Working towards New Zealand risk-based soil guideline values for the management of cadmium accumulation on productive land

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Contents	Page
Summary	1
Project	1
Objectives	1
Methods	1
Results and conclusions	1
Recommendations	1
Introduction	1
Objectives	2
Protection endpoints for cadmium soil guideline values Protection of human health Protection of ecological receptors Food safety standards and trade Protection of groundwater	2 2 9 21 25
Sensitivity of different endpoints and information required to develop NZ specific guideline values Protection of human health Protection of ecological receptors Protection of food safety standards Protection of groundwater	27 28 28 28 29 30
Summary and conclusions	32
Recommendations	34
Acknowledgements	34
References	35
Acronyms and glossary	47
Appendix A – Detailed description of method used to derive soil guideline values for protection of ecological receptors	or the 49
Appendix B – Details for methodology to protect groundwater	53
Appendix C – New Zealand studies on cadmium	55
Appendix D – Proposed methodology for the derivation of cadmium soil guideline values for the protection of ecological receptors in production land	59

Summary

Project

• This project was conducted to assist the Cadmium Management Group to identify how it will develop a set of New Zealand-derived, risk-based soil guideline values (SGV) to manage cadmium accumulation in soils on production land. The project was funded by the Ministry for Primary Industries and conducted by Landcare Research between December 2011 and May 2012.

Objectives

• To identify a preferred approach and research priorities for deriving a set of risk-based soil guidelines for use in the Tiered Fertiliser Management System (TFMS) specified in the Cadmium Management Strategy.

Methods

- We reviewed New Zealand and international methodologies used to derive risk-based soil
 guideline values for cadmium for different endpoints relevant to the TFMS, and assessed
 the research required to derive New Zealand-specific values.
- The four endpoints considered: protection of human health, protection of ecological receptors (e.g. microbial processes, soil invertebrates, plants), protection of food standards, and protection of groundwater quality.

Results and conclusions

- Of the endpoints considered, protection of food standards and ecological receptors are the
 most relevant to agricultural land. However, there are limited data available to develop
 New Zealand-specific values for these endpoints.
- Protection of human health is considered in the *National Environmental Standard for assessing and managing contaminants in soil to protect human health*. Soil contaminant standards have been developed for cadmium and incorporated in this National Environmental Standard, so there is limited need for further research.
- Protection of groundwater should be considered on a site-specific basis, and is particularly important for soils prone to leaching, e.g. stony soils.

Recommendations

To develop New Zealand-specific values for use in the Tiered Fertiliser Management System we recommend the following actions (stated in order of priority):

- Undertake research to better understand the pathway of cadmium accumulation in animal agricultural systems in New Zealand.
- Undertake research to establish how plant uptake of cadmium is influenced by species, cultivar, and soil properties (for relevant plant species). This would establish the relative

sensitivity of protection of food safety standards compared to other endpoints. Industry input is required to determine what species and cultivars are most economically important and widely grown to maximise the value of the research being undertaken. This research should include both low accumulators and high accumulators.

- The methodology proposed in this report for deriving SGVs for ecological receptors is agreed by all members of the Cadmium Management Group.
- Use this methodology to generate preliminary SGVs to enable assessment of the relative sensitivity of ecological receptors and protection of food standards. New Zealand toxicity data for plant species relevant to New Zealand agricultural soils are required to confirm the validity of preliminary values.
- Undertake research to better establish the risk of leaching to groundwater, in particular for vulnerable soils (such as stony soils), and the effects of land use change on leaching.

1 Introduction

MPI released the strategy document *Cadmium and New Zealand Agriculture and Horticulture: A Strategy for Long Term Risk Management* in February 2011 (MAF 2011). The strategy has the objective:

To ensure that cadmium in rural production poses minimal risks to health, trade, land use flexibility and the environment over the next 100 years.

The Tiered Fertiliser Management System (TFMS) is a central part of the strategy and aims to minimise cadmium (Cd) accumulation in soil by imposing increasingly stringent fertiliser management practices as Cd concentrations increase. There are five tiers and four trigger values, based on increasing soil Cd concentrations, which result in different levels of action primarily related to fertiliser application (Table 1). The soil Cd concentrations currently used as trigger values in the TFMS were agreed to by the Cadmium Working Group (CWG), following international review and recommendations (Warne 2011), at a meeting in September 2010 (MAF 2011) and are from a variety of sources (Table 1). The CWG agreed that these trigger values will be reviewed after 5-7 years and compared to New Zealand-specific values (MAF 2011). This report outlines options and information required to develop New Zealand-specific soil guideline values for Cd.

