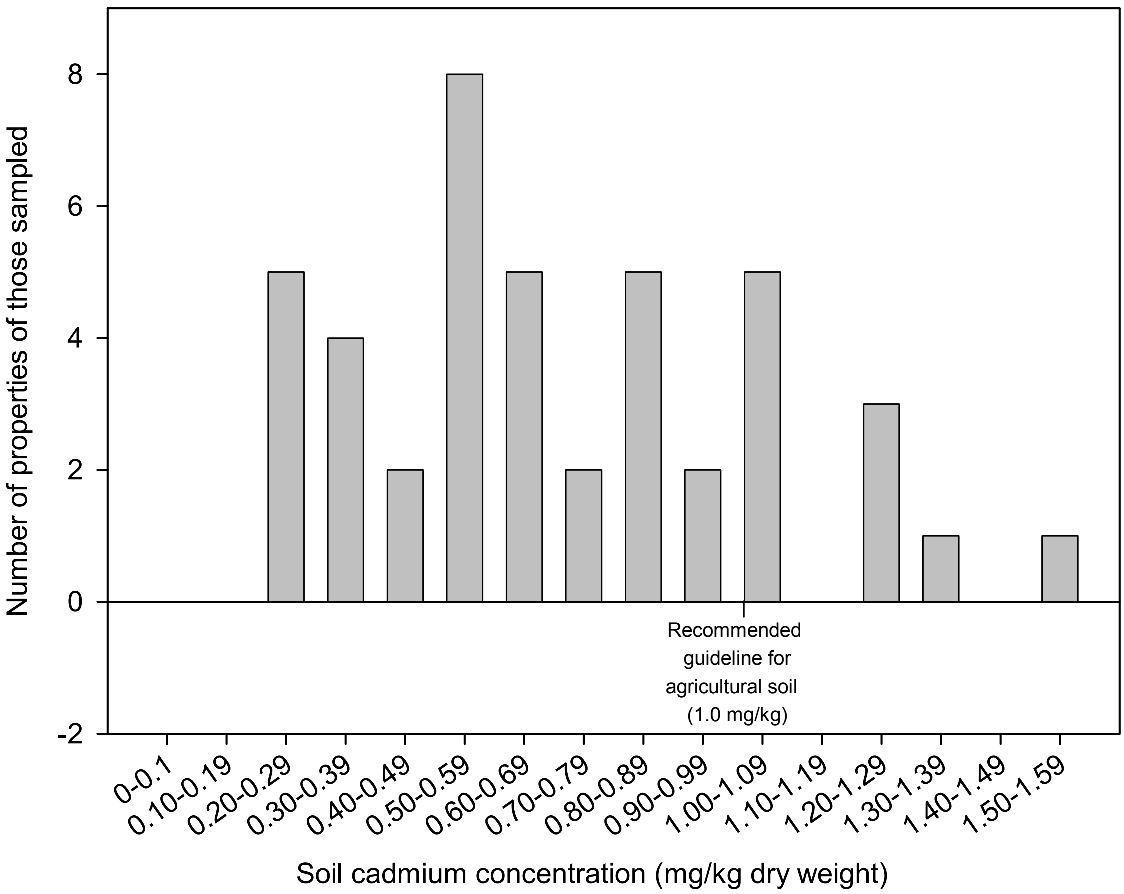

Figure 8 Histogram of soil cadmium levels found for Waikato horticultural soils (N=43) sampled 2001-2003.

The 23% figure is based on raw exceedances of 1 mg/kg cadmium in properties sampled, and does not take the underlying sample distribution in to account. Based on a percentile analysis of the log-normalised data for horticultural cadmium, it is estimated that somewhere between 13-22% (best estimate **17.5%**) of the underlying horticultural soils sample distribution is likely to exceed 1.0 mg/kg. This would represent approximately 1775 ha in land area (**Appendix 7**).

5.2.3 Pastoral soils

Pastoral soils average the same concentration of cadmium as horticultural soils (within statistical error), at about 0.72 mg/kg (**Tables 9** and **10**). **Figure 9** is a histogram of soil cadmium levels found for Waikato pastoral properties.

Six of the 43 properties sampled (14% of pastoral properties) exceeded the recommended limit for cadmium in agricultural and residential soils of 1 mg/kg. All of these were dairy farms, which receive higher than average superphosphate loadings (**Section 6.3**). As noted above, this figure is based on raw exceedances of 1.0 mg/kg cadmium in properties sampled, and does not take the underlying sample distribution in to account. Based on a percentile analysis of the log-normalised data for pastoral cadmium, it is estimated that 10.5–12% (best estimate **11%)** of the underlying pastoral soils sample distribution is likely to exceed 1 mg/kg. This would represent approximately 157000 ha in land area (**Appendix 7**).

Two pastoral properties sampled exceeded the threshold which might be used to define contaminated agricultural land (1.4 mg/kg). These were both dairy farms. Within the pastoral soils sample set, dairy soils appear to contain the greatest average cadmium. For those properties within the pastoral data set that could be identified as dairy farms, the average concentration was **0.83 mg/kg** (rather than 0.72 mg/kg).

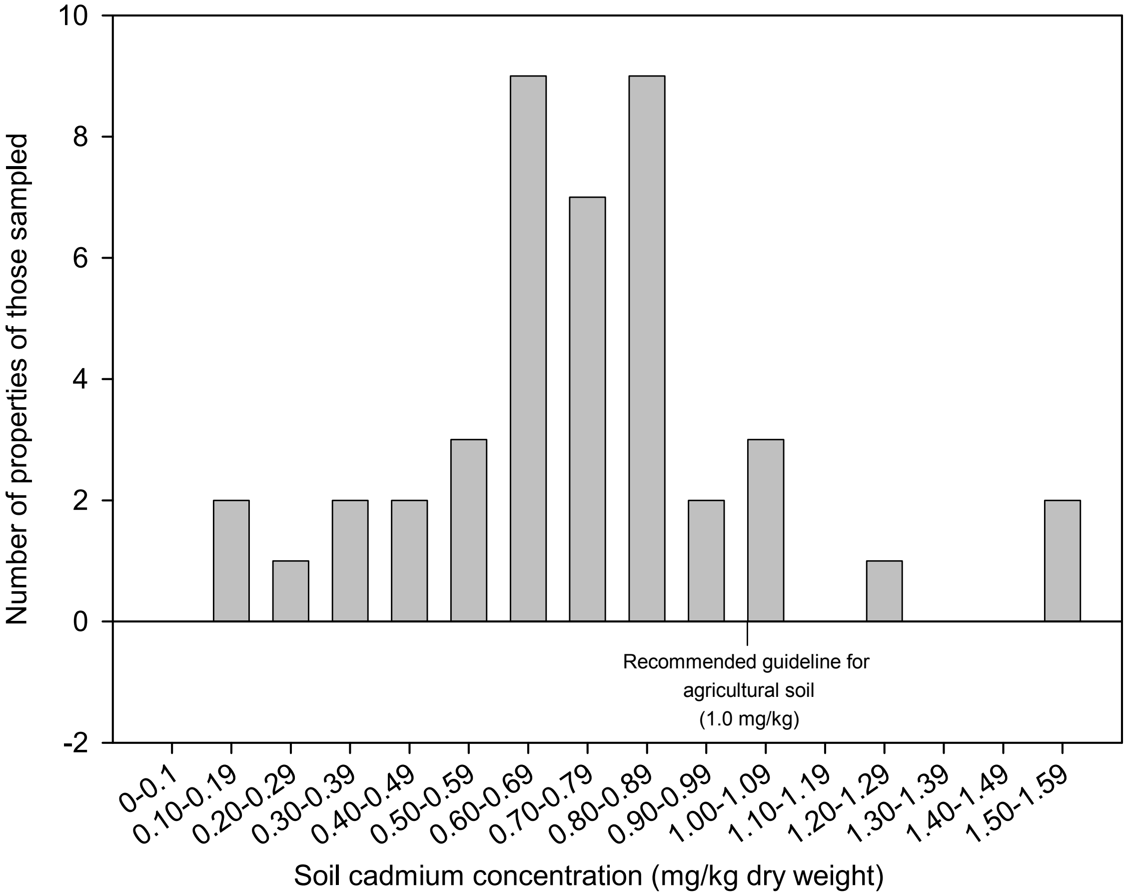

Figure 9 Histogram of soil cadmium levels found for Waikato pastoral properties (N=43) sampled 2001–2004.

The distribution of cadmium concentrations seen for pastoral soils is slightly different to that for horticultural properties (compare **Figure 8** and **Figure 9**). The more binomial looking sample distribution of cadmium in pastoral land is likely to reflect the lower variability in sources and soil processes in this land-use, compared with horticultural cropping.

- In terms of potential sources of cadmium, superphosphate fertiliser (and pesticide) use is more variable between various types of horticultural crops than on pastoral land. For example, superphosphate is not routinely applied to apple orchards, whereas potato crops receive 800-1000 kg/ha/yr. The typical range for pasture is 200-500 kg/ha/yr, which dairy farms being at the upper end of this range.[239]
- In terms of chemical processes, horticultural soils appear to be relatively dynamic. For example, in soils under pasture, soil organic carbon levels tend to increase; whereas in soils used for cropping, organic carbon levels typically decrease (**Appendix 6**). Use of dithiocarbamate pesticides is also higher in horticulture than pastoral farming, and within horticulture will be higher for some forms of cropping than others. Variation in the use of such compounds could lead to a wider spread

[239] Mills T, Robinson B and Clothier B, **2004**. The accumulation of heavy metals in Waikato's productive sector environments. HortResearch Client Report 13155/2004. Final report to Environment Waikato. Hard copy: EW Document **928390**. Electronic copy: EW Document **938788**.

of soil cadmium in horticulture through enhanced leaching, and/or lower retention, of cadmium in soils receiving higher loadings of dithiocarbamates.

5.2.4 Arable soils

Sample numbers in arable soils are fewer (only 9 samples), but the cadmium pattern appears to be similar to that seen for pastoral soils, with most observations in the upper midrange (**Table 9; Appendix 8**). The average cadmium concentration over these samples is **0.64 mg/kg**.

5.2.5 Reserves

As would be expected, no guidelines are even closely approached in the reserve soils. These samples yield and an average cadmium concentration of **0.15 mg/kg (Appendix 8)**, which is about six times below the recommended agricultural soils limit. This suggests that the natural concentration of cadmium in Waikato soils is likely to fall slightly below the assumed background value of 0.2 mg/kg (**Section 3.2.1**),[240] when all anthropogenic inputs are accounted for. The natural abundance of cadmium in the Earth's crust is also estimated to be 0.15 mg/kg.[241]

5.3 Used and residual soil capacity in terms of concentrations

There are various ways to assess residual soil capacity, but in this case, use of averages probably gives the clearest picture of the amount of resource used and the amount remaining. In area, the majority of the total productive soil resource is pastoral.

The background concentration of cadmium in Waikato soils is about 0.15 mg/kg (parts-per-million), or 150 μg/kg (parts-per-billion) (**Section 5.2.5**). The recommended upper limit for agricultural soils (and human health protection value applicable to residential subdivision) is 1 mg/kg (1000 μg/kg) (**Section 3.8.4**). The recommended upper limit does not protect against the possibility that some crops may take up more cadmium than the food standard, but it is the appropriate figure to represent the point where soil resource is lost, partly because it corresponds with current and projected expectations of international trading partners.[242] It follows that the resource initially had the capacity to accumulate **0.85 mg/kg (850 μg/kg)** of additional cadmium; corresponding to the limit less the background value.

The current average concentration in Waikato arable, pastoral and horticultural soils is about 0.7 mg/kg (700 μg/kg) (**Section 5.2**) which is an extra **0.55 mg/kg (550 μg/kg)** cadmium over the background value. This represents 65% of the resource's capacity.[243]

Therefore, it would appear that in soils used for food and fibre production, cadmium contamination is now at a point where on average, two-thirds of the resource's capacity to assimilate cadmium to the 1 mg/kg threshold value has been consumed. Used and residual resource capacity in relation to the 1 mg/kg threshold is illustrated (in parts-per-billion units) in **Figure 10**.

240 Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.

241 CRC Handbook of Chemistry and Physics, 80th Edition, **1999-2000**. 14-14. CRC Press

242 New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand*, **Section 5.2.2**.

243 *i.e.* 550/850 μg/kg.

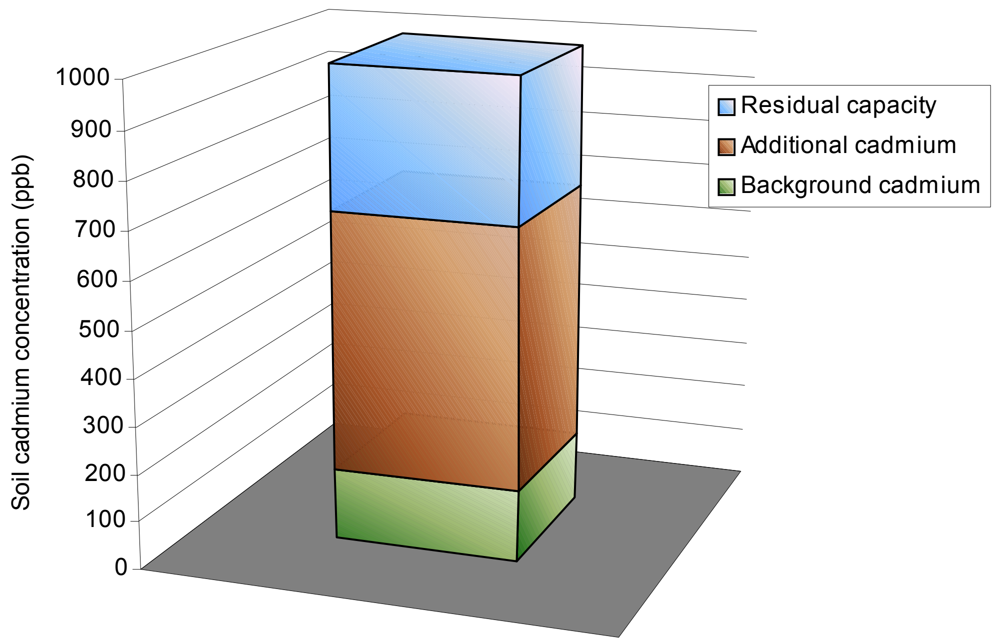

Figure 10 Estimated used and residual capacity of the Waikato productive surface soil resource in terms of cadmium concentrations.

It is worth noting that some properties significantly exceed this average—specifically, 23% of horticultural properties and 14% of pastoral properties recently surveyed already exceed the recommended guideline for cadmium in agricultural soils (**Sections 5.2.2** and **5.2.3**). Assuming that sampling was representative of these soils across the Waikato region,[244] consideration of the underlying sample distribution suggests that perhaps 17% of horticultural properties and 11% of pastoral properties probably exceed the recommended guideline for cadmium in agricultural soils (1 mg/kg) (**Sections 5.2.2** and **5.2.3**).

Horticultural and arable land are not major land uses by area, but in terms of crop uptake and food chain effects, these may be the first sectors needing to re-locate due to the cadmium accumulation issue. This is because, as cadmium continues to accumulate, the probability of food standards being exceeded in selected crops and grains also steadily increases. For each property, there will be a specific point where the soil is no longer fit for production of a given crop. Under such circumstances, other less contaminated land will be required. Current national activity in the horticultural sector amounts to $4.5 billion.[245] The main source of alternative land (by area) is pastoral land; however, the average cadmium content of this land is the same as for horticultural and arable areas. This raises a question about where arable farming and some types of horticulture will re-locate to, once land currently set aside for agricultural production is contaminated to levels which cause food standards to be exceeded. There may be future pressure for substantial conversion of land that is currently used for production forestry, because cadmium levels and accumulation rates in such soils are low (see, for example: **Appendix 7**, **Table 18**, **Section 6.4.3**).

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[244] This is thought to be likely, because the Regional Soil Quality Monitoring Programme uses the same representative sites as used in Landcare Research's national *500 Soils* programme, and the other surveys have incorporated a reasonably randomised approach.

[245] HortResearch, **2004**. *New Zealand Horticulture Facts & Figures 2003.* Available from: http://www.hortresearch.co.nz/files/2004/facts-figs-2003.pdf

6 Ongoing cadmium accumulation

6.1 Introduction

There are several sources of cadmium to agricultural soils. These include application of fertilisers or soil conditioners, use of specific animal remedies and pesticides, and atmospheric deposition (**Section 3.2**).

In commercial products, cadmium is always present as an impurity, rather than as any form of active ingredient. Cadmium is present as a substantial impurity in rock phosphate, which is used to manufacture superphosphate fertiliser, because it shares certain chemical similarities with the major nutrient calcium (**Section 8.2**). Cadmium is also present at lower concentrations in other calcium-containing soil treatments, the most significant of which is lime.

In addition, cadmium has a geochemical association with minerals of lead, zinc and copper (**Section 2.1**). A number of key fungicides used in horticulture contain zinc or copper. Large amounts of zinc are also used in pastoral farming to protect stock against sporodesmin, the fungal toxin that causes liver damage and facial eczema.[246] Whenever these products are used, small amounts of cadmium will be added to agricultural soils. Whether these small amounts are also significant amounts will depend on both the product loading rate, and the trace cadmium content it contains.

The aim of this section is to quantify cadmium loadings to New Zealand agricultural soils from all significant sources. In order to do this, information will be provided on loading rates and impurity levels for specific commercial products most likely to contain significant amounts of cadmium. Sources considered include phosphate fertilisers, zinc compounds (both fungicides and animal remedies), copper compounds, agricultural lime, sewage sludges, and atmospheric deposition.

6.2 Source data

6.2.1 Phosphate fertilisers

Pastoral soils

Most phosphate fertiliser applied to New Zealand pastures is in the form of superphosphate. Application rates are typically 200-500 kg/ha/yr. Intensive dairy units usually apply superphosphate at or near the upper extreme of this range, whereas the more extensive farming operations (sheep, beef and deer) tend to apply the smaller amounts.[247] Superphosphate contains approximately **24 mg/kg** cadmium, which in this product corresponds to the voluntary industry limit of 280 mgCd/kgP (**Table 7**, **Section 4.2.1**).[301] In line with this, two brands of superphosphate tested as part of an associated project were found to contain cadmium at 23.8 mg/kg and 22.5 mg/kg.[248]

Horticultural soils

According to Mills *et al*,[249] very little superphosphate is applied to most horticultural and vegetable crops.

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246 Some of these products (for example, zinc-based facial eczema remedies) may represent significant sources of metal contamination to the wider environment in their own right. However, the focus of this report will remain on cadmium, for the reasons outlined in **Section 1.4**.

247 Mills T, Robinson B and Clothier B, **2004**. The accumulation of heavy metals in Waikato's productive sector environments. HortResearch Client Report 13155/2004. Final report to Environment Waikato. Hard copy: EW Document **928390**. Electronic copy: EW Document **938788**.

248 EW Documents **861279** and **856432**.

249 Mills T, Robinson B and Clothier B, **2004**. The accumulation of heavy metals in Waikato's productive sector environments. HortResearch Client Report 13155/2004. Final report to Environment Waikato. Hard copy: EW Document **928390**. Electronic copy: EW Document **938788**.

Some exceptions exist. Potatoes require very high loadings of superphosphate—typically 800-1000 kg/ha/yr. Mills *et al*[249] also report from discussion with growers that, although not general practice, asparagus and apples can also receive superphosphate at application rates of 200-400 kg/ha/yr and 100-200 kg/ha/yr, respectively.

For most other crops, more refined (but expensive) sources of phosphorus are preferred: these include diammonium phosphate and monoammonium phosphate. As a result of the higher phosphorus content, application rates of the more refined phosphates are lower than those of superphosphate. The P content of single or double superphosphate is 8.7%, whereas that of monoammonium phosphate $(NH_4)H_2PO_4$ is 26.9% and that of diammonium phosphate $(NH_4)_2HPO_4$ is 23.5%. This translates to about 3 times less fertiliser required by mass, to deliver the same amount of P.

Cadmium levels in one brand of monoammonium phosphate are reported (by the manufacturer) as being less than 0.4 mg/kg.[249] It is hard to ascertain whether such low concentrations of cadmium are a general rule for the more refined phosphate fertilisers, but it seems unlikely. For example, the cadmium concentration of a sample of dicalcium phosphate was found to be 5.83 mg/kg, and the average cadmium content of eight specialty fertiliser products sold to home gardeners was 7.4 mg/kg.[250]

Single samples of two specialty plant foods not included in that average were actually found to contain more cadmium than superphosphate: 54.0 mg/kg and 83.6 mg/kg (**Appendix 10**). In the latter case this was despite the fact that the product label specified it as containing less than 9 mg/kg cadmium.

In addition, on about two-thirds of sampled Waikato horticultural properties, measured accumulation of cadmium is observed to be substantial (**Section 5.2.2**, **Figure 8**). Although phosphate fertilisers are not the only source of cadmium, they are usually the most significant source.

For these reasons, for the purposes of loading calculations for crops other than potato, asparagus and apples, a cadmium content of **10 mg/kg** will be assumed. For the purposes of estimating cadmium loadings from phosphorus equivalents, it will be assumed that phosphorus is applied as mono- and diammonium phosphate. Total phosphorus application rates have been supplied by Mills *et al.*[249]

Production forest soils

Superphosphate is not applied to production forestry blocks on a routine or yearly basis; however, some is added on occasion. During a 25-30 year rotation, something in the order of 100-300 kg/ha may be applied two or three times.[249] Assuming that 200 kg/ha is applied on three occasions over a 30 year rotation, the equivalent yearly loading would be **20 kg/ha/yr**.

[250] EW Document **856432**: selected products were general garden food, acid fertilizer, citrus fertilizer, general garden fertilizer, dicalcium phosphate, nitrophoska blue special fertilizer, tomato food, and soluble all purpose plant food.

Home gardens

During 2003, a range of composts, manures and fertilisers marketed for use on home gardens were sampled and analysed for a range of contaminants, as part of an associated project. Samples were collected from three commercial outlets.[251] Results for cadmium are provided in **Appendix 10**. Summary statistics for the fertilisers are given in **Table 13**.

Table 13 Summary statistics for cadmium levels measured in a range of fertilisers used on home gardens.

Source data is provided in Appendix 10.

Variable	All fertilisers tested	Phosphate-containing products
Number of samples	24	15
Mean cadmium concentration (mg/kg dry weight)	13.7	19.2
Standard deviation (mg/kg)	20.4	22.0
Median (mg/kg)	8.7	11.6
Minimum (mg/kg)	0.03	0.11
Maximum (mg/kg)	83.6	83.6

In the 2003 surveying of houses built on former orchard sites in Hamilton,[252] it was found that approximately one in three houses has a garden in which home produce is grown. Home gardens varied in size and complexity from simple fenceline plots through to extensive operations which occupied most spare ground of the section.

The main difficulty in estimating loading rates on home gardens is the wide variety of potential approaches to gardening adopted by homeowners. There will be considerable idiosyncratic variation in the amount and types of products applied from one home garden to the next. For these reasons, cadmium loading estimates derived in this work should be taken as indicative of potential accumulation, rather than predictive of typical, best or worst case.

For the purposes of these loading estimates, a number of 'reasonable assumptions' will be made:

- Firstly, the mean cadmium content of all fertilisers applied will be taken as 14 mg/kg (**Table 13**);
- Secondly, it will be assumed that the home owner applies 0.5 kg of fertiliser per year to their home garden, of size 4 m x 5 m (over 1 hectare, this would be equivalent to a 250 kg/yr);
- Thirdly, it will be assumed that the homeowner also applies commercial compost or manure to the garden, at a rate of 20 kg per year, and that the mean cadmium content of this material is 0.24 mg/kg (**Appendix 10**). At soil cadmium concentrations exceeding 0.24 mg/kg, application of compost or manure will work in the direction of dilution, lowering the overall cadmium content in the receiving soil.

Estimated cadmium accumulation rates in home garden soils, and the potential significance of home produce, are discussed in **Section 6.6** and **Section 7.5**, respectively.

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[251] Mitre 10, The Warehouse, and Palmers Garden World, Hamilton. Further information is provided in EW Documents **861279** and **856432**.

[252] Summary reports for each of the four areas sampled are EW documents **834533**, **841897**, **844302**, and **859176**. A general summary is provided in EW Document **869565**.

6.2.2 Zinc compounds

Usage

As at January 2004, approximately 370 zinc-containing products are registered for use as veterinary medicines or animal remedies.[253] In pastoral farming, zinc-containing compounds are used as antibiotics, antidotes, antifungals, anti-inflammatories, antimicrobials, bactericides, coccidiostats, ectoparasiticides, endoparasiticides, fungicides, oral nutrient/electrolytes, parenteral nutrient/electrolytes, probiotics, and skin/coat conditioners.[254] The main use in pastoral farming is as facial eczema remedies.

Zinc is also contained as part of the active ingredient of 35 registered pesticides, used as anti-fouling paints, bactericides, fungicides, and insecticides. Of these, dithiocarbamate fungicides are probably the most significant in horticulture (**Appendix 6**). Mancozeb and Propineb appear to be the two most important of these.

Persistence of geochemical co-contaminant ratios

Geochemically, cadmium is associated with minerals of zinc, lead and copper (**Section 2.1**). Almost all cadmium produced commercially (**Appendix 1**) is recovered as a by-product during the smelting of zinc ores, in which it is a minor (about 0.2%) isomorphic component.[255,256] The zinc-to-cadmium ratio in zinc ores is in the order of **500**. The natural ratio of zinc-to-cadmium in the earth's crust is **470**.

Galvanised iron products appear to have less cadmium than would be otherwise expected, because they are made using zinc metal, from which cadmium has been recovered during zinc refining. In earlier work[257], the mean concentrations of zinc and cadmium in a sample of galvanized-iron were (54 000 ± 5 400) mg/kg for zinc and (0.225 ± 0.039) mg/kg for cadmium—giving a zinc-to-cadmium ratio in the galvanized-iron of **240000**. In simulated rainfall leaching experiments, galvanised iron was found to lose substantial amounts of zinc, but very little cadmium.[257]

Products made from many zinc salts (rather than metallic zinc) are expected to retain a similar zinc-to-cadmium ratio to that of zinc ores (about **500**), unless these have been specifically purified in some way.

There is some empirical validation of this idea. In a recent contamination assessment on a subdivision in Franklin, one soil sample collected from the spray-shed area was found to contain 4800 mg/kg zinc and 9.8 mg/kg cadmium.[258] High zinc and cadmium concentrations in this sample were attributed to spillage of a zinc dithiocarbamate pesticide formulation. The useful thing about this spill is the characteristic zinc-to-cadmium ratio for the pesticide spilled, which (with soil backgrounds subtracted) was **490**. Further support for a general zinc-to-cadmium ratio of **500** unless otherwise indicated comes from the analysis of home composts and manures (**Table 14**).[259] These are useful for assessing natural geochemical ratios because (unlike some fertilisers) they are not fortified with additional zinc.

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[253] A register of veterinary medicines, animal remedies and plant compounds is maintained by the New Zealand Food Safety Authority (NZFSA); a register of licensed pesticides is maintained by the Environmental Risk Management Authority (ERMA).

[254] Details of product names and other summary data is provided in EW Documents **885913** and **887639**.

[255] Förstner U, **1980**. Cadmium. **In** Hutzinger O (Ed.) *The handbook of environmental chemistry, Vol. 3, part A; anthropogenic compounds.* Springer-Verlag, New York.

[256] Schulte-Schrepping KH and Piscator M, **1985**. Cadmium and cadmium compounds. **In** Gerhartz W (Ed.) *Ullman's Encyclopedia of Industrial Chemistry Vol. A4, 5th edn.* Verlagsgesellschaft mbH (VCH), Federal Republic of Germany.

[257] Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury, Ch. 13.

[258] Environment Waikato file **25 04 02**. Murray Peter Aarts subdivision: assessment carried out by *Vegcon Services* and reviewed by *Environmental & Earth Sciences Ltd.* (Area remediated prior to subdivision.)

[259] Source data: Environment Waikato Document **856432**.

Table 14 **Zinc-to-cadmium ratios for a range of composts and manures used on home gardens.**

Product	Zn/Cd ratio
Organic compost	865
Organic sheep pellets	403
Pot tub & barrel mix	320
Potting mix	153
Seed raising mix	1270
Peat moss	80
Compost	2020
Patio & tub mix	103
Potting mix	180
Pelletised sheep manure	325
Potting mix	360
Seed mix	780
Power-50 vermicast	117
Organic compost	423
Black magic seed raising mix	380
Patio & tub mix	220
Average ratio	**500**

In the case of facial eczema remedies, the relative cadmium content is usually much lower than this. This is because maximum cadmium limits are specified for these products, of not more than 10 mg/kg cadmium in zinc oxide or zinc sulphate heptahydrate, and not more than 15 mg/kg in zinc sulphate monohydrate.[260] These limits are likely to be met in most instances.[261] For the loading estimates in this work, a mean zinc-to-cadmium ratio of **80000** will be assumed for zinc from facial eczema remedies.