Table 1 Relationship between tiers in the Tiered Fertiliser Management System (TFMS), with trigger values and their source.

Tier	Management action required	Cadmium concentratio n (mg/kg)	Trigger value (mg/kg)	Source of value
0	Five-yearly screening soil test for cadmium status	0-0.6	0.6	99th percentile of natural background concentrations in Taylor et al. (2007)
1	Application is restricted to a set of products and application rates to minimise accumulation, and landholders are required to test for cadmium every five years using approved programmes	>0.6-1.0	1.0	NZ Biosolids guidelines (NZWWA 2003)
2	Application rates are further managed by use of a cadmium balance programme to ensure that cadmium does not exceed an acceptable threshold within the next 50 years	>1.0-1.4	1.4	Canadian SQG (human and ecological) for agricultural land use (CCME 1999)
3	Application rates are further managed by use of a cadmium balance programme to ensure that cadmium does not exceed an acceptable threshold within the next 50 years	>1.4–1.8	1.8	UK Soil Guideline value for allotments (Environment Agency 2009)
4	No further accumulation above the trigger value	>1.8		

2 Objectives

To identify a preferred approach and research priorities for deriving a set of risk-based soil guidelines for use in the TFMS specified in the Cadmium Management Strategy.

3 Protection endpoints for cadmium soil guideline values

Soil guideline values for Cd can be developed for a range of purposes, and for protection of an array of endpoints ranging from food standards to groundwater. Soil guideline values developed to protect different endpoints may well specify different soil Cd concentrations. Consequently protection of different endpoints may provide a suitable basis for defining trigger values. Alternatively, different levels of protection for one endpoint (e.g. protection of 95% of species from harm, protection of 80% species from harm) might provide a more suitable basis. The current interim values used in the TFMS have largely been selected on the basis of protecting different endpoints. However, the methodologies and data used, as well as policy decisions (e.g. level of protection), will influence derived values, and the difference in the selected values may simply reflect these variations, as opposed to providing differing levels of protection.

The following sections describe approaches and methodologies for providing protection of different endpoints that could be used to develop New Zealand-specific trigger values for use in the TFMS. Where there is already a nationally agreed methodology (e.g. for soil contaminant standards used in the *National Environmental Standard for assessing and managing contaminants in soil to protect human health* (MfE 2011a), then only this method will be discussed. Where there is no agreed methodology (e.g. for the protection of ecological receptors), an overview of approaches used in New Zealand and internationally is provided. Where appropriate, the parameters influencing derived guideline values for Cd are discussed.

3.1 PROTECTION OF HUMAN HEALTH

Cadmium can cause kidney failure and has been statistically associated with an increased risk of cancer (via inhalation exposures) (US EPA 1992, 1994; WHO 2004; Nawrot et al. 2006; Julin et al. 2012). It is primarily toxic to the kidney, especially to the proximal tubular cells where it accumulates over time, eventually causing renal failure (WHO 2004; EFSA 2009; FAO/WHO 2010). Cadmium can also cause bone demineralisation, either through direct bone damage or indirectly as a result of renal dysfunction (WHO 2004; ATSDR 2008). Food is the dominant source of human exposure in the non-smoking population (WHO 1992; ATSDR 2008; EFSA 2009; FAO/WHO 2010).

Contaminants may be referred to as either threshold or non-threshold contaminants with regard to their effects on human health. Threshold contaminants are those considered to manifest toxic effects only if exposure exceeds a threshold dose level, and primarily include non-carcinogens. Non-threshold contaminants are carcinogens and are considered to have effects at all levels of exposure.

'Acceptable' intakes of threshold contaminants are termed Tolerable Intakes and are defined as an estimate of the amount of a contaminant—expressed on a body weight basis, e.g. mg/kg body weight (bw)—that can be ingested daily (weekly or monthly) over a lifetime without appreciable health risk (based on the available scientific information). 'Acceptable' intakes of non-threshold contaminants are based on intakes over a lifetime that leading to an acceptable increased likelihood of cancer. An 'Acceptable risk level' is used to define the acceptable increased risk, with an acceptable increased risk level of 1 in 100 000 used in New Zealand.

However, there are contaminants, including Cd, that may elicit both carcinogenic (typically non-threshold) and non-carcinogenic (typically threshold) effects. In this case the most sensitive toxicological endpoint is used to set the final value. Cadmium is typically treated as a threshold contaminant, with adverse effects on kidneys as a result of low level, long term exposure to Cd considered to be the critical health effect in humans (US EPA 1994; Jarup et al. 1998; WHO 2004; EFSA 2009; FAO/WHO 2010).