Zinc loading rates

Loading rates for zinc on Waikato horticultural crops can be estimated based on a detailed knowledge of spray schedules and the chemical formulation of each pesticide. Similarly, zinc loading rates for pastoral systems can be estimated based on knowledge of dosing routes and rates and estimates of the proportions excreted which do not leave the farm system by other routes (for example, in wool or meat).

As part of this work, *HortResearch* Palmerston North was contracted to investigate and provide estimates of zinc and copper loading rates on Waikato's top ten crops, production forests, and pastoral land.[262] A summary of zinc loadings for Waikato's top ten horticultural and arable crops, pastoral and production forest land is provided in **Table 15**.

[260] New Zealand Food Safety Authority, **2004**. ACVM Registration Standard and Guideline for the Chemistry of Veterinary Medicines. ISBN-0478-07722-X. PDF saved as Environment Waikato Document **938934**.

[261] Neil Kennington, New Zealand Food Safety Authority, **2004**. Personal communication.

[262] Mills T, Robinson B and Clothier B, **2004**. The accumulation of heavy metals in Waikato's productive sector environments. HortResearch Client Report 13155/2004. Final report to Environment Waikato. Hard copy: Environment Waikato Document **928390**. Electronic Copy: Document **938788**.

Table 15 Zinc loading rates and total applied zinc on Waikato's top ten horticultural and arable crops, pastoral and production forest land.[263]

On pastoral land, figures for total applied zinc represent maximum values (see text).

Produce class	Produce type	Land area (ha)	Zinc loading rate (kg/ha/yr)	Total zinc applied in Waikato (tonnes/yr)	Percent of total accounted for
Arable and horticultural crops	Maize	3364	0	0	0.000
	Potatoes	2309	7.48	17.27	0.203
	Onions	2102	2.4	5.04	0.059
	Kiwifrit	800	0	0	0.000
	Asparagus	560	0	0	0.000
	Field/seed peas	364	0	0	0.000
	Apples	300	1.4	0.42	0.005
	Wine grapes	200	4.5	0.90	0.011
	Avocadoes	200	1.4	0.28	0.003
	Broccoli	136	0	0	0.000
Pasture and plantation forests	Pasture: dairy	623013	6.72	4187 (upper limit)	49.2
	Pasture: sheep	333442	5.77	1924 (upper limit)	22.6
	Pasture: beef	471345	5.04	2376 (upper limit)	27.9
	Forestry (pine)	329780	0	0	0.0
All productive land accounted for				8510	

Data for total applied zinc in **Table 15** relating to pastoral land (sheep, beef and dairy farms) represents maximum loadings. This is because facial eczema remedies are not used on all farms every year, but only a portion of total farms. Loading rates (kg/ha/yr) for pastoral areas are regarded as being realistic for those farms where facial eczema remedies are used during a given year. By contrast, estimates of total applied zinc (and loading rates) relating to arable and horticultural crops, and areas of plantation forest, are regarded as being realistic. This is because these estimates are based on known pesticide spray regimes for each crop.

In all, an upper limit of 8500 tonnes of zinc might be added to Waikato productive soils each year (**Table 15**), but true region-wide loadings are likely to be only a portion of this figure. Most of the zinc used in pastoral areas will be accounted for by facial eczema remedies, which have been in widespread use for approximately the last decade and a half.

[263] Mills T, Robinson B and Clothier B, **2004**. The accumulation of heavy metals in Waikato's productive sector environments. HortResearch Client Report 13155/2004. Final report to Environment Waikato. Hard copy: Environment Waikato Document **928390**. Electronic Copy: Document **938788**.

Zinc loadings estimated by *HortResearch*[263] (**Table 15**) will made use of in this work to estimate the amount of additional cadmium that might also be added to Waikato surface soils through use of zinc-based sprays and animal remedies. In making this assessment, it will be assumed that all sheep, beef and dairy farms routinely use zinc for control of facial eczema, at the recommended application rates. This assumption had the potential to cause an over-estimate of cadmium contributions from facial eczema zinc in relation to other cadmium sources: however, on analysis, this error became negligible due to the comparatively high contribution of cadmium from superphosphate fertilisers (see **Table 18**).

6.2.3 Copper compounds

Approximately 430 copper-containing products are registered for use as veterinary medicines or animal remedies. In pastoral farming, these have a similar range of uses as zinc compounds, and these include use as analgesics, antibiotics, anti-inflammatories, antimicrobials, bactericides, bloat remedies, coccidiostats, endoparasiticides, fungicides, herbicides, nutrient/electrolytes (oral and parenteral), and skin/coat conditioners. One of the major uses in pastoral farming is as an essential trace element supplement.

Copper is also contained as part of the active ingredient of 128 registered pesticides: these cover the classes anti-fouling paint, anti-sapstain, bactericide, fungicide, herbicide, insecticide, and timber preservative (CCA). In horticulture, copper-based fungicides (*e.g.* copper oxychloride) probably represent the biggest use.

Little information is available for copper-to-cadmium ratios in copper salts and sprays, and a small sample of these were therefore analysed as part of this work in order to gain an indicative picture. Analytical results are provided in **Table 16**.

Table 16 Cadmium, copper and copper-to-cadmium ratios in copper sulphate and four copper-based fungicides.

Product	Cadmium concentration (mg/kg)	Copper concentration (mg/kg)	Cu/Cd ratio
Bluestone Copper Sulphate	8.5	241000	28353
Champ DP Copper Fungicide	0.4	340000	850000
Copper Oxychloride Fungicide	1.3	466000	358462
Liquid Copper Natural Fungicide	0.025	35600	1424000
Summer Garden Disease Control; Natural Fungicide	0.05	29800	596000
Average			**650000**

Results showed a very low relative content of cadmium (**Table 16**), and suggest that significant co-contamination with cadmium is unlikely to result from the widespread use of copper-based products. In the loading estimates, a copper-to-cadmium ratio of **650000** will be assumed when estimating proportional contributions of cadmium from this source.

A summary of copper loadings for Waikato's top ten horticultural and arable crops, pastoral and production forest land is provided in **Table 17**. As with zinc from facial eczema remedies, data for copper in **Table 17** relating to pastoral land (sheep, beef and dairy farms) represent maximum loadings. By contrast, data in **Table 17** relating to arable and horticultural crops, and areas of plantation forest, is regarded as being realistic. This is because loadings in these areas are estimated based on known pesticide spray diaries.

Table 17 **Copper loading rates and total applied copper on Waikato's top ten horticultural and arable crops, pastoral and production forest land.**[264]

On pastoral land, figures for total applied copper represent maximum values (see text).

Produce class	Produce type	Land area (ha)	Copper loading rate (kg/ha/yr)	Total copper applied in Waikato (tonnes/yr)	Percent of total accounted for
Arable and horticultural crops	Maize	3364	0	0	0.00
	Potatoes	2309	0.6	1.39	0.88
	Onions	2102	6	12.6	8.08
	Kiwifruit	800	2.2	1.76	1.13
	Asparagus	560	1.3	0.73	0.47
	Field/seed peas	364	0	0	0.00
	Apples	300	4.48	1.34	0.86
	Wine grapes	200	4.4	0.88	0.56
	Avocadoes	200	16.93	3.39	2.17
	Broccoli	136	0	0	0.00
Pasture and plantation forests	Pasture: dairy	623013	0.086	53.6	34.3
	Pasture: sheep	333442	0.016	5.34	3.42
	Pasture: beef	471345	0.065	30.6	19.6
	Forestry (pine)	329780	0.135	44.5	28.5
All productive land accounted for				156	

6.2.4 Lime

There is conflicting evidence relating to the cadmium content of lime. In 1995, Roberts *et al.* reported a measured content of 4 mg/kg in lime used in South Auckland market gardens, sourced from Waitomo and Redvale.[265] However, this seems unusually high. Mills *et al.* (citing McLaughin *et al.*), suggest typical figures of 1-2 mg/kg for agricultural lime sourced from Australian limestones.[264]

Environment Waikato's in-house records relating to cadmium in lime are limited. Those that exist relating to a lime manufacturing consent holder (McDonald's Lime) show significantly lower concentrations of cadmium, of 0.23 mg/kg.[266] Three different brands of lime sold for home gardens also had comparatively low cadmium concentrations, averaging 0.25 mg/kg (**Appendix 10**).

In these estimates, a geometric mean cadmium concentration based on available data (4 mg/kg, 1.5 mg/kg, 0.23 mg/kg and 0.25 mg/kg) will be used. This is **0.8 mg/kg**.

[264] Mills T, Robinson B and Clothier B, **2004**. The accumulation of heavy metals in Waikato's productive sector environments. HortResearch Client Report 13155/2004. Final report to Environment Waikato. Hard copy: Environment Waikato Document **928390**. Electronic Copy: Document **938788**.

[265] Roberts AHC, Longhurst RD and Brown MW, **1995**. *Cadmium Survey of South Auckland Market Gardens and Mid Canterbury Wheat Farms.* Report prepared for the New Zealand Fertiliser Manufacturers Research Association. AgResearch: Hamilton.

[266] Environment Waikato Document **812398**.

This is in reasonable agreement with a comment of Mills *et al.*,[267] that although the cadmium content of agricultural lime can be as high as 2 mg/kg, it is generally lower.

Effects of liming last for some time. In this assessment it will be assumed that lime is applied at intervals of four years. For pastoral soils, Cornforth[268] notes that the acidity caused by grazing animals can be neutralised by applying lime at 10-20 kg/ha per stock unit. One ewe raising one lamb is equivalent to one stock unit, whereas a 350 kg dairy cow producing 280 kg of milk solids is equivalent to 6.5 stock units. For the purposes of these estimates, it will therefore be assumed that annual lime addition to sheep and dairy pastures are **4 kg/ha/yr** and **25 kg/ha/yr**, respectively. For beef, Mills *et al.*[267] provide a figure of 65 kg/ha, which translates to **16 kg/ha/yr** if applied once every four years. In reality, it appears that lime use on sheep and beef farms is limited.[269] Assuming that the assumed cadmium content of lime (0.8 mg/kg) is realistic, cadmium loadings to sheep and beef farms from lime may be slightly over-estimated. However, on calculation, this potential error for pastoral soils becomes insignificant in relation to cadmium loadings from superphosphate fertilisers (**Table 18**).

For cropping and arable soils, lime use is higher. Roberts *et al.*[270] report application rates averaging 3.4 tonnes/ha for lettuce, potato and onion crops in South Auckland, and 2.8 tonnes/ha for arable soils. For these estimates, equivalent annual application rates of **850 kg/ha/yr** and **700 kg/ha/yr** will be assumed for cropping soils and arable soils, respectively.

6.2.5 Biosolids

Some background on biosolids (sewage sludge) is provided in **Section 3.8.2**, and industry guidelines for use of this product have recently been developed.[271] Biosolids can contain cadmium at a range of concentrations. The biosolids guidelines specify cadmium limits depending on product grade and date: 10 mg/kg (*Grade b*), 3 mg/kg (*Grade a* before December 2012), and 1 mg/kg (*Grade a* after December 2012). A typical value for cadmium in biosolids might be 2 mg/kg.

Although this figure appears reasonably low, cadmium loading rates from biosolids can be significant, as a result of substantial application rates: a nitrogen-limited application rate for biosolids is of the order of 6.7 dry tonnes/ha/yr.[271]

Use of biosolids in the Waikato is currently limited, and where applied would currently be subject to resource consent control (as a result of being classified as an industrial waste product). For these reasons, potential loadings from biosolids will not be estimated as a baseline part of this assessment, but in terms of additional loadings in cases where biosolids could be applied to productive soils.

6.2.6 Atmospheric deposition

Atmospheric deposition can become significant on agricultural land proximate to industrialised areas **(Sections 2.1** and **3.2.2)**. In most New Zealand agricultural areas, the influence of atmospheric deposition is expected to be minor or negligible in relation to other sources. This has been empirically confirmed by Gray *et al*,[272] who comment that the low rates of metal deposition in New Zealand reflect the general low density of high temperature industrial processes.

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267 Mills T, Robinson B and Clothier B, **2004**. The accumulation of heavy metals in Waikato's productive sector environments. HortResearch Client Report 13155/2004. Final report to Environment Waikato. Hard copy: Environment Waikato Document **928390**. Electronic Copy: Document **938788**.

268 Cornforth IC, **1998**. *Practical soil management.* Lincoln University Press, Canterbury, New Zealand.

269 Roberts AHC, Ravensdown Fertiliser Co-operative Ltd., **2004**. Personal Communication.

270 Roberts AHC, Longhurst RD and Brown MW, **1995**. *Cadmium Survey of South Auckland Market Gardens and Mid Canterbury Wheat Farms.* Report prepared for the New Zealand Fertiliser Manufacturers Research Association. AgResearch: Hamilton.

271 New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand.*

272 Gray CW, McLaren RG and Roberts AHC, **2003.** Atmospheric accessions of heavy metals to some New Zealand pastoral soils. *Science of the Total Environment*, Vol. 305, No. 1-3, pp 105-115.

6.3 Loading estimates

6.3.1 Loading estimates from the bottom up

Application rates of various cadmium sources, and cadmium loadings, on a representative range of Waikato productive land classes, are summarised in **Table 18**.

Table 18 **Estimated loadings of various cadmium sources, and cadmium, on Waikato's top ten horticultural and arable crops, pastoral and production forest land.**[273] Cadmium loading estimates from each source are in columns with grey shading.

Cadmium content assumptions: copper:cadmium ratio: 650000 (**Section 6.2.3**); zinc:cadmium ratio for facial eczema remedies: 80000; zinc:cadmium ratio for horticultural sprays: 500 (**Section 6.2.2**); cadmium content of superphosphate fertiliser: 24 mg/kg (**Section 6.2.1**); cadmium content of other phosphate fertilisers: 10 mg/kg (**Section 6.2.1**); cadmium content of lime: 0.8 mg/kg (**Section 6.2.4**). Total cadmium loadings are upper limits in the sense that not all products will necessarily be used on each land parcel every year.

Land use	Land area in Waikato (ha)	Copper loading rate (kg/ha/yr)	Cadmium loading from copper (mg/ha/yr)	Zinc loading rate (kg/ha/yr)	Cadmium loading from zinc (mg/ha/yr)	P loading (kg/ha/yr)	Super-phosphate loading (kg/ha/yr)	Mono/di-ammonium phosphate equivalent loading	Cadmium loading from super-phosphate (mg/ha/yr)	Cadmium loading from other phosphates (mg/ha/yr)	Assumed lime loading (kg/ha/yr)	Cadmium loading from lime (mg/ha/yr)	Total cadmium loading (mg/ha/yr) (upper limit)
Asparagus	560	1.3	2	0	0	30		119		1190	850	680	**1872**
Field/seed peas	364					40		159		1587	850	680	**2267**
Broccoli	136					50		198		1984	850	680	**2664**
Kiwifruit	800	2.2	3	0	0	60		238		2381	850	680	**3064**
Avocadoes	200	16.93	26	1.4	2800	38		151		1508	850	680	**5014**
Apples	300	4.48	7	1.4	2800	75		298		2976	850	680	**6463**
Onions	2102	6	9	2.4	4800	65		258		2579	850	680	**8069**
Grapes	200	4.4	7	4.5	9000	9		36		357	850	680	**10044**
Maize	3364	0	0	0	0	40	460		11040		700	560	**11600**
Potatoes	2309	0.6	1	7.48	14960	80	900		21600		850	680	**37241**
Forestry	329780	0.07	0	0	0	1.7	20		480		0	0	**480**
Pasture: sheep	333442	0.016	0	5.77	72	30	350		8400		4	3.2	**8475**
Pasture: beef	471345	0.065	0	5.04	63	30	350		8400		16	12.8	**8476**
Pasture: dairy	623013	0.086	0	6.72	84	44	500		12000		25	20	**12104**

[273] Spreadsheet: Environment Waikato Document **939495**.

6.3.2 Loading estimates from the top down

In the context of Waikato's total land area, almost all (97.9%) cadmium added to soil each year is added to sheep, dairy and beef pastures. Just over half of this total amount is added to dairy pastures (**Table 19**).

Table 19 Upper limits for total cadmium added to various land types, and percentages of totals.

Upper limits assume that the loading rate derived applies to all land of a given type: in reality, not all farms will receive superphosphate routinely or at the rates assumed in Table 18.

Land use	**Land area (ha)**	**Cadmium loading rate from** Table 25 **(mg/ha/yr)**	**Upper limit for total cadmium added (kg/yr)**	**Percent of total cadmium added**
Maize	3364	11600	39.0	0.27
Potatoes	2309	37241	86.0	0.59
Onions	2102	8069	17.0	0.12
Kiwifruit	800	3064	2.5	0.02
Asparagus	560	1872	1.0	0.01
Field/seed peas	364	2267	0.8	0.01
Apples	300	6463	1.9	0.01
Avocadoes	200	5014	1.0	0.01
Grapes	200	10044	2.0	0.01
Broccoli	136	2664	0.4	0.00
Forestry	329780	480	158	1.08
Pasture: sheep	333442	8475	2826	**19.3**
Pasture: dairy	623013	12104	7541	**51.4**
Pasture: beef	471345	8476	3995	**27.2**

Although accumulation rates themselves can be significant on other land types (and should not be discounted in their own right), the fact that pastoral land accounts for almost all of the cadmium added, and superphosphate used, means that loadings on pastoral land can be also estimated from the top down, starting with overall superphosphate use in the Waikato region. This will give a more realistic estimate of total loadings on pastoral land as a whole.

Fert Research have estimate that total sales of fertiliser in New Zealand now exceed 3 million tonnes per annum; approximately two-thirds of this (2 million tonnes) is superphosphate.[274] The same document also notes that government sales volume figures underestimate actual use. This appears to be the case: *Statistics New Zealand* Agricultural Census 2002 figures put total fertiliser use at about 2.4 million tonnes excluding lime.[275]

Sales of superphosphate have also increased in recent years relative to earlier periods. As noted in the Ravensdown Fertiliser Annual Report 2000:[276]

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274 Fert Research, **2004**. Fertiliser Matters. New Zealand Fertiliser Manufacturers' Research Association Newsletter, 20 March 2002: http://www.fertresearch.org.nz/attachments/document/FM%20March%202002.pdf

275 Statistics New Zealand, **2004**. 2002 Agricultural Production Census (Final Results): June 2002: Fertiliser tables are available from: http://www.stats.govt.nz/domino/external/web/prod_serv.nsf/Response/Fertiliser+tables

276 Ravensdown Fertiliser Cooperative, **2000**. Annual Report 2000, CEO's report. Available from: http://www.ravensdown.co.nz/AnnualReport2000/index.cfm?page=10

"The increased phosphorous [sic] application was achieved by a very significant growth in our sales of Superphosphate. Some years ago Superphosphate had been seen as a sunset product, being replaced by high analysis fertilisers such as DAP. This trend has reversed over recent years as farmers have valued the calcium and sulphur that Superphosphate provides as well as the phosphate."

Although 2002 Agricultural Census figures may underestimate total fertiliser use, relative proportions of phosphatic fertilisers used by region are likely to be reliable. On this basis, estimates of actual superphosphate use for each region can be obtained by multiplying the proportional figures derived from the Agricultural Census 2002 by the total estimated superphosphate fertiliser sales volume of 2 million t/yr. This is done in **Table 20**.

Table 20 Estimates of superphosphate use by region, and implied cadmium loadings for each region assuming a cadmium content of 24 mg/kg.

Region	Phosphatic fertiliser use from Agricultural Census 2002 (t/yr)	Percent of New Zealand use	Corrected phosphatic fertiliser use estimate (t/yr)	Estimated cadmium loading (t/yr)
Northland	84,507	6.86	137165	3.3
Auckland	29,907	2.43	48543	1.2
Waikato	213,397	17.32	346368	**8.3**
Bay of Plenty	37,532	3.05	60919	1.5
Gisborne	45,248	3.67	73443	1.8
Hawkes Bay	90,026	7.31	146123	3.5
Taranaki	58,564	4.75	95056	2.3
Manawatu-Wanganui	165,398	13.42	268460	6.4
Wellington	44,976	3.65	73001	1.8
Tasman	10,289	0.84	16700	0.4
Nelson	1,415	0.11	2297	0.1
Marlborough	13,500	1.10	21912	0.5
West Coast	13,910	1.13	22578	0.5
Canterbury	164,274	13.33	266636	6.4
Otago	110,552	8.97	179439	4.3
Southland	148,433	12.05	240924	5.8
Chatham Islands	269	0.02	437	0.0
	1,232,197		**2000000**	**48.0**

Over New Zealand, an estimated **48 tonnes** of cadmium is added to soils each year (**Table 20**). The total mass added in the Waikato is the highest of any region, at **8.3 t/yr**. Half of this is added to dairy farms. Other regions receiving high total masses of cadmium are Canterbury, Manawatu-Wanganui (both 6.4 t/yr), Southland (5.8 t/yr), Otago (4.3 t/yr) Hawkes Bay (3.5 t/yr) and Northland (3.3 t/yr) (**Table 20**).

6.4 Projected accumulation rates

6.4.1 Estimates

In order to best estimate likely net accumulation rates in surface soils, potential leaching of cadmium below the surface layer should be taken into account. Loganathan and Hedley[277] studied downward movement of cadmium and phosphorus from phosphate fertilisers in a New Zealand pasture soil, and found that approximately 90% of the applied cadmium was retained in the top 12 cm (in other words, 10% was lost to leaching). Similarly, Gray et al.[278] reported leaching losses of between 5–15% for New Zealand pasture soils. On these basis of these findings, a leaching loss of 10% of applied cadmium is assumed in estimating surface accumulation rates.[279]

A summary of cadmium loadings, and estimated accumulation rates for cadmium in surface soils, is provided in **Table 21**.

Table 21 Cadmium loadings and estimated surface soil accumulation rates for Waikato's top ten horticultural and arable crops, pastoral and production forest land.[280]

Assumptions: soil bulk density: 1.0 g/cm^3; soil mixing depths as indicated, taken as those appropriate for each type of land use; loss of applied cadmium through leaching: 10%; current average soil cadmium concentrations are based on recent data for Waikato soils (Section 5).[281]

Land use	Land area in Waikato (ha)	Bottom up cadmium loading estimate (mg/ha/yr)	Soil mixing depth assumed (cm)	Soil mixing mass for 1 ha area (kg)	Accumul-ation rate (µg/kg/yr)	Current average soil cadmium (mg/kg)	Time to 1 mg/kg soil guideline (years)
Maize	3364	11600	15	1500000	6.96	0.70	42.1
Potatoes	2309	37241	15	1500000	22.3	0.67	13.8
Onions	2102	8069	15	1500000	4.84	0.67	67.2
Kiwifrit	800	3064	15	1500000	1.84	0.67	179
Asparagus	560	1872	15	1500000	1.12	0.67	293
Field/seed peas	364	2267	15	1500000	1.36	0.67	242
Apples	300	6463	15	1500000	3.88	0.67	84.1
Avocadoes	200	5014	15	1500000	3.01	0.67	109
Grapes	200	10044	15	1500000	6.03	0.67	53.8
Broccoli	136	2664	15	1500000	1.60	0.67	205
Forestry	329780	480	4	400000	1.08	0.20	738
Pasture: sheep	333442	8475	7.5	750000	10.2	0.72	25.5
Pasture: dairy	623013	12104	7.5	750000	14.5	0.72	17.3
Pasture: beef	471345	8476	7.5	750000	10.2	0.72	25.5
					Average: 6.4		

277 Loganathan P and Hedley MJ, **1997**. Downward movement of cadmium and phosphorus from phosphatic fertilizers in a pasture soil in New Zealand. *Environmental Pollution*, Vol. 95, No. 3, pp 319-324.

278 Gray CW, McLaren RG and Roberts AHC, **2003**. Cadmium leaching from some New Zealand pasture soils. *European Journal of Soil Science*, Vol. 54, No. 1, pp 159-166.

279 It is appreciated that the exact leaching loss at a given site will depend on soil type, slope, rainfall, crop cover, and presence or absence of preferential flow paths: however, 10% seems a reasonable average generic leaching assumption to use for general accumulation estimates, based on empirical field results such as those cited.

280 Spreadsheet: Environment Waikato Document **939495**.

281 Note that 'time until guideline reached' figures assume a starting year of 2002 for pastoral soils and 2003 for horticultural soils, because current soil survey data is for samples collected during these years (**Section 5**). Year at time of loading estimates is **2005**.

These estimates relate to properties where fertilisers are faithfully applied, and this is not always the case.

However, the overall average loading and accumulation rate on Waikato pastoral land can also be calculated using the top-down approach. Most (97.9%) added cadmium is deposited on sheep, dairy and beef pastures (**Table 19**), and superphosphate fertiliser use accounts for most (99.1%) of this cadmium (**Table 18**). Estimates of the average accumulation rate for pastoral land can be made by taking these factors in to account, and this is done in **Table 22**. As with previous estimates, a leaching loss of 10% is presumed when calculating residual accumulation rates.

Table 22 Estimates of average cadmium loading and accumulation rates on Waikato pastoral land.[282]

Variable	Value
Mass of cadmium added to Waikato soils from superphosphate fertiliser use (kg/yr)	8300
Adjusted figure[a] (kg/yr)	8200
Area of sheep, beef and dairy land in Waikato (ha)	1427800
Average cadmium loading rate on this land (g/ha/yr)	5.74
Average cadmium accumulation rate on this land to 7.5 cm assuming 10% leaching loss (μg/ha/yr)	6.89
Current average soil cadmium (mg/kg)	0.72
Time to 1 mg/kg soil guideline (years)	39

[a] Adjusted figure: 97.9% represents the proportional amount of superphosphate fertiliser used on sheep, beef and dairy land only (**Table 19**), and the finding that superphosphate fertiliser accounts for 99.1% of added cadmium for these land uses (**Table 18**). The mass of cadmium added is therefore (0.979 x 1.009) = 0.988 of that represented by total superphosphate fertiliser use for the Waikato region.

6.4.2 Overall picture

Over the Waikato region, an estimated **8.3 tonnes** of cadmium is applied to productive soil each year. Of this, 98% is applied to pastoral land, and 2% to other land.

In the following sections, accumulation rates will be expressed primarily in units of μg/kg/yr (parts-per-billion per year), for convenience.

Over the land-uses examined, the average estimated future accumulation rate of cadmium in surface soils is **6.4 μg/kg/yr** (0.006 mg/kg/yr) based on bottom-up loading estimates (**Table 21**). This matches, fortuitously, the average *observed* cadmium accumulation rate for pastoral and horticultural soils, which was **6.6 μg/kg/yr** (**Table 2, Section 3.3**), and the top-down estimate based on superphosphate sales figures and Waikato's grasslands areas, of **6.9 μg/kg/yr (Table 22).** The ten year average cadmium accumulation rate across Waikato productive soils is therefore estimated to lie in the range **6–7 μg/kg/decade** (0.06–0.07 mg/kg/decade).

6.4.3 Pastoral and forest soils

Accumulation rates

For pastoral and forest soils, superphosphate fertiliser always accounts for over 99% of the total cadmium added (**Table 18**). On forest soils, however, application rates are sufficiently low that cadmium accumulation is not significant. For Waikato pastoral soils, the average accumulation rate over the period 1939 to 2002 was **9.0 μg/kg/yr** (0.009 mg/kg/yr) (**Table 2**). The projected future average accumulation rate for Waikato pastoral soils is 77% of this figure, at **6.9 μg/kg/yr** (0.007 mg/kg/yr) (**Table 22**). This average figure takes into account that fact that not all sheep, beef or dairy properties in the region will be applying phosphate fertiliser at 'typical', or

[282] Spreadsheet: Environment Waikato Document **945008**.

recommended, rates; some may receive very little fertiliser, or receive it less routinely. The absolute accumulation rate on some properties will therefore be higher than this average: for the subset of sheep, beef and dairy farms routinely applying superphosphate at rates assumed in **Table 18**, the weighted mean future accumulation rate is estimated to be **12 µg/kg/yr** (0.012 mg/kg/yr) (based on data in **Table 21**), all other factors remaining constant.

Time remaining from 2005

On pastoral soils, projected accumulation rates are rapid. Where superphosphate fertiliser use is routine and at 350 kg/ha/yr, soils carrying sheep and beef would have approximately **25 years** (2030) before the soil guideline value is reached. Dairy soils receiving the standard reported superphosphate fertiliser application rate of 500 kg/ha/yr would have about **16 years** (2021) until the 1 mg/kg cadmium guideline also becomes the surface soil average (**Table 21**).

At a broader level, the Waikato region contains about 2.5 million hectares of land. Twenty-five percent of this is in dairy farming, 19% in beef, and 13% in sheep. Overall, **1.43 million ha**, or 57%, is used for pastoral production. This land receives an estimated **8.3 tonnes** of cadmium per annum. When variation in fertiliser usage rates are taken into account, it is projected that at current superphosphate use rates and cadmium concentrations, the average cadmium content over all pastoral soils in the Waikato region will reach the soil guideline value in about **38 years** (2043) (**Table 22**).