3.1.1 Tolerable intake values

Tolerable intakes for Cd have been determined to protect people from kidney damage arising from Cd accumulation over a lifetime, with different intake values determined by a number of agencies.

The provisional tolerable intakes established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) have been used in a regulatory setting in New Zealand. Most recently, JECFA withdrew the provisional tolerable weekly intake (PTWI) of Cd that had been established in 1988 and established a provisional tolerable monthly intake (PTMI) of 25 µg/kg bw (FAO/WHO 2010). This revision was driven by concerns about the small margin of safety between the PTWI and estimated dietary intakes (FAO/WHO 1993, 2000, 2004). A monthly intake was established because of the long half-life of cadmium and the small to negligible influence of daily ingestion on overall exposure.

The approach used by JECFA was similar to that used by the European Food Safety Authority's panel on contaminants in the food chain. The EFSA panel derived a tolerable weekly intake (TWI) of 2.5 μ g/kg bw per week (EFSA 2009), approximately half that of JECFA's monthly intake equivalent to 5.8 μ g/kg bw per week. Because of the difference between the EFSA and JECFA values, EFSA was asked by the European Commission to confirm whether the TWI established in 2009 was still considered appropriate (EFSA 2011). Based on review, EFSA found that:

Both assessments used the same epidemiological dataset and have two primary components, a concentration-effect model that relates the concentration of Cd in urine to that of beta-2-microglobulin (B2M), a biomarker of renal tubular effects, and a toxico-kinetic model that relates urinary Cd concentration to dietary Cd intake. The following methodological differences were identified: i) the identification of the reference point on the basis of the urinary Cd and the B2M concentration data; ii) the statistical approach to account for the variability and uncertainty of the biomarker of exposure (urinary Cd concentration) and the biomarker of response (B2M concentration) in the concentration-

effect model; and iii) the methodology for transforming urinary Cd concentrations into dietary intake values.

They further concluded that the current TWI of 2.5 µg/kg bw established in 2009:

...should be maintained in order to ensure a high level of protection of consumers, including subgroups of the population such as children, vegetarians or people living in highly contaminated areas.

Thus the intake values developed by EFSA and JECFA could be considered to represent a more and less conservative estimate of the tolerable intake of Cd respectively (Table 2). While the EFSA value is not used in a New Zealand regulatory setting per se, it forms the basis of some international soil guideline values that are used here (e.g. the allotment value specified in Environment Agency (2009) and used in the TFMS).

Table 2 Summary of tolerable intakes for cadmium developed by JECFA (FAO/WHO 2010) and EFSA (EFSA 2009).

JECFA (FAO/WHO 2010)	EFSA (EFSA 2010)
25 μg/kg bw/month (~5.8 μg/kg bw/week)	2.5 µg/kg bw/week

3.1.2 Total diet surveys

Dietary intake is the primary source of Cd in non-smokers (FAO/WHO 2010). Total diet surveys provide a means to assess the significance of this source of Cd intake in the New Zealand population, and are undertaken on a five-yearly basis. They estimate dietary exposure by analysing the most common retail foods in simulated diets for different sex- and age-groups (e.g. Vannoort & Thomson 2005, 2011). The foods are analysed in a 'normally consumed' state for a range of compounds, including Cd. Estimated dietary intakes are then compared to relevant tolerable intakes to assess risk—for Cd this intake is that established by JECFA.

The most recent total diet survey indicates that dietary intake of Cd is less than half the tolerable intake (Table 3) and that dietary intake is decreasing in the New Zealand population (Vannoort & Thomson 2011). Oysters can represent a significant dietary source of Cd, and, as noted in Vannoort and Thomson (2011),

Inclusion of oysters represents a worst case scenario because for most New Zealanders, oysters are likely to be a very minor or seasonal component of the diet, if consumed at all.

Potatoes and related products, and bread, were other significant contributors to dietary intake.

Table 3 Summary of dietary intakes* of cadmium for different age groups in the 2003/2004 and 2009/2010 Total Diet Surveys (Vannoort & Thomson 2005, 2011).

		<u> </u>			1				
Element	International standard	25+ yr males	25+ yr females	19-24 young males	11-14 yr boys	11-14 yr girls	5-6 yr children	1-3 yrs toddlers	6-12 month infants
2009/2010	25 µg/kg bw/month	6.8	5.5	6.9	7.7	6.5	11.5	10.9	9.0
% PTMI		27	22	27	31	26	46	44	36
2003/20041	7 µg/kg	2.1	1.5	1.8	1.7	1.4	2.6	2.6	2.1
	bw/week	2.1	1.5	1.0	1.7	1.4	2.0	2.0	Z. I
Monthly ²		9.1	6.5	7.8	7.4	6.1	11.3	11.3	9.1

^{*} Dietary intakes including oysters are shown; intakes excluding oysters are lower; ¹Weekly intakes as shown in Vannoort and Thomson (2005); ²Calculated monthly intakes for comparison with 2009/2010 results.

3.1.3 National Environmental Standard for assessing and managing contaminants in soil to protect human health

The Resource Management (National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health) Regulations 2011 (hereafter referred to as NES) came into effect on 1 January 2012. The NES includes soil contaminant standards (SCS_{health}) for Cd. Soil contaminant standards are contaminant concentrations in soil at or below which people's direct exposure to soil is judged to be acceptable because any adverse effects on human health are likely to be minor. They have two functions, acting as:

- health-based trigger values, to identify a human health risk threshold above which the
 effects on human health may be unacceptable over time or further assessment of a site is
 required to be undertaken, and
- remediation targets, where soil concentrations are greater than the SCS_{health}.

The methodology for the derivation of the soil contaminant standards is outlined in MfE (2011a) and an overview is provided here. Briefly, an SCS_{health} is the soil contaminant concentration that does not result in a specified intake (tolerable intake) of a contaminant being exceeded under a given exposure scenario and taking account of background exposure, e.g. diet. The basis for tolerable intakes (called Toxicological intake values in MfE 2011a, b) and background exposures used to derive the SCS_{health} for different contaminants are set out in MfE (2011b). Five generic land use scenarios are considered, which utilise standardised receptors and exposure parameters. A summary of the exposure scenarios, the routes of exposure relevant for those scenarios, and the $CdSCS_{health}$ for each scenario, is given in Table 4.

Different methodologies are used to develop SCS for non-threshold and threshold contaminants. SCS for non-threshold contaminants are derived to ensure that the potential for detrimental effects arising from contaminant intake does not exceed a risk of 1 in 100 000. They are based on exposures of children and adults (residential scenarios) or adults only (commercial scenarios) and averaged over a lifetime.

Table 4 Summary of land use scenarios and soil contaminant standards (SCS_{health}) for cadmium specified in the NES (MfE 2011a).

Landuse	Description	Exposure pathways considered	SCS _{health} (mg/kg)
			(pH 5)
Rural residential / lifestyle block	Lifestyle blocks and rural residence in the immediate vicinity of the farmhouse or farm staff houses; greater potential for a higher proportion of home-grown vegetables (e.g. compared to urban residents). 25% of produce consumed is assumed to be home grown.	Soil ingestion, dermal absorption, produce consumption	0.8
Residential	Separate houses with gardens, and potential to grow vegetables. 10% of produce consumed is assumed to be home grown.	Soil ingestion, dermal absorption, produce consumption	3
High density residential	The high density residential scenario has lower soil ingestion rates than standard residential, and does not include home-grown vegetable consumption.	Soil ingestion, dermal absorption	230
Recreation	Includes playing fields, residential reserves where children play, secondary school playing fields, public green areas, reserves and gardens used for passive recreation. Children's playgrounds and primary schools should be considered on a site-specific basis.	Soil ingestion, dermal absorption	400
Commercial / industrial outdoor worker	Based on an outdoor worker who carries out maintenance activities involving soil exposure to surface or near-surface soil through gardening and other landscaping activities, and occasional shallow excavation for routine underground service maintenance activities.	Soil ingestion, dermal absorption	1,300

For threshold contaminants, such as cadmium, the background exposure (e.g. dietary intake) is subtracted from the tolerable intake, and the residual intake is used to derive the SCS. Estimates of the dietary intake of various substances are primarily based on the 2003/04 New Zealand Total Diet Survey (NZTDS) (Vannoort & Thomson 2005) or national nutrition studies (copper only: Russell et al. 1999; MoH 2003). Mean dietary intakes are used and are considered to represent a long-term average. Where data from the NZTDS is used, dietary intakes are provided for a child 1–3 years old and the mean of an adult male and female aged 25+. Dietary intake from water is based on data provided in a survey of the chemical quality of drinking water supplies (Davies et al. 2001). For threshold contaminants, SCS_{health} is based on exposure of a child for all scenarios except commercial/outdoor industrial, for which SCS_{health} is based on an adult.