Essential findings for pastoral soils are summarised in **Figure 11**.

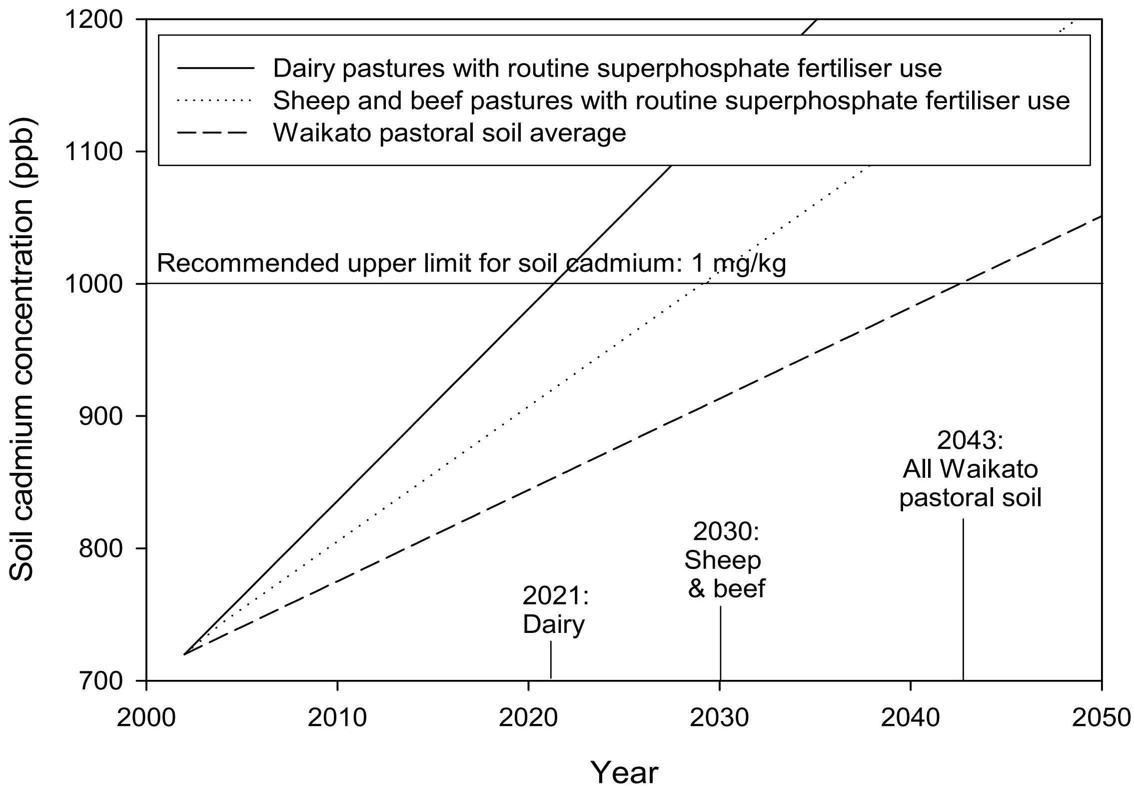

Figure 11 Estimated times remaining until the recommended upper limit for average soil cadmium is reached in Waikato pastoral land at current cadmium loading rates.

In general terms, results of these loadings estimates are supported by industry figures. According to the Ballance Agri-Nutrient fact sheet for cadmium,[283] it will take an estimated **27 years** before the average cadmium in soil of New Zealand dairy pasture

[283] Ballance Agri-Nutrients, **2005**. Fact sheet for cadmium.; accessed 10 August 2005. Available from: http://www.ballance.co.nz/fscadmium.html

exceeds the recommended agricultural guideline of 1 mg/kg (**Section 3.8**). In these estimates for Waikato dairy soil, the estimated time until this happens on a typical Waikato dairy farm where superphosphate fertiliser is routinely used is one decade less than this at **16 years** (**Table 28**).

Minor differences between the two estimates relate to assumptions made in modelling cadmium accumulation on average New Zealand and Waikato soils, and the fact that Ballance's estimate is likely to be slightly dated (given that other items in the fact sheet are up to four years out of date—see **Section 3.5.2**), with the most extensive previous survey of cadmium in national soils having been carried out in 1992. The mean cadmium accumulation rate in Waikato soils may also be marginally higher than national averages, due to the preponderance of yellow brown loams, which tend to be reasonably adsorptive.[284]

The 16 year figure is regarded a conservative estimate for Waikato dairy soils, because the average cadmium concentration (the starting point) for Waikato dairy soils appears to be slightly higher than the pastoral soil average that has been assumed in these loading estimates. Where soil guideline exceedances were seen, they were for dairy farms, and the present mean for the dairy farms surveyed was closer to 0.8 mg/kg than 0.7 mg/kg (**Section 5.2.3**). Starting cadmium concentrations in the range 0.7–0.8 mg/kg would yield accumulation times in the range **8-16 years**, and therefore the 16 year figure for dairy soils to average soil cadmium of 1 mg/kg or above should be seen as an upper estimate.

Significance in relation to guidelines

With respect to pastoral soils, the first practical significance of soil cadmium exceeding the recommended upper limit of 1 mg/kg is that this may cause future barriers to international trade. This is because the recommended upper limit for agricultural soils is partly set on the basis of expectations of international trading partners, and the European Community in particular (**Sections 3.8.2** and **4.3.1**).[285]

In terms of human exposure, the significance of the soil guideline being exceeded on operating pastoral properties is limited. Cadmium levels in milk and muscle meat are low. Cadmium does accumulate in liver and kidney meat (**Section 3.6**), but overall dietary intakes attributable to muscle meat or milk are small to insignificant compared with those from grain and vegetables (**Section 2.4.2**). Liver and kidney comprise only a minor component of the average diet, and management practices are also in place for these meats. For example, offal from animals older than 2.5 years is not permitted to be sold for human consumption.[286] However, it is worth reiterating that to the sheep and beef industries, this already represents a significant lost income stream (**Section 3.6**).

A second aspect of resource capacity loss is the potential inability to subdivide pastoral properties for residential or rural residential use, once the soil guideline value of 1 mg/kg is exceeded (**Sections 3.8.3** and **3.8.4**).

Significance of accumulation in its own right

It is important to note that soil guidelines do not represent the full story in terms of soil resource loss, when changes in land use are taken in to account.

Irrespective of soil guidelines, the fact of ongoing cadmium accumulation itself is causing a third type of soil resource loss in pastoral surface soils. Instead of soil guidelines, this relates to food standards, and concerns the total area of land that

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284 Longhurst RD, Roberts AHC and Waller JE, **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.

285 New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand*, **Section 5.2.2**.

286 Fert Research, **2002**. *Cadmium in New Zealand—Its Presence and Management.* Addendum 8 to the Code of Practice (COP) for Fertiliser Use: http://www.fertresearch.org.nz/attachments/document/UpdatedCodeAddenda.pdf

would remain suitable for future production of certain horticultural or arable crops at any point in time. As soil cadmium concentrations continue to increase, progressively more land will become unfit for conversion to specific horticultural or arable use, due to the steadily increasing likelihood of food standards being exceeded in certain crops (mainly grains and vegetables) if they were grown in such soil.

Therefore, although the soil guidelines for cadmium in agricultural and residential soils (both 1 mg/kg) represent a definable point of significant resource capacity loss, the fact of cadmium accumulation itself is concurrently causing a steady background loss of a future potential use of the soil resource.

This third type of background loss of the soil resource is inherently more difficult to quantify, because it covers a range of possible scenarios. Relevant factors include the new intended land use, the intended crop, the soil type, and the soil mixing depth. However, it is possible to provide an indication of its order of magnitude.

This highlights a weakness in current approach to managing the cadmium issue, which is that it is implicitly based on a presumption that cadmium accumulation will cause no adverse consequence until a specific soil guideline is reached (1 mg/kg cadmium). This is not a valid presumption, for the reason that food standard exceedances are possible in given crops at soil cadmium levels that are below the nominated soil guideline. As outlined in **Section 3.5.2**, this has already been demonstrated as part of research carried out on cadmium levels in soil and crops of 90 South Auckland market gardens and 70 mid-Canterbury wheat farms.

At a more general level, a reviewer of the draft edition of this report has also noted the following:[287]

"The concept of a "residual capacity" of soil to assimilate contaminants is worth further consideration from a philosophical viewpoint. Many environmental authorities do not subscribe to the philosophy that the soil can be used as a recipient of contaminants and concentrations allowed to accumulate up to a defined guideline or trigger value i.e. a reservoir to be filled up. Rather the philosophy of "as low as reasonably achievable" or a "mass balance" approach is often favoured. Indeed, the latter is the underlying philosophy of the European Union risk assessment for cadmium in phosphatic fertilisers."

6.4.4 Horticultural and arable soils

Accumulation rates
Horticultural crops show a wide variation in projected cadmium accumulation rates, compared with pasture (**Table 21**). This is consistent with observations. A wide spread of observed cadmium enrichment was noted for horticultural land (**Figure 8**, **Section 5.2.2**), compared with pasture (**Figure 9**).

For Waikato horticultural soils, the average accumulation rate over the period 1939 to 2002 was **8.1 µg/kg/yr** (**Table 6**). The projected future average accumulation rate for Waikato horticultural and arable soils (taken over the Waikato's top ten crops) is 65% of this figure, at **5.3 µg/kg/yr** (**Table 21**).

Time remaining from 2005
Within horticultural soils studied, potatoes are the crop showing the shortest interval between current soil status and the point where the 1 mg/kg recommended upper limit is reached: **13 years** (2018). Once again, in general terms, results of these loadings estimates are supported by the fertiliser industry figures. According to the Ballance Agri-Nutrient fact sheet for cadmium,[288] it will take an estimated **16 years** before the

[287] McLaughlin M, **2005**. Centre for Environmental Contaminants Research CSIRO Land and Water. Personal communication: comment made in peer review.
[288] Ballance Agri-Nutrients, **2005**. Fact sheet for cadmium.; accessed 10 August 2005. Available from: http://www.ballance.co.nz/fscadmium.html

average cadmium in soil under potato crops exceeds the recommended agricultural guideline of 1 mg/kg (**Section 3.8**).

Two main factors are responsible for this high rate of accumulation under potatoes. Firstly, potatoes receive high loadings of superphosphate fertiliser (**Section 3.7.2** and **Table 18**). Secondly, in these estimates it has been assumed that in zinc-containing dithiocarbamate sprays, the geochemical zinc:cadmium ratio of 500 persists (**Section 6.2.2**). If this is indeed the case, zinc sprays would constitute an important second source of cadmium to potatoes. Of the additional cadmium received by soil under potatoes, 58% is estimated to come from superphosphate fertilisers, 40% from zinc-containing sprays, and the remaining 2% from lime.

The high accumulation rate in soils used for potato growing is of significance to the Waikato region (**Section 3.7.2**). Reasons for this are outlined in **Section 7.1**. As far as the author is aware, no specific sector-wide programme is in place to monitor or manage cadmium accumulation in soils under potatoes.

After potatoes, maize shows the shortest interval between current levels and the recommended soil limit, of **42 years** (2046) (**Table 21**).

Overall, the projected average accumulation rate for Waikato horticultural and arable soils (taken over the Waikato's top ten crops) is lower than that of pastoral soils, at **5.3 µg/kg/yr**. At this rate, the recommended upper limit would be reached on average over all horticultural soils in **62 years** (2066). However, in making these estimates, the lower average accumulation rate of horticultural soils (compared with pastoral) hinges on two factors:

1. The assumption that more refined phosphates tend to be preferred over superphosphate fertiliser in horticulture. Where this is not the case, loading rates and soil concentration increases will be more rapid than indicated;

2. An assumption that soil is mixed to at least 15 cm (rather than 7.5 cm assumed for pasture).

Essential findings for horticultural and arable soils are summarised in **Figure 12**.

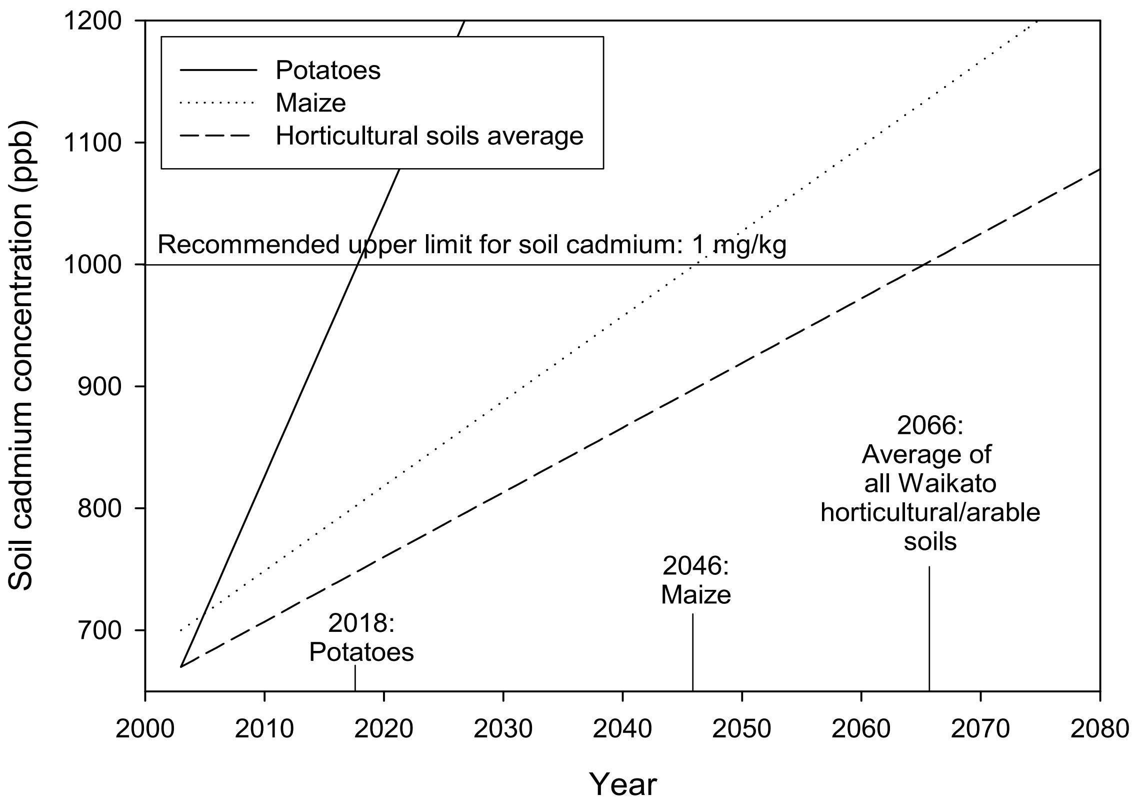

Figure 12 Estimated times remaining until the recommended upper limit for average soil cadmium is reached in Waikato horticultural and arable land at current cadmium loading rates.

Significance

Cadmium accumulation in horticultural and arable soils has the greatest direct influence on human intakes of cadmium.

In horticultural areas, loss of resource capacity is best defined as the point at which crops grown on the soil routinely exceed food standards. Under these conditions, it will not be possible for growers to continue production of a given crop, if it is recognised that the food standard is routinely being broken. With this in mind, it is worth reiterating that the recommended upper limit for soil cadmium of 1 mg/kg is **not** sufficiently low to protect against cadmium in at least a proportion of crops exceeding food standards, under typical soil pH conditions (**Section 3.8.3**). Loss of production capacity in horticultural and arable areas may come about at cadmium concentrations lower than 1 mg/kg, due to food standards being exceeded.

For crops showing lower cadmium uptake, where food standards are not likely to be breached, the soil concentration of 1 mg/kg represents the next identifiable resource capacity loss-point. As with pastoral soils, this limit represents a point at which soil cadmium may cause international trade access issues, and difficulty may be encountered in allowing properties to be subdivided for more sensitive land uses.

6.4.5 Policy significance of ongoing cadmium accumulation

In relation to objectives of the Waikato Regional Policy Statement (**Section 1.1**), the significance of ongoing cadmium accumulation in agricultural land is that the range of existing and foreseeable uses of the soil resource, versatility and productive capacity are being progressively reduced. Therefore, this objective of the Waikato Regional Policy Statement is not currently being met. This loss of current and future soil resource capacity is felt at both the operating farm level, and the future land-use level.

As outlined in **Sections 1.2.5, 6.4.3** and **6.4.4**, mechanisms of this soil resource capacity loss include:

- Lesser ability to subdivide land to residential or rural residential use without some form of assessment and/or remediation, caused by the residential soil guideline (for human health protection, 1 mg/kg) being exceeded;

- Progressive increase in the total land area unsuitable for specific (current and future) horticultural or arable uses, due to the increasing likelihood of food standards being exceeded as overall soil cadmium concentrations continue to increase;

- Possible hindrances to international trade, caused by the recommended limit for agricultural soils (1 mg/kg) being exceeded.

6.4.6 Improvements over the last decade

There is some evidence to suggest that cadmium accumulation rates have decreased in recent years, at least in relation to the average previous accumulation rate over the period 1939-2002.

- When making comparisons, it is worth noting that exact shape of the cadmium accumulation curve would have changed over time. It is likely that average accumulation in the immediate decade after 1939 was low, but increased significantly when aerial topdressing became established after 1949. Use of superphosphate fertiliser did not become widespread until after WWI, and aerial topdressing was first trialled in May 1949.[289] Peak accumulation rates would therefore be expected during the period 1949 to 1997, depending on economic circumstances (which have an impact on fertiliser use). In 1997, the fertiliser industry initiated progressive reduction of the cadmium level in superphosphate by one-third (**Section 4.2.1**), but subsequently also experienced increased sales growth of superphosphate (**Section 6.3.2**).

However, in overall terms, projected accumulation rates for pastoral and horticultural soils are 77% and 65% of average rates over the period 1939-2002, respectively (**Sections 6.4.3** and **6.4.4**). Most of this decrease is likely to be attributable to the main management strategy adopted by the fertiliser industry to date, which involved introduction of a voluntary limit on the cadmium content of superphosphate fertiliser (**Section 4.2.1**). This brought the average cadmium content down by at least one-third.

6.5 Potential impact of biosolids

Biosolids (sewage sludge) as a source of cadmium to soil are discussed in **Section 6.2.5**. In the Waikato region, biosolids use is currently regulated, and does not form a significant part of the baseline addition of cadmium to productive soils. However, it is useful to estimate potential contributions of cadmium from this source, in order to guide future decision making. Loading calculations have been carried out to quantify inputs of cadmium from the cleanest grade of biosolids (*Grade a*) in relation to various other sources, in the theoretical event that biosolids were applied to various types of cropping or pastoral soils. *Grade a* biosolids might typically contain cadmium at 2 mg/kg (dry weight) (**Section 6.2.5**).[290]

Other potential sources of cadmium considered were as previously, with source contributions, loading and soil mixing assumptions as indicated in **Table 18** and **Table**

289 *New Zealand Listener*, **2004**. 65 Events that Shaped a Nation; 65th Celebration Issue, July 10-16, p 17.
290 New Zealand Water and Wastes Association (NZWWA), **2003**. *Guidelines for the Safe Application of Biosolids to Land in New Zealand*.

21. Relative contributions of cadmium from each source assuming concurrent *Grade a* biosolids use are listed in **Table 23**.[291]

Table 23 Potential percentage (%) contributions to cadmium loadings to the Waikato region's top ten arable and horticultural crops, forest and pastoral soils, assuming concurrent N-limited application of *Grade a* biosolids.

Land use	Super-phosphate	Other phosphates	Lime	Zinc compounds	Copper compounds	Grade a biosolids	Total
Maize	44.2	0.0	2.2	0.0	0.0	53.6	100.0
Potatoes	42.7	0.0	1.3	29.5	0.0	26.5	100.0
Onions	0.0	12.0	3.2	22.4	0.0	62.4	100.0
Kiwifrit	0.0	14.5	4.1	0.0	0.0	81.4	100.0
Asparagus	0.0	7.8	4.5	0.0	0.0	87.7	100.0
Field/seed peas	0.0	10.1	4.3	0.0	0.0	85.5	100.0
Apples	0.0	15.0	3.4	14.1	0.0	67.5	100.0
Avocadoes	0.0	8.2	3.7	15.2	0.1	72.8	100.0
Grapes	0.0	1.5	2.9	38.4	0.0	57.2	100.0
Broccoli	0.0	12.4	4.2	0.0	0.0	83.4	100.0
Forestry	3.5	0.0	0.0	0.0	0.0	96.5	100.0
Pasture: sheep	38.4	0.0	0.0	0.3	0.0	61.3	100.0
Pasture: dairy	47.1	0.0	0.1	0.3	0.0	52.5	100.0
Pasture: beef	38.4	0.0	0.1	0.3	0.0	61.3	100.0

If or where biosolids are applied to productive soils, it would be expected that they would be responsible for more cadmium input than the sum of all other sources combined, the most significant of which is usually superphosphate fertiliser (**Table 23**, **Figure 13**). This is in fact the general experience for biosolids sites in Australia and elsewhere in the world.[292]

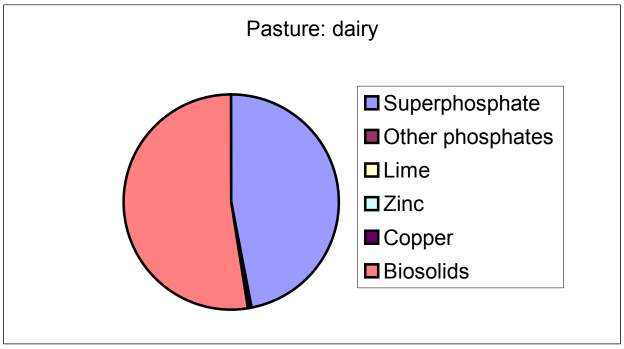

Figure 13 Example pie-chart of proportional contribution which would be made to anthropogenic cadmium in the event that biosolids were applied to dairy pasture (based on data in **Table 23**).

Put another way, when biosolids are used on productive soils, the rate of cadmium accumulation would be expected to more than double. Correspondingly, time periods before which various soil guidelines are reached would be halved.

[291] See also Environment Waikato Documents **939495** and **939496**.
[292] McLaughlin MJ, **2000**. Unwanted passengers in fertilizers: a threat to sustainability? Soil Research: a knowledge industry for land-based exporters. Proceedings of the workshop held by the Fertilizer and Lime Research Centre, Massey University, Palmerston North (Eds. Currie, L.D. and Loganathan, P.), 9-10 February, 2000.

In some scientific circles, there is concern that the desire to dispose of sewage sludges and biosolids by land application has resulted in undue emphasis being placed on beneficial re-use aspects, with less attention being paid to risks of metal accumulation from this source.[293]

6.6 Accumulation in home vegetable gardens

Cadmium accumulation rates in soil of home vegetable gardens will be variable, depending on the size of the garden, soil mixing depth, and amount and types of soil conditioners, fertilisers and manures that are applied to each garden.

Based on survey results, typical cadmium concentrations in phosphate fertilisers and manures sold for home garden use have been taken as 14 mg/kg, and 0.24 mg/kg, respectively (**Section 6.2.1**, **Appendix 10**). Potential loadings and accumulation rates were modelled for a 4 m x 5 m garden, assuming annual fertiliser and manure application rates of 0.5 kg/yr and 20 kg/yr, respectively, a soil mixing depth of 15 cm, and a leaching loss beyond this depth of 10%.

Under these conditions, the rate of cadmium accumulation cadmium is estimated as **3.25 µg/kg/yr**.

This is not particularly rapid. If the soil started with natural cadmium concentrations (0.15 mg/kg), accumulation to the recommended guideline value of 1 mg/kg would take 290 years. At the other end of the scale, in a property that is subdivided from horticultural or pastoral land containing the current average cadmium concentration of 0.7 mg/kg, accumulation to the guideline value would still take 96 years.

The finding that cadmium accumulation rates in home garden soils are likely to be at the lower end of the scale should not be taken to imply that home produce grown in home gardens will necessarily meet food standards for cadmium. For example, results of recent limited uptake experiments for a type of lettuce reported to be popular with home gardeners (Buttercrunch) suggest that under some circumstances, food standards may be reached at soil cadmium concentrations as low as 0.2 mg/kg (**Section 7.5**).

However, at pH values of Waikato soils, 1 mg/kg is also (coincidentally) the regulatory point at which residential soil would be regarded as contaminated with cadmium (**Table 11**). This distinction is useful, because contaminated land guidelines of this type are risk-based numbers which already take home produce consumption into account (**Section 3.8.2**). This implies that in the context of total residential cadmium exposure, a home soil limit of 1 mg/kg cadmium should be protective even in cases where cadmium concentrations do exceed food standards in some items of home produce.

6.7 Brief overview of management options

The primary aim of this report is to provide a technical assessment of how well the Waikato Regional Council is meeting its own policy objectives in relation to cadmium accumulation in agricultural soils (which are outlined in **Section 1.1**). Technical and policy management options that might be applied to avoid, remedy or mitigate cadmium accumulation in agricultural soils are not the subject of this report. These areas are substantial enough to require a broader investigation and separate report on identified issues and management options. Production of such a report is suggested as a recommendation of this work (**Section 9.2**).

[293] McBride, M.B., **2003**. Toxic metals in sewage sludge amended soils: has promotion of beneficial use discounted the risks? *Advances in Environmental Research*, Vol. 8, pp 5-19.

However, the types of options that might be available are outlined briefly below by request of a reviewer. Technical management and policy options might include, but are not necessarily limited to:

- Source controls, *e.g.* further reductions in cadmium content of phosphate fertiliser; reduced phosphate fertiliser use through nutrient budgeting; reduced use of zinc pesticides where these contain significant cadmium.
- Practical decontamination measures, *e.g.* complexation and assisted leaching; soil blending; active phyto-accumulation and offsite disposal.
- Manipulation of soil chemistry or plant biochemistry, *e.g.* development of crops with lower capacity for cadmium uptake; use of soil additives that work to reduce crop uptake by increasing adsorption; development of chemical reagents designed to release soil phosphorus (allowing reduced fertiliser use).
- Review of the recommended soil guidelines.
- Review of risks associated with low level dietary cadmium, and how these relate to food standards.

6.8 Role of the Waikato Regional Plan

Under the Resource Management Act (1991) and amendments, regional councils are the regulatory agencies responsible for managing discharges of contaminants. This management may take a number of forms, ranging from requiring discharge consents through to accommodating and permitting the discharge by covering it as a rule in the Regional Plan.

Loading estimates presented in **Section 6.3** of this assessment have confirmed that for most productive soils in the Waikato region, phosphate fertilisers account for most cadmium being added. Confirmation that fertiliser is the dominant source of cadmium has significance for the *Permitted Activity Rule – Fertiliser Application* set out in the Waikato Regional Plan. Under this rule, fertiliser application is subject to a number of conditions, but does not require resource consent.[294] In cases where the Regional Plan is found to allow outcomes that are inconsistent with objectives of the Regional Policy Statement (**Section 1.1**), the latter usually has precedence. The policy is seen to set the framework within which the plan operates.

7 Baseline survey of cadmium in selected crops

7.1 Rationale and overview

As part of this assessment, samples of commercial produce sold in the Waikato region were collected and analysed for cadmium. The aim of this part of the work was to ascertain current average cadmium concentrations in some key Waikato crops, as a baseline for future comparison. It should be noted that:

- The purpose of this survey was not to assess the quality of produce being grown in local soils, but to assess what was being consumed by people resident in the Waikato region, on average, in 2004.

- The results of this work can not be used to derive statements about food risk, which is usually defined in relation to how cadmium over the total diet compares with the tolerable weekly intake (PWTI) for cadmium in food. Risks of dietary cadmium are

[294] Waikato Regional Plan, Section 3.9.4.11 Permitted Activity Rule – Fertiliser Application. Available from: http://www.ew.govt.nz/policyandplans/wrpintro/wrp/wrp3.9.4.htm

examined in the New Zealand Total Diet Surveys administered by the New Zealand Food Safety Authority.

Statistics for the areas of land used for growing horticultural and arable crops in the Waikato region are provided in **Appendix 9**.

Crops selected were potatoes, onions, lettuce and silverbeet. The first two of these are the Waikato's most significant outdoor horticultural crops in terms of land area used (**Appendix 9**). Potatoes are also significant for four other reasons:

- The Waikato region is now the second largest potato growing region of New Zealand, after Canterbury (**Section 3.7.2**);

- Potato crops require high loadings of superphosphate fertiliser (**Section 3.7.2**), which is a significant source of cadmium (**Section 6.3**, **Table 18**);

- Potatoes represent a significant contribution to daily cadmium (**Section 2.4.2**).

Lettuce and silverbeet were sampled in more limited numbers. These are not significant crops in terms of land area, but may be useful indicator plants to cross-check mean rates of cadmium uptake in the future. In the last published New Zealand Total Diet Survey,[295] silverbeet was identified as one of the foods making a significant individual contribution to dietary cadmium intakes (others were potatoes, breads, and carrots) (**Section 2.4.2**).

7.2 Sample collection

7.2.1 Potatoes and onions

Potatoes and onions (usually bagged) were purchased from the top 24 cities and towns in the Waikato region by population. Numbers of samples or bags purchased (**Appendix 11**[296]) were broadly related to population density in each city or town, and product availability. Overall, 53 bags of potatoes were purchased, and 36 bags of onions. Pack size ranged from less than 1 kg for some onions through to 10 kg for some potatoes.

Different varieties of potatoes are available at different times of the year. For this reason, sampling was split into two runs. The first collection took place between the dates 2-7 March 2004: in this run, samples were purchased from supermarkets in Hamilton, Mangakino, Matamata, Putaruru, Taupo, Tokoroa and Turangi. The second collection took place between the dates 11-13 and 17 May 2004: in this run, samples were purchased from supermarkets and growers in Cambridge, Coromandel, Huntly, Morrinsville, Ngaruawahia, Otorohanga, Paeroa, Pauanui, Raglan, Te Aroha, Te Awamutu, Te Kuiti, Thames, Tuakau, Waihi, Whangamata and Whitianga.

Supermarkets were appropriate for much of this sampling, because these represent areas where most food is purchased.

Many (but not all) of the potatoes and onions collected were grown in the Pukehohe area and surrounds: for example, one bag of potatoes purchased at the Southernmost town on the collection route (Turangi) was packed in the Northernmost town (Tuakau). A small number of samples were also grown outside the Waikato region.

Twenty-two of the potato samples collected came with no variety name indicated, particularly in the second sampling run: it is suspected that a number of these were Rua. For the 32 samples where variety was indicated, these were: Agria (3); Desiree

[295] Vannoort R, Cressey P and Silvers K, **2000**. 1997/98 *New Zealand Total Diet Survey Part 2 : Elements. Selected Contaminants & Nutrients.* ESR Client Report FW 99/47.
[296] Further details are provided in Environment Waikato **Document 891061.**

(3); Draga (6); Fianna (1); Frisia (2); Ilam hardy (1); Karaka (2); Nadine (8); Oamaru (1); Peru Peru (1); Red rascal (2); Stroma (2). Four samples were red potatoes (of which the identified Red Rascal were two).

Very few of the onions were labelled as to variety (apart from use of the odd generic term such as 'pickling onions'). Four samples were red onions, and the other 32 samples were brown.

7.2.2 Lettuce and silverbeet

Silverbeet and lettuce were purchased during 1-2 May 2004 from supermarkets, fruit and vegetable shops, and growers in the Hamilton, Te Awamutu, Morrinsville and Gordonton areas. These comprised 11 samples of lettuce (all Iceberg), and 11 samples of silverbeet (variety or varieties unknown).

7.3 Sample preparation

Details of sample preparation for analysis are provided in **Appendix 12**.

7.4 Results

7.4.1 Summary statistics and general comments

Measured cadmium concentrations in 53 different potato samples and six cooked composites are provided in **Appendix 13**. Concentrations measured in 36 different onion samples and four cooked onion composites are provided in **Appendix 14**. Cadmium in 11 samples of Iceberg lettuce and 11 samples of silverbeet are given in **Appendix 15**.

Summary statistics for cadmium and moisture contents of the commercial food samples tested in this work are listed in **Table 24**. A histogram showing the spread of cadmium results for the 53 uncooked potato samples is provided in **Figure 14**.

Table 24 Summary statistics for cadmium and moisture contents of the commercial food samples tested in this work (2004).

	Fresh potatoes (N=53)	Potato composites (boiled, mashed) (N=6)	Fresh onions (N=36)	Onion compo-sites (fried) (N=4)	Iceberg lettuce (N=11)	Silverbeet (N=11)
Cadmium, µg/kg						
Mean	25.4	27.2	16.0	18.1	19.0	25.9
Median	20.0	22.5	10.0	16.8	14.5	18.7
Geometric mean	19.8	26.0	11.3	17.5	16.4	22.2
Standard deviation	19.6	9.5	15.1	5.6	10.4	18.7
95% confidence error on mean	5.3	11.8	5.0	6.9	7.0	12.5
Minimum	2.2	19.5	3.0	12.8	4.3	10.4
Maximum	106.0	43.6	65.4	25.9	42.4	76.4
Moisture (%)						
Mean	81.9	82.4	88.9	75.4	96.3	90.5
Median	82.7	82.4	88.7	75.4	96.3	90.6
Geometric mean	81.8	82.4	88.9	75.4	96.3	90.5

Standard deviation	3.7	1.6	1.3	1.9	0.5	0.4
95% confidence error on mean	1.6	2.0	0.7	2.4	0.3	0.3
Minimum	74.5	80.0	87.1	73.3	95.2	89.6
Maximum	87.0	85.1	92.3	77.4	97.0	91.0

In general, there was a reasonably wide spread of results for cadmium in each food tested (**Table 24**; **Figure 14**; **Appendices 13-15**).

Mean cadmium concentrations in potato and onion samples collected from throughout the Waikato region in 2004 (this work) are **25.4 µg/kg**, and **16.0 µg/kg**, respectively (**Table 24**). The figures will be useful as an indicative benchmark for future studies.

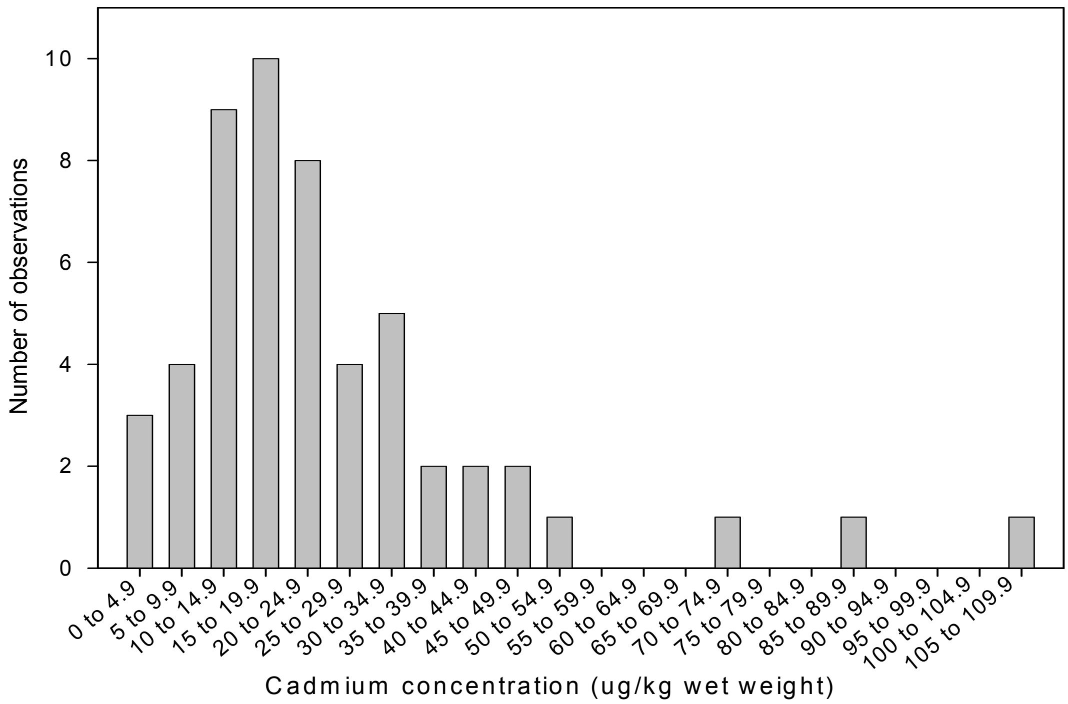

Figure 14 Histogram of cadmium concentrations in 53 samples of potato purchased in the Waikato region.

The average concentration measured for potatoes in this survey is analytically indistinguishable from the figure reported from the first quarter of the latest New Zealand total diet survey 2003-04, which is **25.8 µg/kg**.[297] In addition to confirming the baseline figure for 2004, this suggests that potatoes grown in the Waikato region have no more or less cadmium in them than potatoes grown in other regions of New Zealand.

Overall, only one sample exceeded the current food standard of 0.1 mg/kg (100 µg/kg). This was 106 µg/kg in a Frisia potato from a bag purchased from a supermarket. The variety of potato was unimportant, because the other identified Frisia sample in the survey contained six times less cadmium (18.2 µg/kg).

Based on a distribution analysis of the log-normalised data, it is estimated that about **1.5%** of potato samples purchased in the Waikato region in 2004 were likely to exceed the food standard for cadmium. Since the average cadmium concentration in Waikato

[297] Shaw IW, Vannoort RW and Thomson BM, **2003**. 2003/04 *New Zealand Total Diet Survey Analytical Results – Q1.* ESR Client Report FW 03/77. Available from: http://www.nzfsa.govt.nz/science-technology/research-projects/total-diet-survey/reports/quarter-1/index.htm

region samples was identical to that reported from the Total Diet Survey (with fewer samples, but collected over New Zealand), and the Waikato is now New Zealand's second largest potato growing region, potatoes sampled in this survey can probably be taken as being representative of a wider New Zealand sample.

All samples were also tested for uranium, because this is another known contaminant of rock phosphate (though less significant than cadmium). No uranium was detected in any potato, onion or lettuce sample, to a detection limit of 0.0004 mg/kg (0.4 parts-per-billion) (fresh weight) (**Appendices 13–15**). Uranium at just above this detection limit was detected in three samples of silverbeet (**Appendix 15**): however, concentrations measured in these samples would not be regarded as significant in any health sense.

Lettuce and silverbeet samples were also tested for iron, as a marker for potential soil contamination. Levels reported were all within the normal range expected for plant tissue and indicative that no soil contamination of samples had occurred (**Appendix 15**). Laboratory cross-checking using a certified reference material also showed good accuracy.

Moisture content was measured for a number of samples. Boiling and mashing had no significant effect on the moisture content of potatoes, with this averaging 82% whether the potatoes were raw or cooked. For this reason, metal concentrations remained the same whether or not the potato was cooked.[298] By contrast, frying caused a small reduction in the moisture content of the onions (from 88.9% to 75.4%), causing the average cadmium concentration in cooked composites to be slightly higher than that of raw onions (**Appendix 13**, **Table 24**).

7.5 Home produce: Buttercrunch lettuce

Gaw (2004)[299] has recently carried out cadmium uptake experiments on ten[300] Waikato soils, in order to estimate uptake under home gardening conditions. Lettuces were grown in pots. In the absence of lime amendments, soil pH values averaged 5.6 (range 5.0 to 5.9). Soil cadmium concentrations were all well below the industry recommended upper limit, ranging from 0.03 to 0.54 mg/kg, and averaging 0.23 mg/kg.

Lettuces used in this case were Buttercrunch (not Iceberg, as sampled in the commercial survey). Buttercrunch is reputed to be popular with home gardeners.

Under these circumstances, cadmium was found to exceed the food standard of 0.1 mg/kg (fresh weight) in lettuce grown in four (40%) of the soils.[301] The lowest soil cadmium concentration associated with a food standard exceedance was only 0.2 mg/kg. Concentrations observed in the lettuce are reported to have closely matched uptake predicted by the UK DEFRA CLEA equation for leafy vegetables (**Section 3.5.1**; illustrated in **Figure 6**).[302]

In **Sections 3.8** and **6.6**, it was noted that at pH values of Waikato soils, 1 mg/kg is the regulatory point at which residential soil would be regarded as contaminated with cadmium (**Tables 5** and **6**). This risk-based guideline is itself derived partly on the basis of cadmium uptake in home produce, predicted by the same uptake equation.

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298 Since trace metal concentrations in water are very low (compared with those in foodstuffs), water absorption during cooking has the potential to cause a decrease in measured metal concentrations. This occurs because the concentration is expressed as mass of metal per mass of substance (mg/kg). A decrease in metal concentration can be observed either by decreasing the amount of metal (decreasing the mg), or increasing the relative mass of substance (increasing the kg). Strictly speaking, the food standards should be taken to apply to food as eaten. In the case of potatoes, moisture content remains the same on boiling and mashing, so that the cadmium concentration in the raw potatoes is the same as that of the cooked potatoes.

299 Gaw SK, **2004**. Department of Chemistry, University of Waikato. Personal communication.

300 Four orchard soils, two pasture soils, two bush-block soils, and two soil mixtures.

301 Note, however, that metal uptake experiments carried out in pot trials are reported to often show increased uptake relative to the field situation; it is therefore possible that uptake from the same soils in home gardens (rather than pots) would not result in any food standard exceedances.

302 UK Environment Agency, **2002.** *Soil guideline values for cadmium contamination.* Department for Environmental, Food and Rural Affairs (DEFRA): http://www.defra.gov.uk/environment/landliability/pdf/sgv3.pdf

This is fortunate, because it means that the amount of uptake observed in the Buttercrunch lettuce trial—which was found to match that predicted by the DEFRA CLEA equation—has already been factored in to the home soil limit of 1 mg/kg cadmium in the jurisdiction where that guideline was derived (the UK). As such, the residential soil limit should generally remain sufficiently protective even in cases where cadmium concentrations do exceed food standards in some items of home produce. The main possible exception to this might be for people with who eat most of their produce from a home garden, rather than a portion of it.

8 Off-site effects in agricultural catchments

8.1 Scope

The focus of this section is to provide some general comments on potential loss of cadmium from agricultural areas to freshwater receiving environments.

A substantial body of work exists on metal stormwater loadings to (particularly estuarine) sediments in New Zealand, predominantly from urban and industrial sources. By contrast, very little work appears to have been carried out to determine the potential impact of metals specifically associated with pastoral farming and horticulture on rural streams, rivers and lakes.

The most significant of these metals is probably zinc, rather than cadmium. Zinc is now widely used as an animal remedy for facial eczema control, and the amount added to Waikato soils each year may be between two and three orders of magnitude greater than the amount of cadmium added (a maximum of 8500 t/yr for zinc compared with and estimated 8.3 t/yr for cadmium) (**Section 6.2.2**). Although this does not translate to a potential human health issue,[303] there are some implications for the health of soils and freshwater systems.[304]

In the absence of substantive research, this section is not intended as a definitive statement on loss of cadmium from agricultural areas to freshwaters, but a preliminary sketch of the factors involved, and an assessment of the potential for adverse effects.

8.2 Dominant source and mobile forms of cadmium

On a regional basis, and in terms of total mass loadings, superphosphate fertilisers comprise the dominant potential anthropogenic source of new cadmium within agricultural catchments. An estimated 8.3 tonnes of cadmium is deposited on Waikato pastoral and horticultural farmland each year, of which 99% is attributable to superphosphate fertiliser use (**Section 6.4**).

Superphosphate fertiliser is produced by reacting sulphuric acid with rock phosphate, which is itself mainly the insoluble mineral fluorapatite: $Ca_5(PO_4)_3F$. Reactions occurring during the manufacture of superphosphate are complex, but can be summarised by the overall equation:[305]

$$\underset{\text{fluorapatite}}{2Ca_5(PO_4)_3F} + \underset{\text{sulphuric acid}}{7H_2SO_4} + \underset{\text{water}}{3H_2O} \longrightarrow \underset{\text{gypsum}}{7CaSO_4} + \underset{\text{calcium dihydrogen phosphate}}{3Ca(H_2PO_4)_2.H_2O} + \underset{\text{hydrofluoric acid}}{2HF}$$

303 In mammalian physiology, zinc is an essential element, whereas cadmium is non-essential.
304 This topic will be the subject of further investigation.
305 Harland CW, Donaldson L Simpson J and Wansbrough H, **1998**. The manufacture of sulfuric acid and superphosphate, **In** Packer JE, Robertson J and Wansbrough H (Eds.), 1998. *Chemical processes in New Zealand*, Second Ed. New Zealand Institute of Chemistry.

Ordinary single superphosphate contains approximately 30% calcium dihydrogen phosphate, 45% gypsum, 10% calcium biphosphate ($CaHPO_4$), 10% iron, silicon and aluminium oxides (*etc.*), and 5% water; overall this supplies 18-21% available P_2O_5.[306]

During mineral formation or precipitation, trace metal cations tend to substitute for major metals of similar size and charge—this is termed isomorphic substitution. Substitution of one metal for another is favoured when the two metals are within ±10% of each other in size, and differ by not more than one unit of charge. Calcium and cadmium have the same charge (2^+), and their ionic radii are sufficiently close in size for substitution to occur readily.[307] The ionic radius of six-coordinate cadmium is 0.95 Å (95 pm); and that of six-coordinate calcium is 1.00 Å (100 pm).[308] Cadmium in rock phosphate, and superphosphate fertiliser, is therefore mainly likely to be present as a trace-level isomorphic replacement for calcium. Major calcium-containing constituents of superphosphate fertiliser are therefore more accurately represented by the formulas:

$(Ca_xCd_{(1-x)})(H_2PO_4)_2.H_2O$ $(Ca_xCd_{(1-x)})SO_4$ $(Ca_xCd_{(1-x)})HPO_4$

(where x is a number slightly less than 1)

Calcium dihydrogen phosphate and gypsum are slightly soluble in water, and when superphosphate fertiliser comes into contact with moisture, some of the cadmium close to the granule surfaces will dissolve as the hydrogen phosphate dissolves:

$$(Ca_xCd_{(1-x)})(H_2PO_4)_2.H_2O \longrightarrow xCa^{2+}_{aq} + (1-x)Cd^{2+}_{aq} + 2H_2PO_4^- + H_2O$$

$$(Ca_xCd_{(1-x)})SO_4 \longrightarrow xCa^{2+}_{aq} + (1-x)Cd^{2+}_{aq} + SO_4^{2-}$$

(where x is a number slightly less than 1)

This is **dissolved**, or **free ionic**, cadmium, Cd^{2+}_{aq}. Use of either term implies that the metal ion is physically dissolved in solution, with each atom being surrounded by a solvent sphere. A more precise representation of this form of cadmium is $[Cd(H_2O)_6]^{2+}_{aq}$, or $[Cd(H_2O)_5OH]^{+}_{aq}$, with the relative proportion of the second form increasing with pH.

Most free ionic cadmium released in this way will rapidly be sequestered by highly adsorptive solid phases in the underlying soil. As noted in **Section 3.4**, soil phases responsible for cadmium fixation, in order of probable importance, include organic matter, hydrated metal oxides, clay minerals, carbonates, and sulphides.[309,310,311,312]

Such sequesterisation is the primary mechanism responsible for the progressive accumulation of cadmium (and retention of phosphate) in soils. Adsorption of cadmium is never entirely quantitative, but better envisioned as an equilibrium process, with small concentrations always persisting in soil solution. The amount of release depends on exact soil conditions (**Table 3**). Over time, with ongoing addition, cadmium retained by the soil becomes a progressively larger reservoir for future release (**Section 3.4**). Two main mechanisms of cadmium re-mobilisation exist: these are desorption of cadmium back in to the soil solution as the free ionic form or simple dissolved complex, and transport of cadmium adsorbed on very fine particles with high surface areas, termed colloids.

306 Budavari S, O'Neil MJ, Smith A, Heckelman PE and Kinneary JF, **1996**. The Merck Index, 12th Ed. Merck & Co., Inc., Whitehouse Station, New Jersey. Entry for calcium phosphate, monobasic (p 276).

307 This is actually the same mechanism which underpinned damage to the skeletal system in *itai itai* disease, an effect which was mainly manifest in persons with a low calcium status.

308 CRC Handbook of Chemistry and Physics, 80tth Edition, **1999-2000**. 12-14. CRC Press.

309 Gray CW, McLaren RG, Roberts AHC and Condron LM, **1998**. Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. *Australian Journal of Soil Research*, Vol. 36, No 2, pp 199-216.

310 Gray CW, McLaren RG, Roberts AHC and Condron LM, **2000**. Fractionation of soil cadmium from some New Zealand soils. *Communications in Soil Science and Plant Analysis*, Vol. 31, No. 9-10, pp 1261-1273.

311 Kim ND and Fergusson JE, **1991**. Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soil. *Science of the Total Environment*, Vol. 105, pp 191–209.

312 Kim ND and Fergusson JE, **1992**. Adsorption of cadmium by an aquent New Zealand soil and its components. *Australian Journal of Soil Research*, Vol. 30, No. 2, pp 159-67.

Colloids are formed in soil through two processes: detachment of fragments of inorganic minerals or organic species from their parent materials as a result of weathering and degradation, and partial-precipitation of dissolved species in groundwater, triggered by pH and redox changes. As a result of their high surface areas and charge characteristics, soil colloids are often responsible for the majority of metal adsorption in soils. However, if small enough, colloids can begin to move with groundwater rather than remain in place. Particles in the range 0.1 to 0.2 µm are the most mobile in groundwater. Whether colloidal transport becomes significant as a means of transporting adsorbed contaminants is site-specific, being mainly determined by soil and groundwater chemistry at a given location. Usually, colloids are more mobile when dissolved ion concentrations are low. In circumstances where colloidal transport is significant, transport of the contaminant is determined by the properties of the colloid, rather than the inherent solubility of the contaminant.[313] Cadmium in this form is termed **colloidally-bound**.

A second fraction of cadmium in the original superphosphate will be less readily available in the first instance, being entrained within the crystal lattice of calcium dihydrogen phosphate inside the superphosphate granules, or associated with smaller particles of the same as the granules degrade. Similarly, much of the cadmium in soil will be adsorbed to solid particles that are too large to move in groundwater in the absence of preferential flow-paths. This is called **particulate-bound** cadmium. Prior to degradation of superphosphate granules, loss of this form of cadmium from a property is most likely to occur as a result of rainfall events or irrigation causing loss of particulate material with surface water runoff.

A summary of expected forms of cadmium that might be mobilised to water in agricultural catchments, and their likely environmental behaviour and fate, is provided in **Table 25**.

Table 25 Forms of cadmium potentially mobilised to water from agricultural catchments.

	Free ionic/soluble	Colloidally-bound	Particulate-bound
Physico-chemical form	Simple hydrated metal ion, simple organic and inorganic complexes	Adsorbed on organic, inorganic, or mixed organic/inorganic colloids	Adsorbed on organic or inorganic solids, incorporated in remains of organisms, incorporated in minerals
Examples	$[Cd(H_2O)_6]^{2+}_{aq}$; $[CdHCO_3]^{+}_{aq}$; Cd-fulvate complex	Cd—humic acid; Cd—Fe_2O_3; Cd—humic acid/Fe_2O_3	$(Ca_xCd_{(1-x)})(H_2PO_4)_2.H_2O$ (from superphosphate) Cd—humic acid (from soil)
Approximate diameter range (nm)	0.8 to 4 (including solvent sphere)	10 to 500	>500
Predominant likely means of transport where mobile	Groundwater; surface runoff following superphosphate application	Groundwater; Surface runoff	Surface runoff
Likelihood of attenuation by readsorption prior to entering nearby surface water environments	High	High for groundwater; Low for surface runoff	Low
Dominant fate on reaching freshwater	Contribution to total dissolved cadmium; Progressive retention in bottom sediments	Contribution to total dissolved cadmium; Retention in bottom sediments	Retention in bottom sediments

313 Weiner ER, **2000**. *Applications of Environmental Chemistry. A practical guide for environmental professionals.* CRC Press LLC, Florida.

8.3 Receptors and guidelines

The significance of contaminant movement depends on the identified receptors living in the receiving environments. Water and sediment guidelines for freshwaters are based on the susceptibility of various ecological receptors, such as fish and sediment-dwelling invertebrates. By contrast, quality of groundwater (itself) is usually assessed against drinking water standards, designed for the protection of human health. Some relevant guidelines are as follows.

Freshwaters[314] (mainly relates to free ionic/soluble cadmium):

- **0.2 µg/L** for protection of 95% of species
- **0.06 µg/L** for protection of 99% of species

Drinking water[315] (groundwater is usually assessed against this standard):

- **3 µg/L**

Sediments:[314]

- **1.5 mg/kg** (dry weight) as a probable 'no-effects' threshold. Termed the *ISQG-Low*.[316]
- **10 mg/kg** as a median level where most organisms would be adversely effected. Termed the *ISQG-High*.

Of metals carried in the water column, considerable evidence exists that the free ionic forms of metals such as copper, lead, cadmium and aluminium are usually the most directly toxic forms to aquatic biota. These tend to readily bind with carrier proteins and be transported across cell walls. Complexation by natural ligands—especially humic substances—usually reduces the toxicity of these metal ions.

8.4 Potential for leaching and movement in groundwater

Fortunately, research on cadmium leaching from a range New Zealand pasture soils that had received superphosphate fertiliser has been carried out by Gray *et al.*[317] These researchers found that annual losses to leaching accounted for between 5 to 15% of the cadmium applied. As might be expected, more cadmium was leached as groundwater pH decreased (greater acidity retards adsorption and enhances desorption processes, **Section 3.4**), and total groundwater drainage volume increased.

However, concentrations of cadmium reaching groundwater were found to be low, and always less than the drinking water standard. Observed results are likely to reflect the net effect of loss of cadmium from the surface followed by progressive re-adsorption of cadmium further down the soil profile. Over time, a plume of cadmium enrichment would be expected to slowly develop in the subsoil itself.

On the basis of this work, it would seem that cadmium is unlikely to become elevated enough in groundwater to pose an issue for drinking or irrigation water in most instances. As cadmium attenuation will increase strongly with distance from the source, it would also seem unlikely that groundwater will contribute a significant flux of cadmium to streams, either now or in the future.

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314 ANZECC, **2000**. Australian and New Zealand Guidelines for Fresh and Marine Water Quality.
315 Ministry of Health, **2000**. Drinking-Water Standards for New Zealand 2000.
316 ISQG is the abbreviation of 'Interim Sediment Quality Guideline.'
317 Gray CW, McLaren RG and Roberts AHC, **2003**. Cadmium leaching from some New Zealand pasture soils. *European Journal of Soil Science*, Vol. 54, No. 1, pp 159-166.

Exceptions may exist in sandy soils of low adsorptive capacity, and in this respect it is worth noting that sandy soils of the Tasman District appear to show a very low rate of cadmium accumulation (**Table 2**, **Section 3.3**). This suggests that groundwater in the Tasman District (and other sandy areas) may contain proportionately higher concentrations of dissolved cadmium than other regions (although it is also possible that this may be compensated for by lower total cadmium inputs).

Exceptions may also exist in cropping horticultural catchments, due to loss of soil organic matter, a dominant adsorptive phase for cadmium in soils. Loss of soil organic matter has the potential to cause a significant increase in cadmium leaching to groundwater, as a result of the remaining soil have a substantially lower overall adsorption capacity (**Appendix 6**).

8.5 Cadmium in surface runoff and direct entry to waterways

The most effective means of cadmium movement from land to surface water is likely to be transport of particulate-bound and colloidally-bound cadmium in runoff. Mobile particulate-bound cadmium may take any of the forms indicated in **Table 25**.

In cropping catchments, a significant cadmium flux would be expected to accompany loss of particulate soil organic matter. At a paddock level in horticultural cropping soils, this loss is estimated at 7-30 tonne/ha/yr[318] (**Appendix 6**).

- Since much of the adsorbed cadmium in horticultural soils is likely to be concentrated in the organic fraction, the cadmium content of the organic matter in the soil is likely to be much higher than that of the whole soil. For example, at a mean whole soil concentration of **0.7 mg/kg**, the concentration in organic matter could be **14 mg/kg** assuming that the soil contained 10% organic matter, and this sequestered half the total cadmium. Annual loss of 20 t/ha/yr in particulate organic matter would then represent concurrent loss of up to 280 g/ha/yr of cadmium.

In pastoral catchments, however, the most important mechanism for cadmium mobilisation to waterways is likely to be transport of superphosphate granules and particles in surface water runoff.

Transfer of phosphorus from land to water can not occur without sources of phosphorus. Globally, sources of phosphorus to soils include native soil phosphorus, phosphate fertilisers, and imported livestock feed concentrates, which are returned to the soil either via direct excretion during grazing or, after storage as spread manure.[319]

Gillingham and Thorrold have recently published a review[320] of New Zealand research relating to phosphate runoff from pasture. In New Zealand pastoral systems, superphosphate fertilisers represent the primary phosphate source, with excreta from grazing animals providing a secondary recycled source. These authors estimate that diffuse agricultural sources contribute about 91% of total phosphorus entering fresh waters annually, with 0.11 to 1.67 kg/ha/yr being removed.