A key point to note is that the NES does not apply to production land unless it stops being production land (i.e. land use change); the exception being if soil near residential buildings or used for farmhouse gardens is disturbed, in which case the SCS_{health} for rural residential land use is applicable. However, consideration of the SCS_{health} in the NES is relevant for managing Cd in production land to ensure future land use flexibility.

Cadmium specific parameters

Cadmium is considered a threshold contaminant, and a provisional tolerable monthly intake (PTMI) of 25 μ g/kg body weight adopted by FAO/WHO (2010) is the 'acceptable intake' of Cd used to derive the SCS (MfE 2011b). The total dietary intake of Cd from food and water was estimated to be 12.5 μ g/kg bw per month for a child and 7.9 μ g/kg bw per month for a 70-kg adult (MfE 2011b).

Residential land use is the most sensitive land use (has the lowest SCS_{health}—see Table 4), and, as can be seen from Table 5, produce consumption is the primary route of exposure to Cd for residential scenarios when included (i.e. rural residential and residential but not high density residential). The Cd SCS is dependent on soil pH and has been developed for a soil pH of 5, which is at the lower end of pH range in New Zealand soils (MfE 2011a). Also provided in Table 5 are soil guideline values calculated for other soil pHs. These are available in MfE (2011a) and illustrate the effect of pH on derived values. Given the significance of the produce consumption pathway in determining SCS_{health} values, further discussion is provided below.

Table 5 Soil guideline values (mg/kg) for each exposure pathway, and final combined value, for soil pH of 5 (from MfE 2011a).

Scenario	Soil	Derm al	Produce consump	tion*	Combined SGV	SGV (mg/kg) (pH 5.5)	SGV (mg/kg)
			10% produc e	25% produc e		(рт 0.0)	(pH 6)
Rural residential/ lifestyle	115	75.5	-	0.83	0.8	1.4	2.3
Residential	115	75.5	3.12	-	3.0	5	7.9
High density	229	151	-	-	229	NA	NA

residential

^{*}Amount of home-grown produce consumed

Produce consumption exposure pathway

Four parameters are considered in the produce consumption pathway (MfE 2011a):

- amount of produce ingested
- the proportion of that which is home-grown
- the amount of Cd taken up by different produce
- soil loading on different produce types.

Vegetables are the primary produce considered, as contaminant uptake and translocation to fruit (in fruit trees) is considered to be negligible (MfE & MoH 1997; MfE 2011c) and fruit is not widely grown in residential gardens. The amount of produce consumed is based on the simulated dietary intakes (Brinsdon 2004) that are used in total diet surveys (e.g. Vannoort & Thomson 2005) and are converted to dry weight. There are limited New Zealand data on proportion of home-grown vegetables consumed and the values used for the different scenarios are a policy- rather than a science-based decision (MfE 2011a).

Plant uptake of contaminants differs between produce types, and for ease of quantitation, vegetables are classified as root, tuber and green vegetables. A detailed description of the method used to determine plant uptake of Cd is provided in MfE (2011a), where a review of the primary literature was undertaken and the relationships between plant uptake of Cd and soil concentrations were examined using regression analysis. Data collated included New Zealand data (although these data were limited), and only data from studies using field soil were used, i.e. studies where Cd was already present in the soils. Cd concentrations in plants and soil were expressed on a dry weight basis. Only studies that reported soil pH, soil Cd concentration and Cd concentrations in the edible portions of plants were used. The final regression equations were based on 188 data points from 21 studies, with 102 data points for green vegetables and 66 for root and tuber vegetables. The equations followed the form:

$$ln(plant \ Cd) = a + b \times ln(soil \ Cd) + c \times soil \ pH$$

with coefficient and constant values shown in Table 6.

Table 6 Coefficients determined for use in Equation (1), and the percentage of the variability in the data explained by them.

Vegetable type	In(plant Cd)				
	а	b	С	%var	
All data (n=168)	4.98	0.728	-0.764	58.0	
Green (n=101)	4.58	0.759	-0.626	68.1	

(Eqn 1)

Root/tuber				
(n=67)	4.73	0.600	-0.838	58.6

All explanatory variables were significant at p<0.001.

Occupational Exposure

Workplace exposure standards are another type of guideline value that aims to protect human health (Department of Labour 2011). These may be applicable to farmers or workers applying fertilisers, although would be unlikely to be applicable in the TFMS. The standards are:

- 0.01 mg/m³ as inhalable dust
- 0.002 mg/m³ as respirable dust.