Perhaps 80% of phosphorus exported in waterways that drain pastoral catchments is in the particulate form: however, only a proportion of this will be accounted for by granules and smaller particles of superphosphate fertiliser itself. This latter fraction would presumably still carry most of its intrinsic cadmium load. The direct contribution made by superphosphate fertiliser to overall phosphorus runoff is highest in the period

[318] Edmeades Consultants Ltd, **2002**. The content and value of nutrients in the topsoils of the Franklin District. Environment Waikato Internal Series IS02/06. Environment Waikato Document **764122**.
[319] Macleod C and Haygarth P, **2003**. A review of the significant of non-point source agricultural phosphorus to surface water. *SCOPE Newsletter No. 51, Special Edition June 2003*. PDF saved as Environment Waikato Document **946497**.
[320] Gillingham AG and Thorrold BS, **2000**. A review of New Zealand research measuring phosphorus in runoff from pasture. Journal of Environmental Quality, Vol. 29, No. 1, pp 88-96.

immediately after fertiliser is applied. After fertiliser application, phosphorus runoff from surface slopes can increase by up to 300 times the baseline level, and after peaking, declines exponentially.[321]

In addition to particulate runoff, a significant contribution to phosphorus in waterways can be made by superphosphate falling directly into water during aerial top-dressing, or spreading too close to waterways. Twenty percent of the annual phosphorus exported from one small New Zealand catchment was attributed to fertiliser falling directly in the waterway or permanently saturated soils (from which surface runoff is significant).[321]

Entry of particulate-bound cadmium to waterways would be expected to follow the same pattern as seen with total phosphorus, with a baseline figure representing loss of cadmium associated with mobilised particulate soil organic matter (*etc.*) and annual peak loadings occurring after application of superphosphate fertiliser.

Interestingly, catchment scale models have been developed for phosphorus runoff, and it may be possible to readily adapt such models to predict cadmium fluxes associated with fertiliser application.

8.6 Dissolved cadmium in freshwaters

Background levels of cadmium in New Zealand freshwaters can be very low by world standards. The usual concentration in the upper catchment of the Manuherikia River, Central Otago, which is fed by rain and snow-fed streams travelling through slightly modified tussock country, has been determined as 0.010 µg/L. In the lower catchment, which is typified by intensive grazing, dissolved cadmium concentrations were found to increase by 50%, to 0.015 µg/L.[322,323] Dissolved cadmium concentrations reported for the lower catchment were well below the most conservative current New Zealand ANZECC guideline value (for protection of 99% of species) of 0.06 µg/L.[324] This is perhaps what might be expected based on the likely attenuation of any free ionic or colloidal cadmium that is mobilised to groundwater (**Table 25**).

- It is possible that dissolved cadmium concentrations in waterways could exceed ANZECC guideline values during and immediately after application of superphosphate fertiliser; however, strictly speaking, for cadmium and most other contaminants, these guidelines relate to longer term (chronic) exposure, rather than transient pulses.

- It is also conceivable that concentrations of dissolved cadmium in freshwaters will eventually increase through the delayed impact on the quality of groundwater reaching streams and rivers; however, the cadmium front (if there is one) would lag well behind the nitrate front.

Environment Waikato monitor for heavy metals (including cadmium) in the water column at five sites[325] on the Waikato River at five-yearly intervals, with four samples collected at each site during the year of sampling. No cadmium was detected in Waikato River water in any sample during the last sampling run for the 2000 year, to a detection limit of 0.04 µg/L.[326]

[321] Gillingham AG and Thorrold BS, **2000**. A review of New Zealand research measuring phosphorus in runoff from pasture. Journal of Environmental Quality, Vol. 29, No. 1, pp 88-96.

[322] Ahlers WW and Hunter KA, **1984**. A baseline survey of water quality and trace metal levels at lignite deposits in the Upper Manuherikia Valley, Central Otago. **In** Trace elements in the eighties. *Proc. of the Conf. of the N.Z. Trace Element Group* 7-8 Aug. 1984, Massey University, Palmerston North, pp 14-23.

[323] Ahlers WW and Hunter KA, **1988**. Mass transport and natural distributions of some trace metals in the Manuherikia River, Central Otago. **In** Trace elements in New Zealand: environmental, human and animal. *Proc. N.Z. Trace Element Group Conf.* 30 Nov.-2 Dec. 1988, Lincoln College, Canterbury, pp 37-46

[324] ANZECC, **2000**. Australian and New Zealand Guidelines for Fresh and Marine Water Quality.

[325] Waikato River sampling sites are the Taupo control gates, Ohakuri tailrace bridge, Narrows Bridge, Horotiu Bridge and Tuakau Bridge.

[326] Wilson B and Smith P, **2001**. Waikato River water quality monitoring programme. Data report 2000. Environment Waikato Document 670412.

On occasion, other authors have reported much higher levels of cadmium in Waikato surface waters,[e.g.327] but these are thought to represent an artefact of contamination introduced during sampling or analysis. Analysis of heavy metals at their natural or near-natural concentrations in fresh and marine waters can be notoriously difficult, being subject to the influence of contamination introduced during or after sampling (through contact with solvents, airborne dust, the analytical instrument, *etc.*). At sub parts-per-billion levels, specific protocols are usually required to prevent trace contamination comprising a more than minor part of the overall measurement.[328] Where significant differences exist between surveys for dissolved heavy metals in natural waters, the lower results are more likely to be the accurate ones.

Based on the Otago results for the Manuherikia River, and Environment Waikato's results for the Waikato River, there is no current evidence to suggest that use of superphosphate fertiliser constitutes an issue in terms of average dissolved cadmium concentrations realised in freshwater receiving environments.[329]

8.7 Cadmium accumulation in freshwater sediments

The main off-site impact of the cadmium in superphosphate fertiliser is expected to be accumulation of the metal in sediments of agricultural receiving environments, rather than average cadmium concentrations in water. This is for two reasons:

- Most of the mobilised cadmium is likely to already be in particulate-bound form (**Section 8.5**; **Table 25**);

- A significant fraction of any dissolved cadmium which does enter streams and rivers is expected to be progressively adsorbed by organic matter and hydrous metal oxide phases present in sediments, by identical processes to those which govern cadmium adsorption in soils (**Section 3.4**).

Reliable empirical survey data in this area is currently very limited. However, recently, a multi-element survey was carried out on surface sediment grab-samples collected from 10 small lakes in the Waikato region (Lakes Hakanoa, Maratoto, Ngaroto, Rotomanuka, Serpentine East, Serpentine North, Te Koutu, Waahi, Waikare, and Whangapae). Of the 32 elements tested, only two elements showed highly significant ($p<0.001$) correlations with total phosphorus in the sediment, and the phosphorus-cadmium correlation was the strongest of these two ($R = 0.944$, $p<0.001$).[330] This is illustrated in **Figure 15**. The high correlation observed suggests that superphosphate fertiliser is likely to be a dominant (although not necessarily the only) source of cadmium to these lake sediments. Summary statistics for cadmium concentrations in sediment of the ten lakes are provided in **Table 26**.

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327 Roldan, RM, **2002**. *Distribution of trace metals in Waikato natural water.* MSc thesis in Chemistry, University of Waikato.

328 Ahlers WW, Reid MR, Kim JP and Hunter KA, **1990**. Contamination-free sample collection and handling protocols for trace elements in natural fresh waters. *Australian Journal of Marine and Freshwater Research*, Vol. 41, No. 6, pp 713-20.

329 However, it should be borne in mind that dilution volumes in the Waikato River are very high, and there may be special cases where involving smaller streams and rivers in well developed catchments, where average dissolved cadmium concentrations do approach guideline values.

330 Source data and correlation matrix: Environment Waikato Document **894590**.

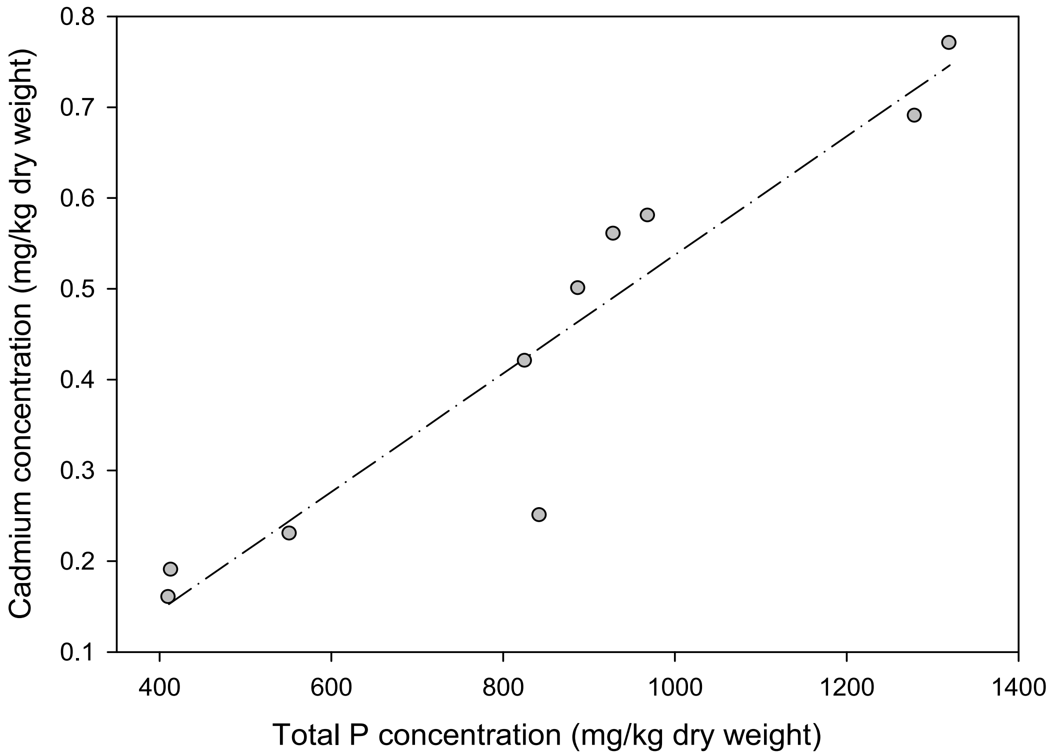

Figure 15 Relationship between concentrations of total phosphorus and cadmium in a small survey of Waikato lake sediments.

Table 26 Summary statistics for cadmium in sediment grab samples of ten small Waikato lakes.

All figures are in mg/kg (dry weight).[331]

Mean	0.44
Median	0.46
Geometric mean	0.38
Standard deviation	0.22
95% confidence error on mean	0.16
Minimum	0.16
Maximum	0.77

Although the sample size is limited, lake sediments in the Waikato region do appear to show elevated cadmium, relative to background values (typically 0.15 mg/kg or below). However, on average, cadmium concentrations in the sediments surveyed are still over three times lower than the ANZECC (2000)[332] 'no-effects' threshold of 1.5 mg/kg.

Results of this preliminary survey therefore suggest that cadmium accumulation in river and lake sediments sourced from agricultural catchments in the Waikato region is likely to be occurring, and that superphosphate fertiliser is likely to be a dominant source.

In the lakes surveyed, a tolerable margin still exists between current concentrations and the level where adverse effects may begin. This may or may not be the case for other lakes, rivers or streams. Further work is necessary to better delineate the rate of cadmium accumulation in the freshwater sediment receiving environment.

[331] Source data: Environment Waikato Document **894590**.
[332] ANZECC, **2000**. Australian and New Zealand Guidelines for Fresh and Marine Water Quality.

8.8 Summary

Essentials of **Section 8** can be summarised as follows.

1. Superphosphate fertiliser is at present the main (99%) source of new cadmium introduced to agricultural catchments.

2. Cadmium in groundwater is unlikely to be a general issue; however, exceptions may exist for sandy soils, or soils subject to substantive loss of soil organic matter.

3. Surface runoff of particulate-bound cadmium comprises the primary means by which cadmium is likely to be transferred from land to surface water bodies.

4. Some New Zealand research suggests that use of superphosphate fertiliser in agriculture causes average dissolved cadmium concentrations in freshwaters to increase. However, in freshwater systems reliably assessed to date, the magnitude of this increase (if any) is modest in relation to relevant guideline values for dissolved cadmium.

5. Despite low dissolved concentrations, the influx of particulate-bound cadmium is apparently resulting in the gradual accumulation of this metal in freshwater (and possibly coastal) sediments.

The main off-site issue associated with use of cadmium in agriculture is therefore expected to be the accumulation of cadmium in receiving sediments. Accumulation of cadmium in sediments would be of concern if net accumulation rates are sufficient to enable sediment cadmium concentrations to eventually pass ecotoxic thresholds.

Further work is required to assess whether cadmium accumulation in rural streams and rivers is sufficient to pose a risk to ecological receptors (and over what term), and which types of freshwater systems would be most susceptible in this regard.

9 Summary and recommendations

9.1 Summary

9.1.1 Policy objectives

A central objective of the Land and Soil section of the Waikato Regional Policy Statement (Section 3.3.8[333]) is that the range of existing and foreseeable uses of the soil resource should not be reduced as a result of the contamination of soils. This rests alongside the complementary objective that versatility and productive capacity of the region's soil resources should be maintained (Waikato Regional Policy Statement Section 3.3.9[333]).

9.1.2 Loss of soil resource

There are three means by which existing and foreseeable uses of the productive soil resource may be lost as a result of cadmium accumulation. These are:

1. Soil cadmium concentrations become such that they pose a potential issue for international market access. The current recommended upper limit for total cadmium in New Zealand agricultural soil is **1 mg/kg** (dry weight). This figure is

[333] Waikato Regional Policy Statement, **2004**. Sections 3.3.8 and 3.3.9. Available from: http://www.ew.govt.nz/policyandplans/rpsintro/rps/RPS3.3.8.htm

partly designed to meet current and projected expectations of international trading partners.[334]

2. Soil cadmium concentrations become such that the property can no longer be subdivided for residential or rural-residential use without some form of investigation and/or remediation. This threshold is also **1 mg/kg** in the Waikato region.[335]

3. Soil cadmium concentrations (in combination with other soil conditions), become such that food standards would be routinely broken in specific crops grown on a property. This impact relates to the capacity of any land to be used, either currently or in the future, for production of specific vegetable and grain crops.

Loss of soil resource can be defined as the point at which any of these outcomes are realised.[336] In the case of cadmium accumulation, loss of soil resource, when it occurs, is largely irreversible.[337]

The first and second outcomes are comparatively straightforward to quantify. In recent surveying, cadmium levels in 23% and 14% of Waikato horticultural and pastoral soil samples (respectively) were found to already exceed the recommended guidelines for cadmium in agricultural and residential soils (both 1 mg/kg).[338]

Assessment of the underlying sample distributions suggest that perhaps 11% of Waikato's pastoral soils and 17% of horticultural soils may already exceed 1 mg/kg soil cadmium. For horticultural soils, this would represent approximately 1775 ha in land area. For pastoral soils (sheep, beef and dairy land), this would represent approximately 157000 ha in land area.[339] Within the pastoral soils sample set, cadmium concentrations were highest for dairy farms. All pastoral soil exceedances of the 1 mg/kg guideline found to date have been for dairy farms.[340]

Based on **average** cadmium concentrations in surveyed soils, relative to the 1 mg/kg soil guideline, about two-thirds of the productive pastoral, horticultural and arable surface soil resource capacity for cadmium assimilation has been used at time of writing.[341] Most of this 'available' capacity was consumed over the 65 year period from 1940 to the present day.[342]

Loading estimates confirm that most of this cadmium is added through use of superphosphate fertiliser, which contains up to 24 mg/kg cadmium.[343] In some cropping horticultural soils, a significant secondary contribution may also be made by zinc-based fungicides.[344]

Current rates of cadmium accumulation may have decreased by up to one-third[345] in response to industry-led initiatives,[346] but are still rapid, and unsustainable even in the medium term.[347] Based on reported superphosphate sales figures, an estimated **8.3 tonnes** of cadmium is applied to Waikato soils per annum.[348] A summary of significant projected soil resource loss points for the Waikato region at current cadmium loadings is provided in **Table 27**.[349]

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334 **Sections 3.8.2**, **3.8.4**, **6.4.3** and **6.4.4**. Comments about default soil depths to which this guideline would generally apply in New Zealand are provided in **Section 3.9.2** (pastoral soils) and **Section 3.9.4** (horticultural soils).
335 **Sections 3.8.2** and **3.8.4**. Comments about soil depths to which this guideline would generally apply in New Zealand are provided in **Section 3.9.3**.
336 **Section 1.2.5**.
337 **Section 3.2**; **Section 3.4.**
338 **Section 5.2.2**.
339 **Sections 5.2.2** and **5.2.3**.
340 **Section 5.2.3**.
341 **Figure 15, Section 5.3**.
342 **Section 3.3**.
343 **Section 4.2.1**.
344 **Sections 6.2.2**, **6.3.1** (see **Table 25**) and **6.4.4**.
345 **Section 6.4.6**.
346 **Section 4.2.1**.
347 **Section 6.4**.
348 **Sections 6.4.1** and **6.4.2**.
349 Based on the findings in **Section 6.4**.

Table 27 Significant projected soil resource loss points for the Waikato region assuming current cadmium loadings.

For graphical representations, see Figures 11 and 12.

Land use	Year soil average reaches the cadmium guideline	Land area (ha)	Loss of soil resource issues[a]	Percent of Waikato land area	Cumulative percent of Waikato region
Potato growing	2018	2309	1, 2, 3	0.09	0.09
Dairy farms receiving superphosphate fertiliser at 500 kg/ha/yr	2021	Up to 623013	2, 3	Up to 24.9[b]	(24.9)[b]
Sheep and beef farms receiving superphosphate fertiliser at 350 kg/ha/yr	2030	Up to 455333[c]	2, 3	Up to 18.2[b]	(38.1)[b]
Average of all Waikato pastoral soil (dairy, sheep and beef farms)	2043	1427800	2, 3	57.1	57.2
Maize	2046	3364	1, 2, 3	0.13	57.3
Average of all Waikato horticultural/arable soil	2066	12636	1, 2, 3	0.51	57.8

[a] Loss of soil resource issues: 1. Non-compliance with food standards; 2. Possible market access restriction; 3. Inability to subdivide to more sensitive land-use.

[b] Exact areas unknown, but total land loss estimated based on current superphosphate fertiliser use rate. It is thought that most dairy farms are routine users of superphosphate fertiliser: the land-loss figure for 2021 based on use rates is essentially the same as the area of dairy farms in the region.

[c] Upper area estimate based on total land area for sheep and beef farms (804787 ha) multiplied by the ratio of actual superphosphate fertiliser use (8.3 t/y) to potential use (14.7 t/yr), based on land areas and loading rates given in **Table 18**.

- In terms of average soil cadmium levels (rather than upper concentrations), the next significant loss of soil resource capacity over wide pastoral land areas might be expected for dairy farms, which cover 623000 hectares, or about one-quarter of the Waikato region. At reported superphosphate fertiliser use rates (500 kg/ha/yr) and current cadmium concentrations, these soils should equal or exceed 1 mg/kg soil cadmium in 8-16 years, with 16 years as the most conservative estimate.[350] This is consistent with the 27 year estimate made for New Zealand dairy soils by the fertiliser industry, when differences in survey years and soil factors are taken into consideration.[351]

- At current cadmium loadings, it is estimated that the average cadmium concentration of all pastoral soils in the Waikato region (57% of the Waikato region) will pass the 1 mg/kg threshold in about 40 years, and the average for the residual horticultural and arable land (another 0.6%) will reach this point a further 20 years beyond this.[352]

Horticultural soils comprise approximately 9270 ha, or 0.37% of the Waikato region's total land area. In horticultural soils, the shortest estimated average time interval between current soil cadmium levels and the threshold representing loss of resource capacity (1 mg/kg) is 14 years, for soils under potato crops.[353] Estimates made in this part of the work are also consistent with fertiliser industry figures, where New Zealand

[350] **Section 6.4.3**.
[351] **Sections 4.2.1** and **6.4.3**.
[352] **Sections 6.4.3 and 6.4.4**.
[353] **Section 6.4.4**.

soils under potatoes are expected to average the 1 mg/kg agricultural guideline in 16 years.[353] The Waikato region is now New Zealand's second largest potato growing region;[354] however, the absolute amount of land involved is relatively small, being estimated at 2309 hectares.[355] These figures are based on horticultural soil averages: it is important to note that cadmium levels in horticultural soils show a wide amount of variation due to differences in soil treatments and pesticide spray regimes between crops.[356]

In all, ongoing cadmium accumulation has the potential to impact 58% of the Waikato region's total land area in the short to medium term, covering pastoral agriculture (primarily dairy, beef and sheep farming), arable cropping and horticulture (**Table 27**).

Superphosphate fertiliser is also used in production forests (19.1% of Waikato's land area[357]), but at rates sufficiently low that cadmium accumulation should not be significant.[358] These areas may be required for other forms of farming in the future.[359]

Soil resource loss that occurs by the third identified mechanism (the inability to grow crops that meet food standards) is inherently difficult to quantify. However, the existence of this mechanism for soil resource capacity loss highlights a weakness in current approach to managing the cadmium issue: that it is implicitly based on a presumption that cadmium accumulation will cause no adverse consequence until a given numeric soil guideline is reached. This is not valid, for the reason that food standard exceedances are possible in given crops at soil cadmium levels that are below the nominated soil guideline. This has already been demonstrated as part of previous work relating to cadmium in New Zealand soil and crops, including an investigation of 90 South Auckland market gardens and 70 mid-Canterbury wheat farms.[360]

Other findings are as follows:

- Land application of biosolids also has the potential to double cadmium loadings, but this is not currently a widespread practice.[361]
- On average, cadmium accumulation in home vegetable gardens through use of various products sold for this use is not likely to be particularly rapid: however, exceptions will exist.[362]

The New Zealand fertiliser industry has reported that preventing further accumulation in New Zealand soils would require an 80% reduction in the cadmium content of superphosphate fertiliser. This New Zealand estimate agrees with a recent opinion delivered by the European Commission's Scientific Committee on Toxicity, Ecotoxicity and the Environment (SCTEE), and with US data.[363]

The area of technical management options that might be applied to avoid, remedy or mitigate cadmium accumulation in agricultural soils is substantial enough to require a separate investigation and report in its own right. Production of such a report is suggested as a recommendation of this work.[364]

9.1.3 Human exposure

Cadmium is a toxic, non-essential and biologically cumulative heavy metal.[365] Classic cadmium poisoning can arise through either acute (short-tem, high dose) or chronic

[354] **Section 3.7.2**.
[355] **Appendix 9**.
[356] **Sections 5.2.2**, **5.2.3** and **6.4.4**.
[357] **Appendix 7**.
[358] **Sections 6.2.1**, **6.3.1** (see **Table 18**) and **6.4.3**.
[359] **Section 5.3**.
[360] **Section 3.5.2**.
[361] **Section 6.5**.
[362] **Section 6.6**.
[363] **Section 4.3.2**.
[364] **Section 9.2**.
[365] **Sections 2.1 and 2.3**.

(long-term, low dose) exposures. The main source of general-population exposure to cadmium is through food,[366] and foods groups making the greatest contribution to dietary intakes are cereals and vegetables.[367] A provisional tolerable weekly intake (PTWI) of 7 µg/kg/week has been set that is designed to prevent chronic cadmium poisoning while leaving a suitable margin for error.[368]

Of all contaminants in the diet, cadmium is the one closest to its provisional tolerable weekly intake (PTWI), in both New Zealand and Australia.[366] Published evidence also exists that in some New Zealand crops, it is likely that the current food standard is routinely being exceeded. This is particularly the case for some varieties of wheat.[369]

In order to provide a reliable benchmark for future work in the Waikato region, a survey was carried out of cadmium concentrations in some key commercial produce sold in the Waikato region. Produce sampled included potatoes, onions, lettuce and silverbeet. The average cadmium concentration measured for Waikato peeled potatoes collected in 2004 was identical to the composite average for New Zealand reported as part of the concurrent New Zealand Total Diet Survey.[370] Based on the survey result sample distribution, it is estimated that approximately **1.5%** of potatoes sold in the Waikato region in 2004 might exceed the food standard for cadmium.[369]

There is some limited evidence that cadmium uptake from home vegetable garden soils may result in food standards being exceeded in home-grown produce.[371] However, this is thought not to be a serious issue in Waikato home gardens, providing the total soil guideline value remains lower than 1 mg/kg, and consumption of home produce forms a limited proportion of the overall diet (as it normally does). This is because the residential soil guideline value for cadmium takes home produce consumption into account in the context of overall exposure, the cadmium uptake equation used in doing this was found to correctly predict the uptake observed.[372]

9.1.4 Off-site effects in agricultural catchments[373]

Superphosphate fertiliser is the main (99%) source of new cadmium introduced to agricultural catchments. Of the potential cadmium mobilisation mechanisms that exist, the one of greatest significance is surface runoff of particulate-bound cadmium. Theory[374] and preliminary evidence[375] suggests that this results in the gradual accumulation of cadmium in stream, river and lake sediments.

Accumulation of cadmium in sediments would be of concern if net accumulation rates are sufficient to enable sediment cadmium concentrations to pass ecotoxic thresholds. Further work is required to assess whether cadmium accumulation in rural streams and rivers is sufficient to pose a risk to ecological receptors in the medium term, and which types of freshwater systems would be most susceptible in this regard.

9.1.5 Evolving significance of the issue: what's changed?

Factors relevant to the cadmium accumulation issue include contamination of land (and the wider environment), human exposure, a developing understanding of the likely effects of dietary exposure, horticultural and pastoral production, residues in produce, and the regulatory role of regional councils in managing contaminant discharges. From each perspective, there are reasons why the cadmium accumulation issue has recently become more serious as a resource management and regulatory compliance problem than it was one or two decades ago. These reasons are as follows.

366 **Section 2.2.1**.
367 **Section 2.4.2**.
368 **Section 2.4.1**.
369 **Section 3.5.2**.
370 **Section 7.4.1**.
371 **Section 7.5**.
372 **Sections 6.6**, **7.5** and **3.5.1**.
373 **Section 8**.
374 **Section 8.5**.
375 **Section 8.7**.

1. Agricultural soil guideline: the recommended guideline for cadmium in agricultural soil has dropped by a factor of three to 1 mg/kg, with the new guideline partly being based on international market access considerations.[376]

2. Residential soil guideline: the effective interim default guideline for cadmium in Waikato residential soil has also dropped to the same level, and this has implications for subdivision of agricultural land to rural-residential or residential.[375]

3. Recent survey data: Cadmium in Waikato soils has not been routinely measured in the past. In recent surveying, cadmium levels in 23% of Waikato horticultural and 14% of pastoral properties sampled were found to exceed the recommended soil guidelines (both 1 mg/kg).[377] Survey results also suggests that on average, cadmium concentrations in Waikato soils are now about five times their natural level. Relative to the 1 mg/kg soil guideline, two-thirds of the 'available' soil capacity to assimilate cadmium has now been used.[378] Accumulation to this point took approximately 65 years.

4. Loading estimates: Loading estimates suggest that if current accumulation rates continue, a large area of the Waikato region (dairy soils) will exceed the agricultural soil guideline in under 16 years.[379]

5. Food standards: The food standard for key crops has dropped by a factor of ten.[380] Cadmium levels in some arable and horticultural crops already exceed this standard on occasion.[381] This relative exceedance rate is projected to increase with time, due to ongoing accumulation of the element in soil.[382]

6. Better understanding of soil resource pressures: a review of soil resource pressures which relate to this issue[383] suggests that factors are at work which may have the net effect of increasing plant uptake of cadmium, even in the absence of further accumulation. These include loss of soil organic matter in cropping soils, which is the dominant adsorptive phase for cadmium, and possible soil acidification.

7. New Zealand scientific evidence gathered in the last decade: most research carried out on the problem of cadmium accumulation in New Zealand soils, which is substantial,[384] has appeared in the last decade. Now is an appropriate juncture to consider the results and implications of this work at policy and regulatory levels.

9.2 Recommendations

Accumulation of cadmium in agricultural soils, and consequent limitations this imposes on future uses of the soil resource, is a national issue. If poorly managed or left unattended, cadmium accumulation has the potential to back horticulturalists, arable, and pastoral farmers in to a cadmium corner. Potential implications range from international trade access issues to population-level consequences of increasing dietary intakes. At the same time, Environment Waikato has its own policy objective and regulatory obligations to consider. Losses of current and foreseeable uses of the soil resource caused by cadmium accumulation are not in keeping with regional council policy objectives.

It would be advisable for this report to be circulated to relevant national agencies, including the Office of the Parliamentary Commissioner for the Environment, the

[376] **Section 3.8.2**.
[377] **Sections 5.2.2** and **5.2.3**.
[378] **Section 5.3**.
[379] **Section 6.4.3**.
[380] **Section 1.2.3**.
[381] **Section 3.5.2**.
[382] **Section 3.3** and elsewhere in this report.
[383] **Section 3.7**.
[384] **Appendix 5**.

Ministry for the Environment, the New Zealand Food Safety Authority, and the Ministry of Agriculture and Forestry.

Other recommendations are as follows:

1. That one or more reports are prepared, preferably at a national level, on issues, technical management and policy options relating to cadmium in New Zealand agriculture.

2. That Environment Waikato investigate whether fertiliser is being applied in accordance with conditions set out in **Waikato Regional Plan section 3.9.4.11 Permitted Activity Rule - Fertiliser Application**, which requires adherence to NZ Fertiliser Manufacturers Research Association Code of Practice for Fertiliser Use. Addendum 8 to this Code of Practice specifies that *"Farmers should have their own Cadmium Management Plan..."*

3. That research be undertaken to assess the rates and significance of agricultural metal accumulation in rural streams, rivers, and lake sediments (primarily cadmium and zinc).