Protection of ecological receptors

Protection of ecological receptors should ensure land productivity is protected and thus is highly relevant for inclusion in the TFMS. There is no agreed methodology for the development of soil guideline values for the protection of ecological receptors in New Zealand. The Ministry for the Environment has recently scoped the policy development required to extend the National Environmental Standard to the protection of the wider environment; however, the status of this work is unclear. Therefore, we provide an introduction to methods used to derive soil guideline values for the protection of ecological receptors, and an overview of the approaches used in New Zealand and internationally.

Three steps are typically used to derive soil guideline values for the protection of ecological receptors:

- 1. Collection and screening of the data.
- 2. Derivation of the soil guideline value—this is typically by using a form of statistical extrapolation if there are sufficient data, or an assessment factor approach if there are insufficient data.
- 3. Normalisation of the values to a 'standard' soil that has specified parameters (e.g. for pH, organic matter content, clay content) that are considered representative of the country developing the guideline values. This step is not always used.

There are three key groups of ecological receptors typically considered:

- microbial processes
- plants

• soil invertebrates (e.g. worms, springtails).

Higher animals may also be considered, with the primary concern being secondary poisoning arising from biomagnification, i.e. contaminant accumulation in a prey species (plant or invertebrate) through association with the soil, and consumption of that prey by a bird or other terrestrial fauna.

For microbial processes and species, different toxicity endpoints may be used. Most often the NOEC (no-observed effect concentration) or EC10 (effective concentration at which effects are observed in 10% of the test population) is used. Other endpoints may be used including the LOEC (lowest observed effect concentration), EC30 (effective concentration at which effects are observed in 30% of the test population), EC50 (effective concentration at which effects are observed in the 50% of the population) or LC50 (the concentration at which mortality is observed in 50% of the population). The endpoint chosen depends, in part, on what is reported in the literature; specifically, older literature typically reports NOEC or LOEC type data, whereas more recent literature tends to report the effect on a certain percentage of the test population (ECx). EC10 can be considered equivalent to a NOEC, while EC30 can be considered equivalent to a LOEC (Heemsbergen et al 2010). For non-lethal toxicity tests on plants and invertebrates, the effects typically considered include seed germination (plants only), growth (various measures are used for plants) and reproduction (invertebrates only).

Where sufficient data are available, statistical extrapolation is generally used and typically results in the generation of a species-sensitivity distribution (SSD) as shown in Figure 1. The SSD is a collation of toxicity data from tested species and is typically assumed to represent the distribution of sensitivity for all species present in the ecosystem being considered. The concentration that provides a certain level of protection can be determined from the SSD. Typically, a protection level of 95% is used, although other levels of protection—for example, 50% or 80%—may be used depending on the land use or purpose of the guideline value.

These levels of protection may sometimes instead be expressed as the hazardous concentration at which x% of species will be affected (HCx). Thus, an HC5 (the hazardous concentration at which effects are observed in 5% of species) protects 95% of species. The level of effect experienced by the population depends on the toxicity data used derive the curve. For example, for soil guideline values derived using NOEC or EC10 data, the potentially affected species would experience slight toxic effects, i.e. up to 10% of the affected species would experience significantly reduced growth compared to controls. For soil guideline values based on EC50 data the potentially affected species/processes would experience a greater level of effect, i.e. up to 50% of the affected species would experience significantly reduced growth compared to controls.

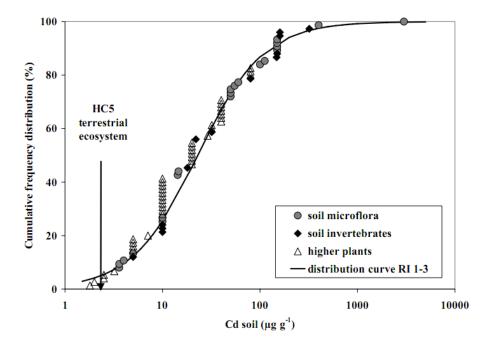


Figure 1 Species-sensitivity distribution curve. HC5 represents the hazardous concentration at which effects are observed in 5% of the tested species (EU 2007).

The level of protection ultimately conferred depends on the toxicity data used to generate the species-sensitivity distribution, as well as the level of protection selected. For example, selection of 95% protection level based on NOEC data will provide a greater level of protection than 95% protection level based on LOEC or EC50 data (typically NOEC or EC10 data are used). Similarly 95% protection level will provide greater protection than 80% protection level.