Appendix 1 Uses of cadmium in industry.[a]

Use	Cadmium forms used	Reasons for use	Examples of use
Cadmium coating and electroplating	Cd metal CdCN CdO $CdCl_2$ Cd complexes $CdSO_4$	Good corrosion protection (alkali and salt water), ductility, good frictional properties, high soldering potential, uniform and high rate of deposition, retention of luster	Coating nuts and bolts, automotive construction, aircraft parts, machine construction, defence industry
Nickel-cadmium, silver-cadmium & mercury-cadmium accumulator batteries	Cd metal $Cd(OH)_2$ $Cd(NO_3)_2 \cdot 4H_2O$	Long life, robust, cell reaction perfectly reversible, cell reaction doesn't release gas (can seal battery)	Power supply in portable appliances such as radios, calculators and pacemakers
Pigments (red, orange, yellow & maroon)	CdS CdSe CdO $CdCl_2$ $CdSO_4$ $Cd(NO_3)_2 \cdot 4H_2O$ Cd thioselenides Cd lithopones organocadmium salts	Bright deep shades, good covering power, high resistance to heat,light H_2S and SO_2	Colouring agent in ceramics, paper, plastics, printing inks, rubber, ruby glass, soaps and textiles
Plastics stabilizers $CdCl_2$	CdO and light, work as $CdSO_4$ organocadmium salts	Stabilize plastics to heat antioxidants to retard discolouration	Production of PVC
Alloys-solders	Various Cd alloys *e.g.* "cerrobend" = 50%Bi; 26.7%Pb; 13.3%Sn; 10%Cd	Added Cd lowers the melting point of Ag, Cu and Zn	Joining dissimilar metals, soldering Al, hard soldering
Alloys-electrical	0.7%Cd; 99.3%Cu	Added Cd increases the strength of Cu wire without reducing conductivity	Overhead power lines to electric locomotives, automotive cooling fins, heavy-duty radiators
	2.5-15%Cd; 97.5-85%Ag	Added Cd reduces sparking	Electrical switches
Alloys-other	Various Cd alloys	miscellaneous properties	Nuclear control rods, fusible alloys in fire-protection devices, white-light lasers, lens grinding blocks

Continued…

Use	Cadmium forms used	Reasons for use	Examples of use
Other electrical uses	CdS CdSe CdTe CdO CdSb	Work as semiconductors, thermoelectric and photoelectric generators	Various electronics applications; thermodetectors, photovoltaic (solar) cells
	Cd arsenides Cd phosphides Cd borates CdF_2	Exhibit laser action, fluoresce	Laser beams, phosphors in television tubes, fluorescent lamps, X-ray screens
Catalysts CdO	Diverse catalytic Cd halides Cd dialkyls	Organic polymerization properties	reactions
Photography	$Cd(NO_3)_2 \cdot 4H_2O$ Cd halides	Various properties	Light-sensitive components of photographic film, flash powder
Pyrotechnics	Cd halides	Flammability and flame colour	Blue colour in fireworks

[a] Complied from the following sources:

- Förstner U, **1980**. Cadmium. **In** Hutzinger O (Ed.) *The handbook of environmental chemistry, Vol. 3, part A; anthropogenic compounds.* Springer-Verlag, New York.
- Hollander ML and Parker PD, **1978**. Cadmium and cadmium alloys *and* cadmium compounds. **In** *Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edn. Vol. 4*, John Wiley and Sons Inc., USA.
- Moore JW and Ramamoorthy S, **1984**. *Heavy metals in natural waters. Applied monitoring and impact assessment.* Springer-Verlag New York Inc., New York.
- Nriagu JO, **1980a**. Production, uses and properties of cadmium. **In** Nriagu JO (Ed.) *Cadmium in the environment; part 1.ecological cycling.* John Wiley and Sons, New York.
- Plunkert P, **1988**. Cadmium. **In** *Minerals Yearbook 1988 Vol.I; metals and minerals.* U.S. Department of the Interior, U.S. Govt. Printing Office, USA.

Appendix 2 Household dust as a source of adventitious cadmium exposure in young children.

In non-occupationally exposed individuals, food accounts for most ingested cadmium **(Section 2.2).** In young children, adventitious ingestion of household dust can also constitute a significant secondary route, because household dust is elevated in cadmium and young children spend most of their time indoors.

For most heavy metals, dust ingestion is usually[385] not an important intake route relative to food. However, in the case of cadmium, where food intakes are a significant fraction of the PTWI, other possible intake routes are worth consideration. A standard assumption in risk assessment (based on experimental evidence) is that an average young child[386] ingests about 100 mg of soil and dust per day, mainly through hand-to-mouth activity and mouthing of non-food objects.[387] The USEPA recommends use of soil ingestion rates for children of 200 mg/day, a value generally viewed as approximating the upper 95% of the distribution for children.[388] In a survey of 120 houses carried out in Christchurch (**Appendix 2, Table 1** and **Appendix 2, Figure 1**), the geometric mean (and median) cadmium concentration in house-dust was found to be 4.2 mg/kg.[389] The upper 95th percentile value was 13.3 mg/kg.

Appendix 2, Table 1. Concentrations of cadmium in indoor dust of 120 Christchurch houses.[390]

Cadmium concentration (mg/kg) (from lowest to highest)					
0.557	2.39	3.06	4.34	5.56	7.35
0.893	2.43	3.20	4.40	5.62	7.56
1.19	2.46	3.28	4.47	5.98	7.95
1.38	2.51	3.31	4.55	6.24	8.09
1.53	2.56	3.34	4.58	6.37	8.41
1.69	2.56	3.40	4.63	6.40	8.62
1.71	2.58	3.54	4.69	6.48	8.88
1.81	2.66	3.57	4.70	6.49	8.94
1.86	2.68	3.77	4.71	6.50	8.94
1.95	2.69	3.89	4.72	6.56	9.06
1.97	2.69	3.92	4.76	6.62	9.19
1.99	2.72	3.94	4.85	6.66	9.32
2.04	2.77	3.97	4.99	6.66	10.3
2.05	2.78	4.05	5.13	6.83	12.8
2.13	2.82	4.07	5.21	6.98	13.7
2.14	2.88	4.16	5.22	7.03	14.6
2.18	2.91	4.16	5.35	7.04	14.6
2.19	2.92	4.17	5.43	7.23	16.8
2.19	2.95	4.20	5.48	7.24	17.5
2.22	3.00	4.32	5.50	7.29	21.0

385 This intake route is still routinely responsible for cases of acute childhood lead poisoning (now listed as a notifiable disease); the usual reason in such cases is that an old lead-painted house was undergoing renovation (Dell Hood, Waikato Medical Officer of Health, Personal communication, 2003).

386 Taken as a non-pica child, aged 1-6 years, weighing 15 kg.

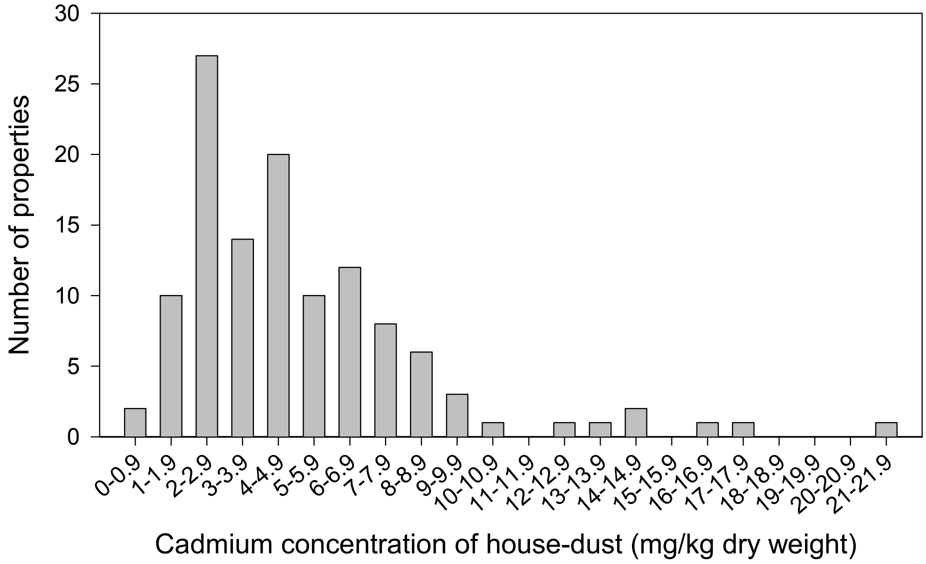
387 See, for example: Ministry for the Environment and Ministry of Health, **1997**. *Health and Environmental Guidelines for Selected Timber Treatment Chemicals*.

388 Stanek EJ and Calabrese EJ, **1995**. Daily Estimates of Soil Ingestion in Children. *Environmental Health Perspectives*, Vol. 103, pp 276-285. Also available at: http://ehp.niehs.nih.gov/members/1995/103-3/stanek-full.html

389 Kim ND and Fergusson JE, **1993**. Concentrations and sources of cadmium, copper, lead and zinc in house-dust in Christchurch, New Zealand. *Science of the Total Environment* , Vol. 138, pp 1-21.

390 Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury, Ch. 4.

Appendix 2, Figure 1. Histogram of cadmium concentrations in Christchurch house-dust.



Based on these numbers, an average child might ingest 2.9 mg cadmium per week from house-dust, whereas a 95th percentile exposure might be up to 18.6 mg/week. At a 15 kg body weight, these would represent about 3% and 18% of the tolerable cadmium intake figure, respectively (**Appendix 2, Table 2**).

Appendix 2, Table 2. Estimates of cadmium intakes from house-dust by young children (a body weight of 15 kg is assumed).

Percentiles for children relate to dust ingestion rates in non-pica children.

Variable	Average exposure: 50th percentile child, median house	95th percentile child, median house	Ordinary child, 95th percentile house	95th percentile child and house[a]
Ingestion rate (mg dust/day)	100	200	100	200
Cadmium concentration in house-dust (mg/kg)	4.2	4.2	13.3	13.3
Amount of cadmium ingested (mg/day)	0.42	0.84	1.3	2.7
Amount of cadmium ingested per week (mg/week)	2.9	5.9	9.3	18.6
Amount of cadmium ingested per kg body weight per week (mg/kg/wk)	0.2	0.4	0.6	1.2
Amount of PTWI remaining for food (mg/kg/wk)	6.8	6.6	6.4	5.8
Percent of PTWI from house dust	2.8%	5.6%	8.8%	17.8%

[a] Note that this represents the 95th percentile intake figure (200 mg) for children who happen to be living in a 95th percentile house. This last intake figure might therefore apply to 0.25% of children, rather than 5%.

House-dust is therefore a relatively minor intake route for cadmium in young children in its own right, relative to average intakes from food.

Appendix 3 Effects and symptoms of cadmium poisoning.[391]

For a full toxicological profile, see Agency for Toxic Substances and Disease Registry: http://www.atsdr.cdc.gov/toxprofiles/tp5.html

Body part	Effects and symptoms	Comments
Kidney	Kidney damage; lesions on the proximal tubules, reduced ability to concentrate urine, cloudy urine, proteinurea (protein in the urine), glycosuria, amino-aciduria, hypercalcuria, presence of cadmium, albumin and excess phosphate in the urine, amyloid deposits in the kidney, kidney-stone formation	Observed in cases of acute and chronic intoxication
Liver	Cirrhosis (distortion and scarring of the liver, with associated loss of function)	Chronic and acute cases
Lungs and related	Anosmia (impaired sense of smell due to damage to the olfactory nerve) persistent coughing and choking, dyspnea (shortness of breath). Usual outcome is pulmonary emphysema (loss of alveolar elasticity) with or without bronchitis and/or pneumonia	From inhaled cadmium, chronic and acute
Bones	Osteomalacia (bone demineralization) due to decreased gastrointestinal calcium absorption, osteoporosis (bone softening) with tendency to fracture, leg myalgia (muscle pain), waddling gait	Chronic poisoning only; required low calcium status
Digestive system	Dryness of mouth and excessive salivation, sore throat, yellowing of the teeth, persistent vomiting, abdominal pains, diarrhoea, severe ulcerative gastroenteritis and congestion, poor appetite (leading to weight loss)	Acute oral poisoning
Other effects	Carcinogenesis (known human carcinogen) Teratogenisis (mis-shapen organ formation) Disruption of hormonal signalling. Growth retardation, impaired reproductive function	Chronic effects

391 Adapted from Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury.

Appendix 4 Overview of acute and chronic cadmium poisoning events.

Although cadmium was not identified as an element until 1817, a possible reference to its harmful effects appeared in the writings of Agricola, a sixteenth-century miner.[392] What are now considered to be the first medically documented cases of cadmium poisoning occurred in 1858. Three servants developed acute respiratory and gastrointestinal problems a short time after polishing silverware with cadmium carbonate dust.[393] However, it was not until 1920 that cadmium poisoning as such was definitively recognized.[394]

During World War I, due to an excessive demand for tinned food and the resulting tin shortage, cadmium was used in food containers as a substitute for tin. By the early 1920s several cases of acute cadmium poisoning had occurred in people who had ingested acidic foods stored in cadmium-lined containers.[395] The practice was temporarily discontinued. Cadmium was also utilized pharmaceutically in the mid-1920s for the treatment of malaria, syphilis and tuberculosis, but this usage was abandoned once the metal's toxicity became widely known.[396] Despite this knowledge, numerous new cases of acute cadmium poisoning (some fatal) were reported during the 1930s, which were traced to the use of cadmium-plated ice-cube trays, coffee-urns and cooking utensils.[392]

A few years later during World War II, cadmium oxide fumes were assessed with regard to their potential as a chemical weapon.[393] Surprisingly, at the same time, due to the loss of Malayan tin, cadmium was again investigated as a possible substitute for tin in cans.[394] Sixty-two New Zealand airmen suffered acute cadmium poisoning in one incident during World War II, after drinking (acidic) fruit juice that had been prepared in a galvanized urn.[397] The juice leached cadmium from the urn's interior, and was later estimated to contain 200 mgCd/L, each airman therefore ingesting an approximate dose of 56 mg cadmium. The minimum lethal dose by ingestion is estimated to be 350 mg Cd.[392] Poisoning was characterized by severe gastroenteritis. All the victims had recovered from the acute effects after three days.

By 1945, the industrial uses of cadmium and its compounds had become firmly established; 4389 tons of the metal were produced worldwide in that year.[398] Unfortunately, concurrent with the emergence of cadmium-based industries came cases of occupational exposure to the element and its compounds.[399] These have taken the forms both of acute and chronic poisonings.

The most frequent cases of acute occupational cadmium poisoning have been among people involved in welding, soldering or cutting cadmium alloys and cadmium-plated metals.[400] One of the characteristics of acute cadmium poisoning is that there is usually some delay before the onset of symptoms. Lethal doses of cadmium fumes have been inhaled without the workers feeling much discomfort.[391]

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392 Nriagu JO, **1980**. Production, uses and properties of cadmium. **In** Nriagu JO (Ed.) *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.
393 Berman E, **1980**. *Toxic metals and their analysis.* Heyden and Son Ltd., Great Britain.
394 Yasumura S, Vartsky D, Ellis KJ and Cohn SH, **1980**. Cadmium in human beings. **In** *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.
395 Schroeder HA, **1974**. *The poisons around us: toxic metals in food, air and water.* Indiana University Press. Pub. by Fitzhenry and Whiteside Ltd., Ontario.
396 Waldbott GL, **1973**. *Health effects of environmental pollutants.* C.V. Mosby Co., U.S.A.
397 Jenner GG and Cuningham JAK, **1944**. An outbreak of cadmium poisoning. *N.Z. Med. J.* Vol. 43, No. 237, pp 282-283.
398 Nriagu JO, **1980**. Production, uses and properties of cadmium. **In** Nriagu JO (Ed.) *Cadmium in the environment; Part 1. Ecological cycling.* John Wiley and Sons, New York.
399 Friberg L, Piscator M, Nordberg GF, and Kjellström T, **1974**. *Cadmium in the environment, 2nd edn.* CRC Press Inc. U.S.A.
400 Schulte-Schrepping KH and Piscator M, **1985**. Cadmium and cadmium compounds. **In** Gerhartz W (Ed.) *Ullman's Encyclopedia of Industrial Chemistry Vol. A4, 5th edn.* Verlagsgesellschaft mbH (VCH), Federal Republic of Germany.

Chronic occupational cadmium poisoning, occurring by exposure to a relatively low concentration of the element over a long time period, remained unrecognised until 1948. In that year Friberg identified the disease among workers in a Swedish alkaline battery factory, who had been exposed to cadmium oxide dust.[398] Emphysema of the lungs and renal damage were observed in exposed workers. Subsequent studies worldwide confirmed Friberg's findings and identified other potentially hazardous cadmium related industries.[392,393,398] As a result of the concern generated by the results of such studies, industrial cadmium abatement programmes were introduced in many countries. However, occupational cases of acute and chronic cadmium poisoning were still common in 1980.[401] Although in recent times (post 1950) the frequency of acute cadmium poisoning cases has been far lower among the general population than it has among occupationally exposed groups, the seriousness of such incidents should not be underestimated. Berman[402] cites the case of a two year old child who died as a result of chewing the cadmium-based paint from his cot.

The other possibility, chronic intoxication among a general population, occurred in 1948 (and was definitively diagnosed as such in 1961) among several hundred people from villages on the banks of the Jintsu River, Toyanna Prefecture, Japan.[403,404,405] Cadmium fumes and particulate matter emitted from a nearby lead and zinc mining company caused an excessive accumulation of the metal in the soil of the Fuchi-machi farming community.[406] Rice and soybeans grown in this soil contained high concentrations of cadmium (mean value 1.0 mg/kg and up to 3.0 mg/kg).[400] The most prominent symptom was that the bones fractured under slight pressure, due to their decalcification and subsequent softening. A large amount of pain was involved in this process, and the sickness became known as *itai-itai* disease, which is variously translated *it hurts-it hurts* or *ouch-ouch* disease. It has been estimated that by the end of 1965, nearly 100 deaths had resulted from the disease.[403] Most of the victims were multiparous women over 50 years of age.

Due to the presence in each of the patients of other factors, such as a low calcium intake, it is now assumed that cadmium is a necessary but not sufficient factor for the development of *itai-itai* disease (in particular).[400] However, *itai-itai* disease served to highlight the insidious nature of environmental cadmium poisoning. The fact that it was many (typically 30–40) years before the onset of symptoms suggested that an accumulation of cadmium sufficient in the long term to cause chronic intoxication may have been already taking place among other communities.

This mechanism of cadmium poisoning—long term exposure of a general population to enhanced cadmium in food—relates most directly to the cadmium status of productive (and in particular, horticultural and arable) soils.

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[401] Piotrowski JK and Coleman DO, **1980**. *Environmental hazards of heavy metals: summary evaluation of lead, cadmium and mercury. A general report.* Monitoring and Assessment Research Centre (MARC), University of London.

[402] Berman E, **1980**. *Toxic metals and their analysis.* Heyden and Son Ltd., Great Britain.

[403] Förstner U, **1980**. Cadmium. **In** Hutzinger O (Ed.) *The handbook of environmental chemistry, Vol. 3, Part A; Anthropogenic compounds.* Springer-Verlag, New York.

[404] Friberg L, Piscator M, Nordberg GF, and Kjellström T, **1974**. *Cadmium in the environment, 2nd Edn.* CRC Press Inc. U.S.A., p 95.

[405] Nogawa K, Honda R, Kido T, Tsuritani I, Yamada Y, Ish izaki M and Yamaha H, **1989**. A dose response analysis of cadmium in the general environment with special reference to total cadmium intake limit. *Env. Res.* Vol. 48, No. 1, pp 7-16.

[406] Waldbott GL, **1973**. *Health effects of environmental pollutants.* C.V. Mosby Co., U.S.A.

Appendix 5 Scientific research papers relating to cadmium in New Zealand agricultural soils.

Key institutions are listed in alphabetical order, with most recent publications first. (Where publications are co-authored between institutions, the citation is listed under the institution of the lead author.)

***AgResearch** (Ruakura Agriculture Centre, Hamilton and NZ Pastoral Agriculture Research Institute, Palmerston North):*

- Longhurst, R.D. Roberts, A.H.C. and Waller, J.E., **2004**. Concentrations of cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, Vol 47, pp 23-32.

- Roberts, A.H.C. and Longhurst R.D., **2002**. Cadmium cycling in sheep-grazed hill-country pastures. *New Zealand Journal of Agricultural Research*, Vol. 45, pp 103–112.

- Lee, J.; Masters, D.G.; White, C.L.; Grace, N.D.; Judson, G.J., **1999**. Current issues in trace element nutrition of grazing livestock in Australia and New Zealand. *Australian Journal of Agricultural Research*, Vol. 50(8), pp 1341-1364.

- Roberts, A.H.C.; Longhurst, R.D.; Brown, M.W., **1997**. Cadmium accumulation in New Zealand pastoral agriculture. *Biogeochemistry of Trace Metals*, pp 1-41. Publisher: Science Reviews, Northwood, UK..

- Roberts, A.H.C.; Cameron, K.C.; Bolan, N.S.; Ellis, H.K.; Hunt, S., **1996**. Contaminants and the soil environment in New Zealand. Contaminants and the Soil Environment in the Australasia-Pacific Region, *Proceedings of the Australasia-Pacific Conference on Contaminants and Soil Environment in the Australasia-Pacific Region*, 1st, Adelaide, Feb. 18-23, 1996, pp 579-628.

- Roberts, A.H.C.; Longhurst, R.D.; Brown, M.W., **1994**. Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research*, Vol. 37(1), pp 119-29.

- Other publications co-authored with researchers at Lincoln University (see separate entry).

***HortResearch** (Environment and Risk Management Group), Palmerston North:*

- Granel, T.; Robinson, B.; Mills, T.; Clothier, B.; Green, S.; Fung, L., **2002**. Cadmium accumulation by willow clones used for soil conservation, stock fodder, and phytoremediation. *Australian Journal of Soil Research*, Vol. 40(8), pp 1331-1337.

- Robinson, B.; Russell, C.; Hedley, M.; Clothier, B., **2001**. Cadmium adsorption by rhizobacteria: implications for New Zealand pastureland. *Agriculture, Ecosystems & Environment*, Vol. 87(3), pp 315-321.

***Landcare Research**, Hamilton:*

- Taylor, M.D., **1997**. Accumulation of cadmium derived from fertilizers in New Zealand soils. *Science of the Total Environment*, Vol. 208(1,2), pp 123-126.

- McIntosh, P.D.; Hewitt, A.E.; Giddens, K.; Taylor, M.D., **1997**. Benchmark sites for assessing the chemical impacts of pastoral farming on loess soils in southern New Zealand. *Agriculture, Ecosystems & Environment*, Vol. 65(3), pp 267-280.

- Taylor, M.D.; Theng, B.K., **1995**. Sorption of cadmium by complexes of kaolinite with humic acid. *Communications in Soil Science and Plant Analysis*, Vol. 26(5&6), pp 765-76.

- Taylor, M.D., **1992**. Comparison of archived soil samples with fresh samples for cadmium and zinc. Trace Elements: Roles, Risks & Remedies, *Proceedings of the New Zealand Trace Element Group Conference*, pp 52-6.

Lincoln University *(Soil, Plant and Ecological Sciences Division), Canterbury:*

- Gray C. W., Moot D. J., McLaren R. G., and Reddecliffe, T., **2002**. Effect of nitrogen fertiliser applications on cadmium concentrations in durum wheat (*Triticum turgidum*) grain. *Journal of Crop and Horticultural Science*, Vol. 30, pp 291-299.

- Gray, C. W.; McLaren, R. G.; Roberts, A. H. C., **2001**. Cadmium concentrations in some New Zealand wheat grain. *New Zealand Journal of Crop and Horticultural Science*, Vol. 29(2), pp 125-136.

- Gray, C. W.; McLaren, R. G.; Roberts, A. H. C., **2003**. Cadmium leaching from some New Zealand pasture soils. *European Journal of Soil Science*, Vol. 54(1), pp 159-166.

- Gray, C. W.; McLaren, R. G.; Roberts, A. H. C.; Condron, L. M., **1999**. The effect of long-term phosphatic fertilizer applications on the amounts and forms of cadmium in soils under pasture in New Zealand. *Nutrient Cycling in Agroecosystems*, Vol. 54(3), 267-277.

- Gray, C. W.; Mclaren, R. G.; Roberts, A. H. C.; Condron, L. M., 1998. Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. *Australian Journal of Soil Research*, Vol. 36(2), pp 199-216.

- Gray, C. W.; Mclaren, R. G.; Roberts, A. H. C.; Condron, L. M., **1999**. Effect of soil pH on cadmium phytoavailability in some New Zealand soils. *New Zealand Journal of Crop and Horticultural Science*, Vol. 27(2), pp 169-179.

- Gray, C. W.; McLaren, R. G.; Roberts, A. H. C.; Condron, L. M., 1999. Cadmium phytoavailability in some New Zealand soils. *Australian Journal of Soil Research*, Vol. 37(3), pp 461-477.

- Gray, C. W.; McLaren, R. G.; Roberts, A. H. C.; Condron, L. M., **1999**. Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. *European Journal of Soil Science*, Vol. 50(1), pp 127-137.

- Gray, C.W., McLaren, R.G., Roberts, A.H.C. and Condron, L.M., **1999**. The effect of long-term phosphate fertiliser applications on the amount and forms of cadmium in soils under pasture in New Zealand. *Nutrient Cycling in Agroecosystems*, Vol. 54, pp 267-277.

- Gray, C.W.; McLaren, R.G.; Roberts, A.H.C., **2003.** Atmospheric accessions of heavy metals to some New Zealand pastoral soils. *Science of the Total Environment*, Vol. 305(1-3), pp 105-115.

- Gray, C.W.; McLaren, R.G.; Roberts, A.H.C.; Condron, L.M., **2000**. Fractionation of soil cadmium from some New Zealand soils. *Communications in Soil Science and Plant Analysis*, Vol. 31(9 & 10), pp 1261-1273.

- McLaren, R.G., Backes, C.A., Rate, A.W. and Swift, R.S., **1998**. Kinetics of cadmium and cobalt desorption from soil clay fractions. *Soil Science Society of America Journal*, Vol. 62: pp 332-337.

Massey University *(Soil and Earth Sciences Group; Fertiliser and Lime Research Centre; and more) Palmerston North:*

- Loganathan, P.; Hedley, M.J.; Grace, N.D.; Lee, J.; Cronin, S.J.; Bolan, N.S.; Zanders, J.M, **2003**. Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine: a review. *Australian Journal of Soil Research*, Vol. 41(3), pp 501-532.

- Bolan, N. S.; Duraisamy, V. P., **2003**. Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies. *Australian Journal of Soil Research,* Vol. 41(3), pp 533-555.

- Loganathan, P.; Hedley, M.J.; Wallace, G.C.; Roberts, A.H.C., **2001**. Fluoride accumulation in pasture forages and soils following long-term applications of phosphorus fertilisers. *Environmental Pollution*, Vol. 115(2), pp 275-282.

- Loganathan, P.; Louie, K.; Lee, J.; Hedley, M. J.; Roberts, A.H.C.; Longhurst, R.D., **1999**. A model to predict kidney and liver cadmium concentrations in grazing animals. *New Zealand Journal of Agricultural Research*, Vol. 42(4), pp 423-432.

- Cronin, S. J.; Hedley, M. J.; Neall, V. E.; Smith, R. G., **1998**. Agronomic impact of tephra fallout from the 1995 and 1996 Ruapehu volcano eruptions, New Zealand. *Environmental Geology*, Vol. 34(1), pp 21-30.

- Zanders, J.M., **1998**. *Studies on the origin, distribution and mobility of cadmium in pastoral soils.* PhD thesis, Massey University.

- Loganathan, P.; Hedley, M.J.; Gregg, P.E.H.; Currie, L.D., **1997**. Effect of phosphate fertilizer type on the accumulation and plant availability of cadmium in grassland soils. *Nutrient Cycling in Agroecosystems*, Volume Date 1996-1997, Vol. 46(3), pp 169-178.

- Loganathan, P.; Hedley, M.J., **1997**. Downward movement of cadmium and phosphorus from phosphatic fertilizers in a pasture soil in New Zealand. *Environmental Pollution*, Vol. 95(3), pp 319-324.

- Andrewes, P.; Town, R. M.; Hedley, M. J.; Loganathan, P., **1996**. Measurement of plant-available cadmium in New Zealand soils. *Australian Journal of Soil Research*, Vol. 34(3), pp 441-452.

- Bolan, N S., **1996**. Cadmium accumulation in New Zealand pasture soils. *Chemistry in New Zealand,* Vol. 60(1), pp 31, 33-5.

- Loganathan, P.; Mackay, A.D.; Lee, J.; Hedley, M.J., **1995**. Cadmium distribution in hill pastures as influenced by 20 years of phosphate fertilizer application and sheep grazing. *Australian Journal of Soil Research*, Vol. 33(5), pp 859-71.

- Bramley, R. G. V., **1990**. Cadmium in New Zealand agriculture. *New Zealand Journal of Agricultural Research*, Vol. 33(4), pp 505-19.

Other:

Christchurch Polytechnic Institute of Technology, Christchurch:

- Hawke, D. J., **2003**. Cadmium distribution and inventories at a pre-European seabird breeding site on agricultural land, Banks Peninsula, New Zealand. *Australian Journal of Soil Research*, Vol. 41(1), pp 19-26.

CSIRO Soils Division, Glen Osmond, Australia:

- Naidu, R.; Bolan, N.S.; Kookana, R.S.; Tiller, K.G., **1994**. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science*, Vol. 45(4), pp 419-29.

DSIR (Chemistry Division), Petone:

- Rothbaum, H.P.; Goguel, R.L.; Johnston, A.E.; Mattingly, G.E.G., **1986**. Cadmium accumulation in soils from long-continued applications of superphosphate. *Journal of Soil Science*, Vol. 37(1), pp 99-107.

ESR Limited, Porirua:

- Speir, T.W.; Kettles, H.A.; Percival, H.J.; Parshotam, A., **1999**. Is soil acidification the cause of biochemical responses when soils are amended with heavy metal salts? *Soil Biology & Biochemistry*, Vol. 31(14), pp 1953-1961.

University of Canterbury (Chemistry Department) Christchurch:

- Fergusson, J.E., **1990**. *The Heavy Elements. Chemistry, Environmental Impact and Health Effects*. Pergamon Press, Oxford.

University of Otago (Medical School) Dunedin:

- Sharma, R. P., **1981**. High blood and urine levels of cadmium in phosphate workers: a preliminary investigation. *Bulletin of Environmental Contamination and Toxicology*, Vol. 27(6), pp 806-9.

University of Waikato (Chemistry Department) Hamilton:

- Kim, N.D.; Fergusson, J.E., **1992**. Adsorption of cadmium by an aquent New Zealand soil and its components. *Australian Journal of Soil Research*, Vol. 30(2), pp 159-67.

Appendix 6 Soil resource pressures that relate to the chemistry of cadmium fixation and release.

1. Baseline factors

There is a limit to the amount of cadmium that agricultural soils can accumulate before various adverse thresholds are reached. For horticultural soils, the key threshold appears to be the point where food standards for cadmium are routinely exceeded. Two baseline factors underpin pressure on the soil resource from cadmium. These are prior history, and the fact of ongoing accumulation.

Prior history

The amount of cadmium that can be added before adverse endpoints are realised represents a specific soil resource. Due to past practice, a substantial proportion of the available soil resource has already been consumed. An estimate of used and residual soil capacity is provided in **Sections 5.2** and **5.3**.

Ongoing accumulation

The fact of ongoing cadmium accumulation (**Section 3.3**) means that whatever capacity is left in the soil resource, this capacity is being steadily reduced with time. Prior initiatives by the fertiliser industry to reduce cadmium in phosphate fertiliser by 30% are outlined in **Section 4.2.1**. Current rates of ongoing cadmium accumulation are estimated in **Section 6**.

2. Soil and plant factors

A number of soil and plant factors are likely to exacerbate the amount of cadmium accumulated in Waikato soils, and/or the amount taken up in crops. These are as follows.

Need for ongoing phosphorus inputs

Phosphorus is an essential plant and animal macro-nutrient. On most farmed soils, phosphorus is initially added at a high rate, in order to provide an optimal baseline for production. Once suitable phosphorus capital has been established, ongoing additions are needed for maintenance, to offset losses from the system. Phosphorus is lost from productive areas of a farm by production (*e.g.* incorporation in meat), fixation to inorganic soil minerals, immobilisation with organic material, and transfer of dung and urine to non-productive marginal areas of the farm.[407] Although exact details of the adsorption chemistry differ, the overall retention of phosphate by soil minerals is broadly similar to that of cadmium,[408] with fixation chemistry being best envisaged as a dynamic equilibrium. Overall, the fact that a proportion of added phosphate becomes lost and unavailable for plant uptake every year, means that more phosphate fertiliser needs to be added than would otherwise be the case.

Predominant soil orders under cultivation in the Waikato region include allophanic soils (aquands) and granular soils (humults). Unfortunately, allophanic soils have high natural phosphate retention capacities,[409] and require higher rates of (capital and maintenance) phosphate fertiliser application than is the case for sedimentary soils.

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[407] Roberts AHC, Ravensdown Fertiliser Co-operative Ltd., **2004**. Personal Communication.

[408] Loganathan P, Hedley MJ, Wallace GC and Roberts AHC, **2001**. Fluoride accumulation in pasture forages and soils following long-term applications of phosphorus fertilisers. *Environmental Pollution*, Vol. 115, No. 2, pp 275-282.

[409] McLaren RG and Cameron KC, **1996**. *Soil science sustainable production and environmental protection.* Oxford University Press, Auckland, New Zealand.

Natural acidity of Waikato soils

Soils of the Waikato region (and many other New Zealand soils) have a very low carbonate content, and are naturally quite acidic. Lime is in widespread use, but soil pH values of most productive properties remain at the acidic end of suitable growing ranges, determined by the optimal cost-benefit of lime use.

Summary statistics for 83 pastoral, horticultural, arable, forest and background sites where soil pH has recently been measured as part of Environment Waikato's Regional Soil Quality Monitoring Programme are provided in **Appendix 7, Table 1**.

Appendix 6, Table 1. Summary statistics for soil pH values of 83 Waikato pastoral, horticultural, arable, forest and background sites in the Waikato region.[410]

Statistic	pH value
Mean	5.47
Standard deviation	0.43
Median	5.44
Minimum	3.95
Maximum	6.49

As reviewed in **Section 3.5.1**, the amount of cadmium taken up by crops depends on soil acidity. Other factors being equal, cadmium uptake will be greater from soils which are naturally acidic, compared with those which more alkaline.

Further acidification of soils through nitrification or natural processes

Recently it has been established that, in broad terms, the pH of surface waters in the Waikato region has dropped over the last decade, by approximately 0.3 units.[411] Given pH is a log scale, this is a significant shift, representing a doubling in hydrogen ion concentration over 10 years. Similar trends are reflected in other parts of New Zealand in data collected by NIWA.[412]

It is thought that the increasing acidity of surface waters represents an integrated average of changes occurring on the land, within stream and river catchment areas. However, it is unclear at this stage whether the underlying processes are natural, anthropogenic, or a mixture of the two. The effect is seen in both developed and less-developed catchments.

It is not unreasonable to speculate that soil weathering should result in a slow shift in soil pH over time, with the wider effects of this not being appreciated previously; detection of such subtle trends against the statistical background of seasonal, diurnal and spatial variation require implementation of long-term monitoring programmes which make use of reliable instruments. Results of such programmes have only recently started becoming available.

In terms of anthropogenic processes, nitrification is a well-known cause of soil acidification. The chemical reactions involved in nitrification are as follows:

$$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 4H^+ + 2H_2O$$ (conversion of ammonium to nitrite)

$$2NO_2 + O_2 \longrightarrow 2NO_3^-$$ (conversion of nitrite to nitrate)

410 Compiled from data held in Environment Waikato Document **712297**. Only four of the 83 samples are from peat soils, but three of these are lime-modified, and the average pH over these four soils is 5.36 (close to the overall average).

411 Vant W and Smith P, **2004**. *Trends in river water quality in the Waikato Region, 1987-2002*. Environment Waikato Technical Report **2004/02**.

412 Vant W, Environment Waikato, **2004**. Personal communication.

The first of these reactions, conversion of ammonium to nitrite, results in the release of two acid equivalents per mole of ammonium ion. Due to combined effects of dairy farming, nitrogen fertiliser use, pasture growth (ion exchange) and nitrogen fixation by legumes and leaching, nitrogen pollution in the Waikato region is a significant issue in its own right. At the same time as the pH of surface waters has been decreasing, total nitrogen levels have been increasing.[413]

Fertilisation also tends to increase microbial respiration in soil: the increased amount of dissolved carbon dioxide produced can then also cause a reduction in the pH of groundwater (and receiving waters), through its direct influence on the carbonate buffer system.[414]

Effects of the fertiliser itself on cadmium uptake may be manifest through more than one mechanism. Gray *et al.*[415] found that increasing amounts of calcium ammonium nitrate fertiliser increased cadmium uptake in durum wheat grain at three test sites. Three possible effects may have been operating in this case to increase cadmium uptake at the higher fertiliser application rates. These are the presence of more exchangeable cations (calcium and ammonium), an increase in soil acidity caused by the nitrification of the ammonium content, and an increase in soil porewater acidity caused by greater microbial respiration.

Apparent acidification of soils represents a resource pressure, because it provides a mechanism by which crop uptake of cadmium may increase even in the absence of further cadmium inputs. Acidity is involved in many of the significant remobilization processes for soil cadmium, which are outlined in **Table 3**.

Upper limit on pH suitable for growing each crop
It has been noted that cadmium uptake in crops can be reduced by increasing the soil pH, by addition of lime. It has also been noted (**Section 3.5.3**) that there is an upper limit on the soil pH suitable for growing each crop. Modification of soil pH is therefore a finite tool as a means of limiting crop uptake of cadmium.

Loss of soil organic matter under cropping
In soils under pasture or forestry, soil organic carbon levels tend to increase. In soils used for cropping, soil organic carbon levels generally decrease. Loss of soil organic matter is a significant issue in horticultural soils in its own right, and occurs for the following reasons:[416]

- Fertilisers provide nutrients which act to assist microbial degradation of organic matter;

- Cultivation causes aeration, which also assist microbial degradation of organic matter;

- Significant erosion of topsoil itself is occurring in cropping areas, and this represents direct loss of the soil fraction which contains the most organic carbon. At a paddock level in horticultural cropping soils, this loss is estimated at 7-30 tonnes/ha/yr.[417]

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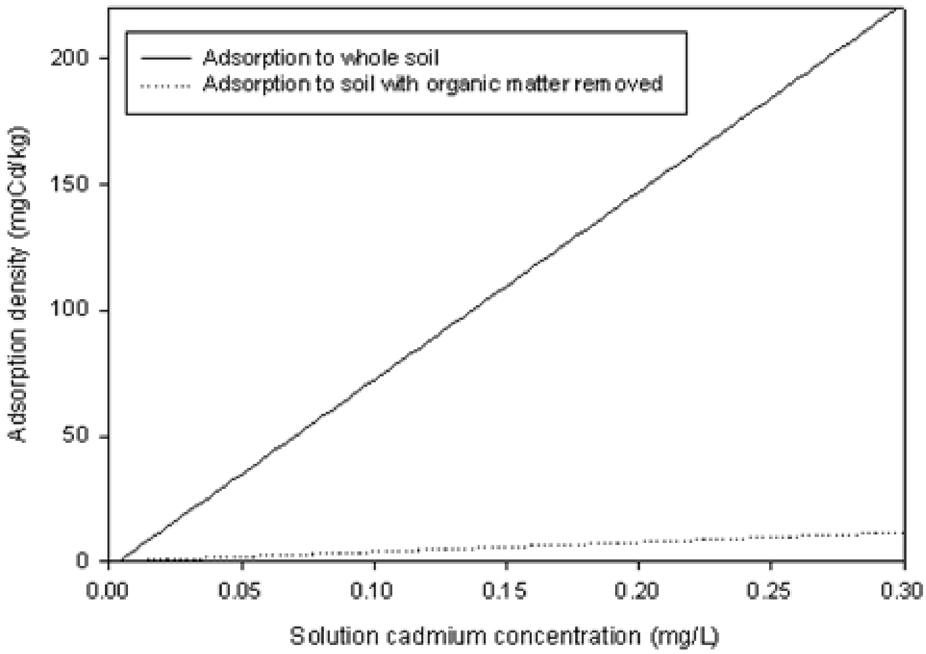
413 Vant W and Smith P, **2004**. *Trends in river water quality in the Waikato Region, 1987-2002*. Environment Waikato Technical Report **2004/02**.
414 Jones JB, Stanley EH and Mulholland, PJ, **2003**. Long-term decline in carbon dioxide supersaturation in rivers across the contiguous United States. *Geophysical Research Letters*, Vol. 30, No. 10, pp 1495-1499.
415 Gray CW, Moot DJ, McLaren RG and Reddecliffe T, **2002**. Effect of nitrogen fertiliser applications on cadmium concentrations in durum wheat (*Triticum turgidum*) grain. *Journal of Crop and Horticultural Science*, Vol. 30, pp 291-299.
416 Singleton P, Environment Waikato, **2004**. Personal communication.
417 Edmeades Consultants Ltd, **2002**. The content and value of nutrients in the topsoils of the Franklin District. Environment Waikato Internal Series IS02/06. Environment Waikato Document **764122**.



Appendix 6, Figure 1. Simple isotherm for adsorption of cadmium to a New Zealand soil (Tai Tapu Silt Loam from Canterbury), and adsorption to the same soil with its organic content removed.[418,419]

In attempts to limit the amount of soil organic matter lost, growers are encouraged to grow cover-crops such as barley or legumes over winter; however, uptake of these ideas is limited.[415] Loss of organic carbon has significant implications for crop uptake of cadmium, because organic matter is a dominant soil phase responsible for cadmium adsorption (**Section 3.4**). This is shown graphically for a particular New Zealand soil in **Appendix 6, Figure 1**.

In this experiment, removal of soil organic matter in a New Zealand soil reduced cadmium adsorption (based on the conditional equilibrium constant) to only 8% of its original level. By comparison, removal or iron and manganese oxides from the same soil reduced cadmium adsorption to 55% of its original level.

Loss of soil organic matter under cropping therefore represents a not insubstantial dynamic change to adsorption conditions primarily responsible for cadmium immobilisation. Lower soil organic matter implies the following consequent changes:

- Part of the pool of previously immobilised cadmium will be remobilised, and become available for crop uptake;

- Residual soil may fix new cadmium at a lower average binding strength, allowing proportionately more cadmium to remain available for plant uptake;

- Residual soil may accumulate new cadmium at a lower relative rate, allowing more cadmium to leach to groundwater.

The amount of cadmium currently reaching groundwater from pasture soils is usually considered low to insignificant in relation to drinking water guidelines.[420] However, this subject may be worth closer investigation in cropping catchments, due to loss of soil

[418] Kim ND and Fergusson JE, **1992**. Adsorption of cadmium by an aquent New Zealand soil and its components. *Australian Journal of Soil Research*, Vol. 30, No. 2, pp 159-67.

[419] Additional data: Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury, Ch. 10.

[420] Gray CW, McLaren RG and Roberts AHC, **2003**. Cadmium leaching from some New Zealand pasture soils. *European Journal of Soil Science*, Vol. 54, No. 1, pp 159-166.

organic matter, and because cadmium is not routinely measured in standard groundwater monitoring programmes. Some New Zealand laboratory research has been carried out on modelling the groundwater transport of cadmium, zinc and lead in alluvial gravels.[421] Whereas lead was strongly sorbed and relatively immobile, cadmium and zinc were both relatively mobile in this medium.

Desorption of cadmium in to soil solution to form dissolved cadmium (Cd^{2+}_{aq}) is not the only means of off-site transport. Loss of particle-bound cadmium in the form of superphosphate fertiliser and cadmium-enriched topsoil also has implications in terms of cadmium contamination of the wider environment. This topic is briefly reviewed in **Section 8**.

Use of dithiocarbamates

Dithiocarbamates (DTCs) are regarded as the most cost-effective and broad spectrum fungicides available for use in horticulture, and the most important fungicide class.[422] As at 1988, world-wide use stood at between 25000 and 35000 tonnes per year,[423] and New Zealand use was estimated as 366 tonnes per year.[421]

- In analytical chemistry, dithiocarbamates are a well known class of metal-complexing agents, which have a particular affinity for sulphur-loving heavy metals. The pyrrolidine-dithiocarbamate anion (PDC^-) (**Appendix 6, Figure 2**) is commonly used to selectively extract and pre-concentrate heavy metals from seawater samples, in the presence of high concentrations of other major cations.[*e.g.* 424,425,426,427,428] To effect an extraction, a water-immiscible solvent (methyl isobutyl ketone, or MIBK) is placed with the seawater in a separating funnel, and PDC^- added to the water phase. Because it carries a negative charge, the uncomplexed PDC^- ligand is soluble in seawater: upon complexation it loses its charge and the metal complex transfers to the organic phase. From there it can be analysed directly, or back-extracted into clean water for analysis.

- Back extraction involves addition of a metal which forms a stronger complex. Of the metals, zinc forms one of the weakest dithiocarbamate complexes, and palladium one of the strongest. In cases where the reagent is supplied as a zinc dithiocarbamate complex, exchange with another suitable metal will occur readily. For example, Schriner found this to be quantitative for the exchange between the complexed zinc and free copper.[429] Dithiocarbamate complexes of copper, cadmium and mercury all exhibit substantially higher equilibrium constants than those of zinc.

A review of environmental health criteria relating to dithiocarbamates has been published as report 78 of the World Health Organisations' International Programme on Chemical Safety (IPCS), and is available online.[430]

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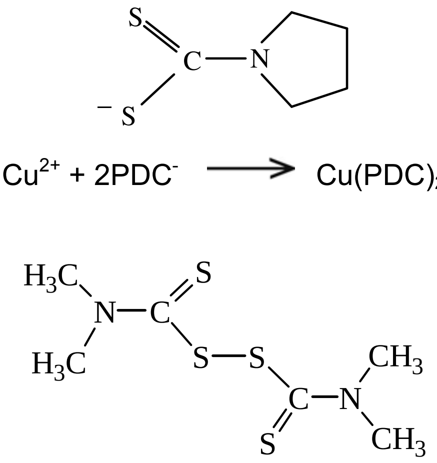
421 Pang L and Close ME, **1999**. Non-equilibrium transport of Cd in alluvial gravels. *Journal of Contaminant Hydrology*, Vol. 36, pp 185-206.
422 Holland P and Rahman A., **1999**. Review of trends in agricultural pesticide use in New Zealand. MAF Policy Technical Paper 99/11.
423 http://www.inchem.org/documents/ehc/ehc/ehc78.htm
424 Brooks RR, Presley BJ, and Kaplan IR, **1967**. APDC-MIBK extraction system for the determination of trace elements in saline waters by Atomic Absorption Spectroscopy. *Talanta*, Vol. 14, pp 809-816.
425 Bruland, KW, Franks, RP, Knauer, GA and Martin JH, **1979**. Sampling and analytical methods for the determination of copper, cadmium, zinc and nickel at the nanogram per litre level in sea water. *Analytica Chimica Acta*, Vol. 105, pp 233-245.
426 Wyttenbach A. and Bajo S, **1975**. Extractions with metal-dithiocarbamates as reagents. *Analytical Chemistry*, vol. 47, pp 1813-1817.
427 Jan TK and Young DR, **1978**. Determination of microgram amounts of some transition metals in seawater by methyl istobutyl ketone-nitric acid successive extraction and Flameless Atomic Absorption Spectrophotometry. *Analytical Chemistry*, Vol. 50, No. 9, pp 1250-1253.
428 Sachsenburg S, Klenke Th, Krumbein WE and Zeeck E, **1992**. A back-extraction procedure for the dithiocarbamate solvent extraction method. Rapid determination of metals in sea water matrices. *Fresenius Journal of Analytical Chemistry*, Vol. 342, pp 163-166.
429 Schriner R, **1994.** *Aspects of the solid-phase speciation of copper in the marine environment.* MSc thesis in Chemistry, University of Waikato, Ch 6.
430 WHO International Programme on Chemical Safety (IPCS). Available from: http://www.inchem.org/documents/ehc/ehc/ehc78.htm



Appendix 6, Figure 2. Top: structure of the pyrrolidine-dithiocarbamate anion (PDC-), and representative complexation reaction between this and copper. Bottom: Chemical structure of the fungicide thiram.

One dithiocarbamate pesticide, Thiram (**Appendix 6, Figure 2**), essentially comprises two tetramethyldithiocarbamate (MDTC) ligands held in close proximity by a disulphide bridge, and would also work as a ligand in its own right.[431] This pesticide is likely to be a strong heavy metal complexing agent, and would probably be comparable in effect to ligands which are used experimentally to extract the plant-available fraction of soil metals. The scientific literature contains at least 19 references to dimeric MDTC complexes of cadmium, $Cd(MDTC)_2$, mainly in the area of synthetic Chemistry.[232] Structures of two relevant analogous cadmium complexes are provided in **Appendix 6, Figure 3**.

Most other dithiocarbamate pesticides already contain a metal (or metals[432]) as stabilising agents. These include sodium, iron, manganese and zinc. Zinc forms one of the weakest metal-dithiocarbabamate complexes, and will be readily displaced by cadmium where it is available. In such cases the dithiocarbabamate ligand is also provided in an already reduced 'metal-ready' form. Such metal-stabilised dithiocarbamate pesticides should therefore also work as effective complexing agents for soil cadmium.

When a dithiocarbamate pesticide is added to a soil containing cadmium, the proportion of cadmium that is complexed and dissolved into soil porewater and groundwater would depend on the loading and nature of the dithiocarbamate ligand (discussed above), coordination of anions, and the degree of involvement of the dithiocarbamate metal (if there is one):

- In terms of coordination of anions, cadmium will tend to form a five or six-coordinate anionic species of the type $[Cd(DTC)_2X_2]^{2-}$, where X is OH^- or Cl^-. Such complexes are reasonably water soluble.

- Involvement of the dithiocarbamate metal is more complicated, with both competitive adsorption and oxidation followed by cadmium sequesterisation being possibilities, depending on the metal. Aspects of the chemistry of cadmium and zinc are similar enough for the two to act as mutual competitors for a number of processes, including soil sorption and plant uptake. Such competition from zinc is more effective where (as is usually the case) zinc concentrations significantly exceed those of cadmium. The depressing effect of zinc on cadmium adsorption is illustrated for a Christchurch soil in **Appendix 6, Figure 4.**

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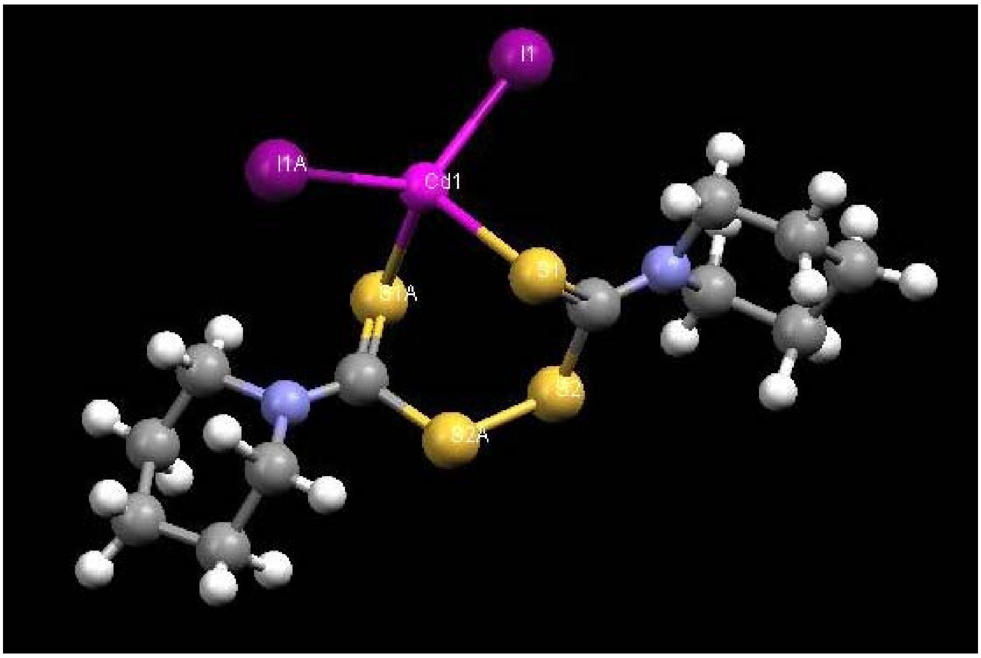
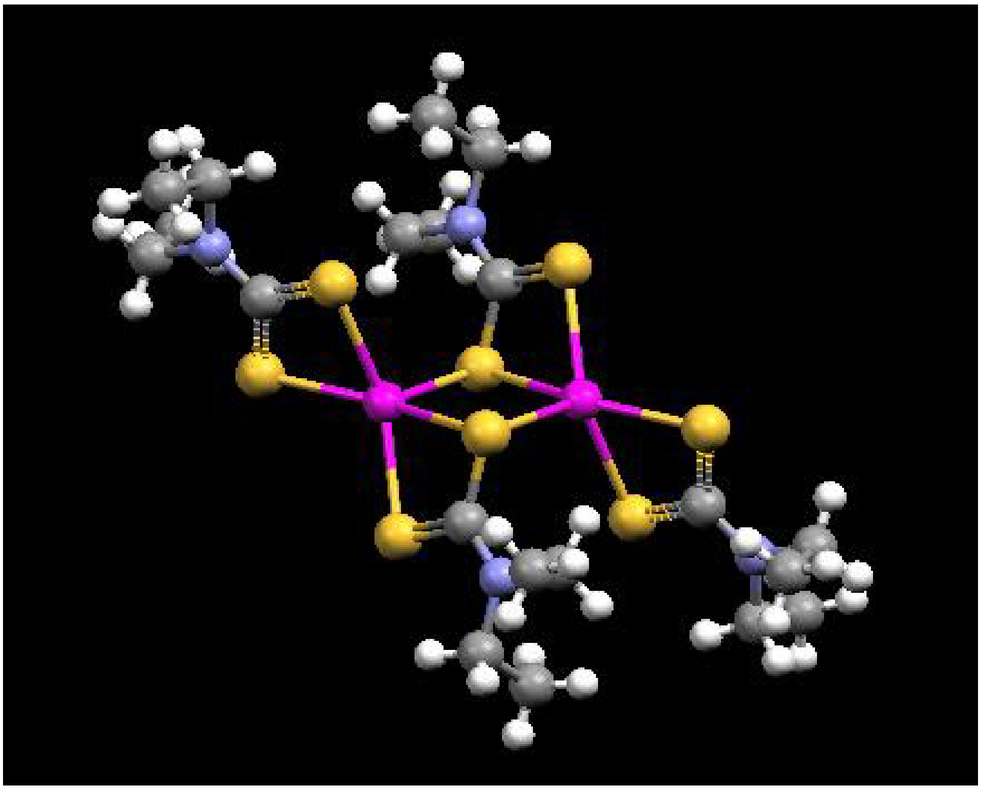
431 Nicholson BK, Department of Chemistry, University of Waikato, **2004**. Personal communication.
432 Mancozeb is a polymeric dithiocarbamate containing both manganese and zinc.



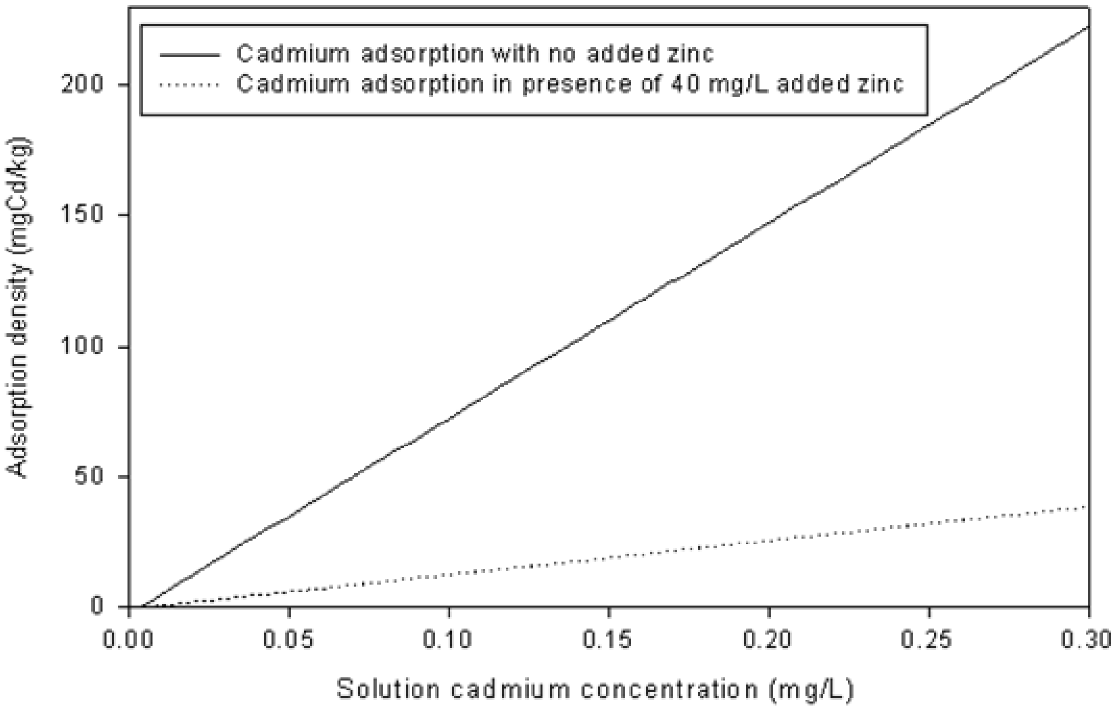


Appendix 6, Figure 3. **X-ray crystal structures of two known cadmium dithiocarbamate complexes analogous to complexes likely to be formed between cadmium and Thiram in soil.**

Top: Seven-membered ring formed by simple complexation of cadmium by two sulphur atoms of the same sulphur-bridged ligand (bipiperidinethiruramdisulphide).