Three main approaches have been used for statistical extrapolation by different agencies:

- The Aldenberg and Slob (1993) method, which fits a log-logistic distribution to the data (used in some European Union Risk assessment reports, e.g. EU 2007).
- The Wagner and Løkke (1991) and Aldenberg and Jaworska (2000) methods which fit a log-normal distribution to the data (used by Dutch agencies, e.g. Lijzen et al. 2001).
- The Burr Type III method (Shao 2000) which fits the best of the Burr Type III family of distributions to the data and includes the log-logistic and log-normal fits. These are used in Australian and New Zealand water quality guidelines (see ANZECC/ARMCANZ 2001), and the proposed methodology for Australian Ecological Investigation Levels for soil (Heemsbergen et al. 2010).

Where sufficient data are not available, an assessment factor approach is used. This is simply the division of a toxicity value (typically the lowest) by an assessment factor, the value of which depends on the type and amount of data available. The assessment factor can range from 2 to 500, where a low value represents greater confidence that the available data will be

protective of the wider environment while a high value indicates less confidence that the available data will be protective of the wider environment.

A summary of the soil guideline values developed for the protection of ecological receptors for Cd in New Zealand and internationally is shown in Table 7, with a description of the approaches used to derive these values provided in the following sections.

Table 7 Cadmium soil guideline values developed for the protection of ecological receptors in New Zealand and internationally.

Country	Value name	Cadmium	Source
		(mg/kg)	
NZ	Soil limit ¹	1	NZWWA 2003
	Minimal risk	1	Cavanagh 2006
	Serious risk	12	
	Minimal risk, microbial	6	
	Serious risk, microbial	86	
Australia	EIL	3	NEPC 1999a
Canada	SQG _e – agricultural ²	3.8	CCME 1999
	SQG _e – residential	10	
	Commercial/ industrial	22	
European Union	PNEC soil	1.15-2.3	EU 2007
	Cd soil,crit	0.9	
USA	Eco-SSL – plants	32	US EPA 2005
	Invertebrates	140	
	Birds	0.77	
	Mammals	0.36	
UK	Soil screening values	1.5-2.3	Environment Agency 2008
The Netherlands	SRC _{eco}	13	Lijzen et al. 2001
	IV	13	VROM 2009

 $EIL-ecological\ investigation\ level;\ SQG_e-soil\ quality\ guideline\ environmental;\ Eco-SSL-ecological\ soil\ screening\ level;\ SRC_{eco}-serious\ risk\ concentration\ ecotox;\ IV-intervention\ value;\ PNEC-Predicted\ no\ effect\ concentration.$

New Zealand

Biosolid guidelines

Soil metal limits contained in the biosolids guidelines (NZWWA 2003) are primarily set on the basis of the lowest-observable concentrations from a literature survey of the available data. The soil limit for Cd was set at 1 mg/kg,

 $^{^{1}}$ Allowable limits in soil to which biosolids have been applied; 2 A value of 1.4 mg/kg was the final combined human health and environmental SQC adopted for agricultural land use.

....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)

and noting that it was important that the limits for Cd were not substantially higher than that of the European Community. This comment was made in relation to the most recent European Community draft directive for biosolids at the time (EC 2000) proposing Cd levels for agricultural soils of between 0.5 and 1.5 mg/kg depending on soil pH (Table 8). These limits are proposed values in the current draft directive (EC 2010), and are noted as being:

...intrinsically precautionary values for the protection of long-term soil quality having a regard to background concentrations in European agricultural soils.

The European Community-proposed Cd limits are based on pH measured using CaCl₂, which is approximately 0.6-0.8 units lower than pH (H₂0), which is primarily used in New Zealand.

Table 8 Proposed limits for Cd in agricultural soil, from EC (2010).

	5≤pH(CaCl₂)<6	6≤pH(CaCl₂)<7	pH(CaCl₂)≥7
Cd	0.5	1	1.5

No review of the Biosolids Guidelines has taken place even though a 5-yearly review (2008) was called for in the Guidelines. However, there are current discussions on updating the New Zealand Biosolids Guidelines, including contaminant limits, and it may also be relevant to consider a common methodology for deriving limits for contaminants in biosolids and Cd in production land.

Auckland Regional Council

In 2006, the Auckland Regional Council contracted Landcare Research to develop soil guideline values protective of on-site and off-site ecological receptors for a range of contaminants, including Cd, to assist in the management of contaminated land.

A detailed description of the approach used is provided in Appendix A. Briefly, soil guideline values were derived by:

- Compilation of toxicity data for soil invertebrates, plants and microbial processes. Data were obtained primarily from international regulatory sources and review articles (no New Zealand data were available).
- Using the statistical extrapolation approach of Aldenberg and Jaworska (2000) where sufficient data were available, or assessment factors.