Bottom: Cadmium dimer formed between reaction of cadmium and the ethyl analogue of Thiram (tetraethyldithiocarbamate instead of tetramethyldithiocarbamate).

Source: Nicholson BK**, 2004**. Department of Chemistry, University of Waikato, Personal communication.



Appendix 6, Figure 4. Simple isotherm for adsorption of cadmium to a New Zealand soil (Tai Tapu Silt Loam from Canterbury), and adsorption to the same soil in the presence of elevated zinc in solution.[433]

Use of dithiocarbamate pesticides on crops could result in a number of subsequent effects on soil cadmium, but these have not been characterised to date. Effects associated with the chelating **ligand** load might involve:

- Complexation and partial extraction of cadmium and other heavy metals into soil solution.
- Complexation and partial extraction of iron into soil solution, accompanied by partial dissolution of the iron oxide phase and release of some of its adsorbed contaminant load.[434]
- Possible increased plant uptake of extracted heavy metals. Small non-polar metal complexes are able to bypass the normal metal uptake process and diffuse through cell membranes directly.[435]
- Reduced soil retention of applied metals, accompanied by increased amounts leaching to groundwater.

Effects associated with the **metal** load might include:

- Deposition of zinc (from Propineb and Mancozeb); causing enhanced cadmium desorption into soil solution (and decreased cadmium adsorption), but probably also decreasing plant uptake.
- Deposition of iron or manganese to soil followed by formation of amorphous iron and manganese oxide coatings and phases. Hydrated manganese oxides tend to be significantly more effective at metal retention than iron oxides, but are usually present (on a mass and surface area basis) at lower concentrations in the soil.

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433 Kim ND, **1990**. *Studies in the concentrations and chemistry of cadmium in the environment.* PhD thesis, University of Canterbury, Ch. 10.

434 Iron is a dominant soil trace metal and iron-dithiocarbamate complexes are reasonably stable: however, these would be less likely to comprise anionic complexes.

435 This parallels the way in which metal dithiocarbamate complexes transfer to the non-polar phase during analytical extraction.

Overall:

- Sodium, ammonium and 'free-ligand' dithocarbamates would be expected to extract a proportion of soil cadmium, and this might increase crop uptake of cadmium;
- Iron and manganese dithocarbamates might also be expected to extract cadmium initially, but this may be countered by iron and manganese oxide formation. It is unclear whether use of manganese or iron dithiocarbamates might cause a net lowering of soil retention capacity for cadmium, or an increase.
- Zinc dithiocarbamates would act as reasonably strong reagents for extraction and leaching of soil cadmium, both through ligand complexation and zinc competition, but it is unclear whether crop uptake might increase or decrease.

It is unclear at present whether dithiocarbamate use represents a soil resource pressure or a partial solution to cadmium accumulation in horticultural soil. Such pesticides may work to reduce net cadmium accumulation in surface soils by moving the metal further down the soil horizon, but if this is the case, would also increase the proportion of cadmium moving in groundwater. However, use of this class of pesticides in New Zealand horticulture continues to increase.[436]

In addition, land-use change will bring about situations where pastoral soils, with no history of dithiocarbamate use, are converted to horticultural soils, where use is high. Release of stored cadmium from a recently converted pastoral soil may be particularly high over the first few growing seasons.

This is because, in pastoral soil, cadmium will have been accumulating, and is mainly associated with soil organic matter, which also tends to accumulate under grass. When the land is converted to horticulture, the organic matter starts to be lost from the soil, at the same time as dithiocarbamates are added. Soil cadmium thus experiences loss of a significant soil sorptive phase (organic matter) at the same time as addition of an alternative complexing agent (a dithiocarbamate), often accompanied by a metal that competes for a fraction of available soil adsorption sites (zinc). Such conditions may result in stripping of the most available fraction of the stored soil cadmium pool. This mobilised cadmium would be expected to move down the soil profile, with a proportion being spread further in groundwater.

Use of facial eczema remedies

Use of zinc compounds in agriculture is summarized in **Section 6.2.2**, where possible cadmium loadings from such sources are considered. Most zinc applied in horticulture is accounted for by use of dithiocarbamate fungicides. By contrast, facial eczema remedies account for most zinc applied to land in pastoral farming areas (either directly or in excreta). Zinc used to prevent facial eczema can be applied to pasture, added to stock water, or administered to animals as a bolus.[437] Based on recommended administration rates, yearly zinc loadings to soil for those sheep, beef or dairy farms where facial eczema remedies are used are estimated to range from 5.0 - 6.7 kg/ha/yr (**Table 15**).

These high zinc loadings to soil, where present, have implications for the chemistry of cadmium retention in soils. High concentrations of zinc work to reduce cadmium adsorption to soil (**Appendix 6, Figure 4**), and would also be expected to cause a certain amount of cadmium desorption from soil. The net expected effect would be to increase dissolved cadmium concentrations in soil pore-water and enhance movement of (some) cadmium further down the soil profile. Uptake in pasture and herbage may also be increased, depending on whether or not zinc competition across the root cell wall is sufficient to counter increased cadmium levels in the soil pore-water. A further

[436] Holland P and Rahman A, **1999**. Review of trends in agricultural pesticide use in New Zealand. MAF Policy Technical Paper 99/11.

[437] Cadmium is present as an impurity in zinc products, but in the case of facial eczema remedies, maximum limits are specified (**Section 6.2.2**). For this reason, the additional amount of cadmium contributed to soil from use of facial eczema remedies appears to be minor in relation to contributions from superphosphate fertiliser (**Table 18**).

result might be to increase cadmium concentrations in groundwater aquifers, depending on their proximity to the soil surface, soil type and local climate.

Use of zinc might therefore work to temporarily ameliorate the accumulation of cadmium in surface soils, by causing it to penetrate more deeply. It is also possible that measured concentrations of cadmium in New Zealand pastoral surface soils (**Section 3.3** and **Section 5**) are moderately lower than they would have been in the absence of the widespread use of zinc treatments.

Overall, it is currently unclear whether zinc-based facial eczema remedies represent an additional soil or groundwater resource pressure in relation to cadmium. Research trials to clarify the range of magnitudes of such effects across a range of soil types would be worthwhile.

Like sporodesmin, the fungal toxin responsible for facial eczema, cadmium is toxic to the liver (hepatotoxic). Based on modeling, it has been suggested by Loganathan *et al.*[438] (**Section 3.6**) that cadmium concentrations in sheep liver and kidneys are most sensitive to fertiliser cadmium concentrations, moderately sensitive to the pasture ingestion rate, and least sensitive to the soil ingestion rate. Phosphate fertiliser, the product responsible for most pastoral cadmium (**Section 6.3**) is generally applied in spring and summer. This being the case, the cadmium ingestion rate in sheep is expected to be highest during spring or summer, over the same period when ingestion of sporodesmin (the facial eczema toxin) also reaches a peak.

It is not known whether fertiliser cadmium might exacerbate the progression of facial eczema in animals whose liver function has already been compromised by exposure to sporodesmin. Usually, a threshold level of cadmium must be exceeded before serious renal or hepatic damage begins.[439] However, if one effect of sporodesmin toxicity is to reduce the liver's ability to express the protein metallothionein (**Section 2.3.2**), then hepatotoxic effects of cadmium could be felt well below this threshold. Mechanistically, the hypothesis that cadmium exposure may exacerbate sprodesmin-induced liver damage appears feasible.

Coincidentally, zinc treatment for sporodesmin would also be effective in reducing an animal's cadmium exposure, because presence of dietary zinc reduces the uptake of cadmium across the gastrointestinal tract (**Section 2.3.2**). By different mechanisms, zinc treatment will work to reduce the hepatotoxicity of both sporodesmin and cadmium.

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438 Loganathan P, Louie K, Lee J, Hedley MJ, Roberts AHC and Longhurst RD, **1999**. A model to predict kidney and liver cadmium concentrations in grazing animals. *New Zealand Journal of Agricultural Research*, Vol. 42, No. 4, pp 423-432.

439 Piotrowski JK and Coleman DO, **1980**. *Environmental hazards of heavy metals: summary evaluation of lead, cadmium and mercury. A general report.* Monitoring and Assessment Research Centre (MARC), University of London.

Appendix 7 Land use in the Waikato region by area. Land uses subject to reasonably rapid cadmium accumulation are indicated by shading.[440]

Land type	Hectares	Percent of Waikato
Tussock and danthonia used for grazing	23471	1.4
Pasture: sheep	333442	13.3
Pasture: dairy	623013	24.9
Pasture: beef	471345	18.9
Arable crop land, fodder crop land & fallow land	16698	1.0
Land in horticulture	10145	0.6
Planted production forest	329781	19.1
Mature native bush	52024	3.0
Native scrub and regenerating native bush	80266	4.6
Other land	62245	3.6

[440] Statistics New Zealand, **2004**. 2002 Agricultural Production Census (Final Results): June 2002. Environment Waikato figures for sheep, dairy and beef pasture.

Appendix 8 Concentrations of cadmium in Waikato soil from recent surveys.

Soil samples were collected from 2001 to 2004; mid-point year of sample collection: 2003. Sample depths relate to surface soil (0-7.5 cm and 0-10 cm): and represent two data sets that were merged on the basis that cadmium results are statistically indistinguishable (see Sections 5.1 and 3.9).

Soil cadmium concentrations by land use (mg/kg dry weight)							
	Arable	*Horticult-ural*	*Horticult-ural (contd)*	*Pastoral*	*Pastoral (contd)*	*Forest*	*Reserve or equivalent*
	<0.1	0.2	0.6	0.11	0.7	<0.1	<0.1
	0.5	0.2	0.6	0.17	0.7	<0.1	<0.1
	0.6	0.2	0.7	0.2	0.76	0.2	<0.1
	0.6	0.2	0.7	0.3	0.79	0.6	<0.1
	0.7	0.2	0.8	0.37	0.8		0.19
	0.8	0.3	0.8	0.4	0.8		0.2
	0.8	0.3	0.8	0.47	0.8		0.2
	0.8	0.3	0.8	0.5	0.8		0.2
	0.9	0.3	0.8	0.59	0.8		0.2
		0.4	0.9	0.59	0.8		0.23
		0.4	0.9	0.6	0.8		0.3
		0.5	1	0.6	0.8		
		0.5	1	0.6	0.81		
		0.5	1	0.6	0.9		
		0.5	1	0.6	0.9		
		0.5	1	0.6	1		
		0.5	1.2	0.6	1		
		0.5	1.2	0.62	1.01		
		0.5	1.2	0.69	1.2		
		0.6	1.3	0.7	1.5		
		0.6	1.5	0.7	1.5		
		0.6		0.7			
Summary statistics							
N	9		43		43	4	11
Mean (mg/kg)	0.64		0.67		0.71	0.23	0.17
Median	0.70		0.60		0.70	0.13	0.20
Standard deviation (mg/kg)	0.25		0.34		0.29	0.26	0.08
Maximum (mg/kg)	0.90		1.50		1.50	0.60	0.30
Percent equal to or exceeding 1.0 mg/kg	0		23		14	0	0

Data sources:

1. Environment Waikato Regional Soil Quality Monitoring Programme, multi-element survey of selected samples by ICP-MS (results: Environment Waikato Document **844227**);
2. Gaw SK, **2003**. *Historic pesticide residues in horticultural and grazing soils in the Waikato region*. Environment Waikato Document **835071**;
3. Gaw SK, **2004**, University of Waikato. Personal communication.

Appendix 9 Hectares used for horticultural and arable crops in the Waikato region in 2002, ranked from greatest to smallest.

Data source: Statistics New Zealand, 2003. 2002 Agricultural Production Census (Final Results).[441]

Category	*Crop*	*Area (hectares)*	*Percent of total horticulture in Waikato region*
Grain and seed crops	Maize grain	3,364	26.6
Outdoor Vegetables	Potatoes	2309	18.3
Outdoor Vegetables	Onions	2102.6	16.6
Other fruit	Kiwifruit	800	6.3
Grain and seed crops	Other crops	786	6.2
Outdoor Vegetables	Asparagus	559.8	4.4
Grain and seed crops	Field / seed peas	364	2.9
Pipfruit and Stonefruit	Apples	300	2.4
Other fruit	Avocados	200	1.6
Other fruit	Wine grapes	200	1.6
Outdoor Vegetables	Broccoli	136.3	1.1
Outdoor Vegetables	Sweet corn	130.2	1
Outdoor Vegetables	Lettuce	111	0.9
Grain and seed crops	Wheat for bread / milling	110	0.9
Other fruit	Olives	100	0.8
Outdoor Vegetables	Other	99.4	0.8
Outdoor Vegetables	Pumpkin	98.6	0.8
Outdoor Vegetables	Cauliflower	93.7	0.7
Outdoor Vegetables	Melon (water/rock)	92.3	0.7
Outdoor Vegetables	Cabbage	91.6	0.7
Horticulture Crops and Flowers Grown Outdoors	Ornamental trees and shrubs	85	0.7
Horticulture Crops and Flowers Grown Outdoors	All other nursery crops	67	0.5
Outdoor Vegetables	Silver beet / spinach	61.4	0.5
Horticulture Crops and Flowers Grown Outdoors	All other flowers and foliage	59	0.5
Grain and seed crops	Oats	54	0.4
Horticulture Crops and Flowers Grown Outdoors	Flower bulb, corm and tuber crops	37	0.3
Horticulture Crops and Flowers Grown Outdoors	Fruit trees	35	0.3
Outdoor Vegetables	Parsnips	30.2	0.2
Outdoor Vegetables	Courgettes / zucchini	24.4	0.2
Horticulture Crops and Flowers Grown Outdoors	Other outdoor crops	19	0.2
Indoor crops	All other flowers and foliage	17.6	0.1
Outdoor Vegetables	Asian vegetables	17	0.1
Horticulture Crops and Flowers Grown Outdoors	Calla lilly	15	0.1
Indoor crops	Tomatoes	14.9	0.1
Horticulture Crops and Flowers Grown Outdoors	Perennials	11	0.1
Indoor crops	Cucumber	9.5	0.1
Indoor crops	Orchids	7.3	0.1
Indoor crops	Other indoor crops	6.4	0.1
Indoor crops	Ornamental trees and shrubs	5.1	0
Horticulture Crops and Flowers Grown Outdoors	Hydrangea	4	0
Horticulture Crops and Flowers Grown Outdoors	Bedding plants	2	0

441 Statistics New Zealand, **2004**. http://www.stats.govt.nz/domino/external/pasfull/pasfull.nsf/7cf46ae26dcb6800cc256a62000a2248/4c2567ef00247c6acc256db000838769?OpenDocument

Horticulture Crops and Flowers Grown Outdoors	Herbs	2	0
Indoor crops	Capsicum	1.7	0
Indoor crops	Flower bulb, corm and tuber crops	1.7	0
Indoor crops	Bedding plants	0	0
Indoor crops	Fruit trees	0	0
Indoor crops	Perennials	0	0

Appendix 10 Measured cadmium concentrations in 40 commercially available compost and fertiliser samples marketed to home gardeners.

Composts and manures		
Brand	*Product*	*Cadmium concentration (mg/kg dry weight)*
Butlers	Organic compost	0.2
Butlers	Organic sheep pellets	0.3
Butlers	Pot tub & barrel mix	0.1
Butlers	Potting mix	0.3
Butlers	Seed raising mix	0.1
Hauraki Gold	Peat moss	< 0.1
Just	Compost	0.1
Just	Patio & tub mix	0.3
Just	Potting mix	0.2
Kiwi	Pelletised sheep manure	0.4
Kiwi	Potting mix	0.1
Kiwi	Seed mix	0.1
Power Organics	Power-50 vermicast	0.7
Results	Organic compost	0.3
Yates	Black magic seed raising mix	< 0.1
Yates	Patio & tub mix	0.2
Fertilisers		
Brand	*Product*	*Cadmium concentration (mg/kg dry weight)*
Butlers	Blood & bone	0.03
Butlers	General garden food	8.7
Butlers	Lawn food	8.62
Kiwi	Acid fertiliser	11.6
Kiwi	Blood & bone fertiliser	< 0.02
Kiwi	Citrus fertiliser	8.9
Kiwi	Garden lime	0.4
Kiwi	General garden fertiliser	10.3
Soil Life	Gypsum	< 0.02
Tui	Dicalcium phosphate	5.83
Tui	Dolomite lime	0.14
Tui	Dried blood	< 0.02
Tui	Nitrophoska blue special fertiliser	1.3
Tui	Potato food	15.8
Tui	Superphosphate	22.5
Yates	Gro-plus blood & bone	0.23
Yates	Gro-plus citrus food	19.8
Yates	Gro-plus complete garden food	83.6
Yates	Gro-plus Garden lime	0.22
Yates	Gro-plus sulphate of potash	0.14
Yates	Gro-plus super phosphate	23.8
Yates	Gro-plus tomato food	12.5
Yates	Thrive. Granular all purpose plant food	54.0
Yates	Thrive soluble all purpose plant food	0.11

Appendix 11 Cities and towns from which potatoes and onions were collected for analysis; population estimates as at the last New Zealand census and numbers of samples/bags purchased.

City/town	*Population estimate*	*Number of samples / bags*	
		Potato	Onion
Hamilton	138792	9	5
Taupo	20307	4	3
Tokoroa	14430	3	2
Cambridge	13890	3	2
Te Awamutu	13446	2	2
Huntly	6822	3	2
Thames	6705	3	2
Morrinsville	6168	2	2
Matamata	6078	1	1
Ngaruawahia	5000	1	1
Waihi	4524	2	1
Te Kuiti	4374	2	1
Paeroa	3882	2	1
Whangamata	3861	1	1
Putaruru	3786	2	1
Te Aroha	3687	2	1
Turangi	3441	2	1
Whitianga	3078	2	1
Tuakau	2853	1	1
Raglan	2667	2	1
Otorohanga	2631	2	1
Coromandel	1437	1	1
Mangakino	1281	1	1
Pauanui	699	0	1
Total samples		**53**	**36**

Appendix 12 Sample preparation protocols followed for the analysis of potatoes, onions, lettuce and silverbeet (Section 7).

Preparation of potato samples
All samples were submitted for analysis within one week of collection.

Four potatoes were taken from each bag. Each of the four potatoes was peeled (with a standard potato peeler in a stainless steel sink), while being washed with reticulated water; during this process, all skin and dirt was removed. Each potato was then cut into four parts (lengthwise) on a clean wooden chopping board, using a stainless steel knife. Excess water was removed from the potato by gently squeezing in a clean linen cloth.

1. Raw samples: one of the quarters from each peeled potato was placed in a labelled zip-lock plastic bag, so that each bag contained four quarters from four different potatoes.

   Bags were rolled to expel air, sealed, and placed in a cooled chilly bin for transport to the laboratory.

   Sub-sampling procedure in the laboratory was to take a cube from each of the submitted quarters from each bag, making a single sample composite for analysis.

2. Cooked potato composite samples: for potatoes collected in the first sampling run, cooked composites were also prepared, in order to ascertain the effect of cooking on moisture content and cadmium status.

   The third quarter from each peeled potato was placed in a stainless steel pot used for preparation of cooked composites. Most composites consisted of 16 potato quarters, these being from four potatoes from each of four randomly selected bags. The final composite consisted of 16 potato quarters from 8 potatoes taken from 2 bags.

   Samples were cooked for 30 minutes in reticulated water. After cooking, water was drained, samples were mashed with a stainless steel potato masher, and allowed to cool to approximately 35 °C.

   After cooling, each sample was transferred to a precleaned 200 mL polypropylene specimen jar using stainless steel teaspoons. Jars were filled to near the top, tightly sealed, and placed in the chilly bin for transfer to the laboratory.

Preparation of onion samples
Four onions were taken from each bag. Each of the four onions was peeled with a stainless steel knife (in a stainless steel sink), and briefly washed with reticulated water to remove any residual dirt or surface skin. Excess water was removed by gently squeezing in a clean linen cloth. Each onion was then cut into four parts (lengthwise) on a clean wooden chopping board, using a stainless steel knife.

1. Raw samples: two of the quarters from each onion were finely chopped, mixed, and placed in a labelled zip-lock plastic bag, so that each bag contained eight quarters from four different onions. Bags were rolled to expel air, sealed, and placed in a cooled chilly bin for transport to the laboratory.

2. Cooked samples: as with potatoes, cooked composites were also prepared from onions collected in the first sampling run. In this case, the third quarter from each onion was chopped and placed in a teflon-lined frying pan used for preparation of fried composites. Composites consisted of 16 onion quarters, these being from four onions from each of four bags.

   The final composite consisted of 16 onion quarters from 8 onions taken from 2 bags. Samples were fried using a minimum of canola oil for about 10 minutes. After cooling, each sample was transferred to a precleaned 200 mL polypropylene specimen jar. Jars were filled to near the top and placed in the chilly bin for transfer to the laboratory.

Preparation of lettuce and silverbeet samples
Lettuce and silverbeet were prepared for analysis by removing the outer leaves, washing under cold running tap-water to remove any loose soil, immersing in deionised water, shaking to remove excess water, and pressing in clean paper towels.

In the case of silverbeet, only the leaves were selected for analysis: the white stalks were discarded. Washed and dried samples were finely chopped, placed in clean zip-lock bags, and homogenised inside the bags.

Chopping involved use of a clean stainless steel knife, a plastic chopping board, and plastic coated bench.

Appendix 13 Measured moisture contents, cadmium and uranium concentrations in 53 different potato samples and six cooked composites. Metal concentrations are in mg/kg on a fresh weight basis.[442]

Moisture, cadmium and uranium concentrations in 53 raw potato samples

Sample #	Moisture (%)	Cadmium (mg/kg)	Uranium (mg/kg)	Sample #	Moisture (%)	Cadmium (mg/kg)	Uranium (mg/kg)
1	85.2	0.0200	< 0.0004	28	-	0.0078	< 0.0004
2	81.0	0.0322	< 0.0004	29	-	0.0105	< 0.0004
3	79.3	0.0178	< 0.0004	30	-	0.0146	< 0.0004
4	81.3	0.0182	< 0.0004	31	-	0.0247	< 0.0004
5	78.6	0.0321	< 0.0004	32	-	0.0453	< 0.0004
6	86.1	0.0084	< 0.0004	33	-	0.0144	< 0.0004
7	84.6	0.0226	< 0.0004	34	-	0.0314	< 0.0004
8	87.0	0.0173	< 0.0004	35	-	0.0054	< 0.0004
9	84.0	0.0204	< 0.0004	36	-	0.0253	< 0.0004
10	75.9	0.0092	< 0.0004	37	-	0.0313	< 0.0004
11	85.6	0.0123	< 0.0004	38	-	0.0108	< 0.0004
12	82.6	0.0149	< 0.0004	39	-	0.0112	< 0.0004
13	81.6	0.0416	< 0.0004	40	-	0.0156	< 0.0004
14	84.3	0.0283	< 0.0004	41	-	0.0022	< 0.0004
15	84.8	0.0188	< 0.0004	42	-	0.0297	< 0.0004
16	84.8	0.0236	< 0.0004	43	-	0.0200	< 0.0004
17	76.5	0.0870	< 0.0004	44	-	0.0045	< 0.0004
18	74.5	0.0738	< 0.0004	45	-	0.0414	< 0.0004
19	82.8	0.0200	< 0.0004	46	-	0.0168	< 0.0004
20	85.1	0.0134	< 0.0004	47	-	0.0189	< 0.0004
21	75.6	0.0114	< 0.0004	48	-	0.0322	< 0.0004
22	81.0	0.0178	< 0.0004	49	-	0.0381	< 0.0004
23	-	0.0275	< 0.0004	50	-	0.1060	< 0.0004
24	-	0.0357	< 0.0004	51	-	0.0045	< 0.0004
25	-	0.0460	< 0.0004	52	-	0.0192	< 0.0004
26	-	0.0506	< 0.0004	53	-	0.0246	< 0.0004
27	-	0.0178	< 0.0004				

Moisture, cadmium and uranium concentrations in 6 cooked composite samples

Sample #	Moisture (%)	Cadmium (mg/kg)	Uranium (mg/kg)
1	82.0	0.0195	< 0.0004
2	82.3	0.0337	< 0.0004
3	82.4	0.0236	< 0.0004
4	80.0	0.0436	< 0.0004
5	85.1	0.0213	< 0.0004
6	82.5	0.0214	< 0.0004

[442] Raw data: Environment Waikato Document **891061**.

Appendix 14 Measured moisture contents, cadmium and uranium concentrations in 36 different onion samples and four cooked composites.

Metal concentrations are in mg/kg on a fresh weight basis.[443]

Moisture, cadmium and uranium concentrations in 36 raw onion samples								
Sample #	Moisture (%)	Cadmium (mg/kg)	Uranium (mg/kg)		Sample #	Moisture (%)	Cadmium (mg/kg)	Uranium (mg/kg)
1	89.0	0.0340	< 0.0004		19	-	0.0078	< 0.0004
2	90.6	0.0045	< 0.0004		20	-	0.0056	< 0.0004
3	89.5	0.0045	< 0.0004		21	-	0.0059	< 0.0004
4	88.7	0.0069	< 0.0004		22	-	0.0448	< 0.0004
5	88.3	0.0165	< 0.0004		23	-	0.0052	< 0.0004
6	87.6	0.0051	< 0.0004		24	-	0.0163	< 0.0004
7	87.1	0.0181	< 0.0004		25	-	0.0136	< 0.0004
8	88.7	0.0105	< 0.0004		26	-	0.0153	< 0.0004
9	88.3	0.0261	< 0.0004		27	-	0.0102	< 0.0004
10	88.9	0.0097	< 0.0004		28	-	0.0089	< 0.0004
11	92.3	0.0161	< 0.0004		29	-	0.0654	< 0.0004
12	87.8	0.0031	< 0.0004		30	-	0.0187	< 0.0004
13	88.2	0.0071	< 0.0004		31	-	0.0092	< 0.0004
14	90.0	0.0095	< 0.0004		32	-	0.0038	< 0.0004
15	-	0.0064	< 0.0004		33	-	0.0184	< 0.0004
16	-	0.0049	< 0.0004		34	-	0.0427	< 0.0004
17	-	0.0513	< 0.0004		35	-	0.0120	< 0.0004
18	-	0.0030	< 0.0004		36	-	0.0355	< 0.0004

Moisture, cadmium and uranium concentrations in 4 cooked onion composite samples			
Sample #	Moisture (%)	Cadmium (mg/kg)	Uranium (mg/kg)
1	76.5	0.0169	< 0.0004
2	77.4	0.0166	< 0.0004
3	73.3	0.0259	< 0.0004
4	74.3	0.0128	< 0.0004

443 Raw data: Environment Waikato Document **891061**.

Appendix 15 Measured moisture contents, iron, cadmium and uranium concentrations in 11 different samples of Iceberg lettuce and silverbeet.

Metal concentrations are in mg/kg on a fresh weight basis.[444]

Iceberg lettuce samples				
Sample #	Moisture (%)	Iron (mg/kg)	Cadmium (mg/kg)	Uranium (mg/kg)
1	96.1	2.3	0.0244	< 0.0004
2	96.3	2.6	0.0043	< 0.0004
3	95.2	2.9	0.0281	< 0.0004
4	96.3	1.7	0.0138	< 0.0004
5	96.5	2.6	0.0254	< 0.0004
6	96.6	1.7	0.0130	< 0.0004
7	96.2	2.6	0.0117	< 0.0004
8	96.7	2.6	0.0137	< 0.0004
9	96.3	2.9	0.0180	< 0.0004
10	97.0	2.7	0.0424	< 0.0004
11	96.3	2.9	0.0145	< 0.0004
Silverbeet samples				
Sample #	Moisture (%)	Iron (mg/kg)	Cadmium (mg/kg)	Uranium (mg/kg)
1	90.5	11.5	0.0245	< 0.0004
2	91.0	16.1	0.0104	0.0011
3	90.8	9.2	0.0432	< 0.0004
4	90.7	9.3	0.0177	< 0.0004
5	90.3	10.6	0.0222	< 0.0004
6	89.6	35.0	0.0157	0.0005
7	90.2	18.2	0.0184	0.0007
8	90.6	9.0	0.0187	< 0.0004
9	91.0	11.9	0.0764	< 0.0004
10	90.6	10.2	0.0198	< 0.0004
11	90.1	10.6	0.0183	< 0.0004

444 Raw data: Environment Waikato Document **891061**.