• No-observable-effects-concentration data (NOEC) was used as the toxicity endpoint to determine soil guideline values.

'Minimal risk' and 'serious risk' guideline values were derived based on protection of soil invertebrates and plants, and a check undertaken to establish whether any effects on microbial processes would occur at the specified concentrations. Minimal and serious risk values were aimed at nominal protection levels of 95% and 50%, respectively, where these denote the percentage of species in an ecosystem protected from detrimental effects. The derived values were also compared to background soil concentrations determined for the Auckland region (Auckland Regional Council 2001). These guideline values were considered most applicable to urban land uses where a functioning ecosystem is desirable (e.g. residential or parkland).

For Cd, sufficient data were available for invertebrate species, plant species, and microbial processes, so it was possible to use statistical extrapolation to derive guideline values. Available data points numbered 233, yielding 14 NOECs from six different invertebrate orders, and also 14 NOECs from plants. The 96 data points from 14 different microbial processes were used to derive proposed minimal risk and serious risk soil guideline values of 6 mg/kg and 86 mg/kg, respectively (Table 9). These values are higher than those derived for protection of species, hence protection of onsite soil organisms will also provide protection of microbial processes.

Table 9 Proposed Auckland Regional Council soil criteria for protection of on-site ecological receptors, from Cavanagh and O'Halloran (2006).

Contaminant	Derive	d value	Background range ¹		Prop	osed criteria
	MRGV ²	SRGV ³	Non-volcanic	Volcanic	$MRGV^2$	SRGV ³
Cadmium	1	12	<0.1-0.65		1	12

¹Auckland Regional Council (2001) ² Minimal risk guideline value ³ Serious risk guideline value

Australia

Guidance on conducting ecological risk assessments is contained within the National Environmental Protection Measure (NEPM) and contains generic principles to be followed in determining ecological risk (NEPC 1999b). Existing interim ecological investigation levels have been collated from ANZECC B-levels (ANZECC/NHMRC 1992) and soil survey data from four Australian cities (NEPC 1999a). The ANZECC B-levels used as interim *ecological investigation levels* (EIL) originate from Environment Canada (1988, cited in ANZECC/NHMRC 1992) and Richardson (1985, cited in ANZECC/NHMRC 1992). The interim EIL for Cd is 3 mg/kg.

Proposed methodology

In 2010, CSIRO proposed a methodology for deriving ecological investigation limits (Heemsbergen et al. 2009). This methodology has been accepted as the Australian national methodology for the development of EILs although the official methodology is yet to be released (pers. comm. Michael Warne, Department of Environmental Resources (DERM), Queensland).

In the proposed approach different land uses are considered and, with the exception of agriculture, the following ecological receptors will be protected:

• biota supporting ecological processes, including micro-organisms and soil invertebrates

- native flora and fauna
- introduced flora and fauna
- wildlife, i.e. secondary poisoning in birds and small rodents

pets

For agricultural land, only agricultural species are proposed for inclusion amongst the plant data and a high level of protection is provided for crop and grass species. Soil processes and soil invertebrates are considered highly important to ensure nutrient cycling to sustain crop species.

The level of protection of the ecological receptors varies depending on the land use and whether the contaminant in question biomagnifies. If a contaminant biomagnifies (as Cd does) a higher level of protection should be provided, although it is only considered when the surface area of land exceeds a minimum value.

Table 9 Percentage of species and soil processes to be protected for different land uses (Heemsbergen et al. 2009).

Land use	Standard % protecti on	Biomagnification protection ^a %
Urban residenti al	80	85 ^b
Public open space	80	85 ^b
Commercial	60	65°
Industrial	60	65°
Agricultural	95 ^d and 80 ^e	98 ^{c,e} and 85 ^{c,e}
National Parks	99	99

^aif a contaminant meets criteria for biomagnification, ^bif surface area exceeds 250 m²; ^cif surface area exceeds 1000 m², ^dagricultural crops, ^efor soil processes and terrestrial fauna.

Of most relevance to the current work is the agricultural land scenario. For this land use a high level of protection is provided for crop and grass species (95%). Tillage and the use of pesticides/herbicides make it unrealistic to protect 95% of soil processes and soil invertebrates and therefore only 80% of these are nominally protected.

The main steps in the methodology outlined in Heemsbergen et al. (2009) are:

- 1. collating and screening the data
- 2. standardising the toxicity data
- 3. incorporating an ageing/leaching factor for aged contaminants
- 4. calculating the added contaminant limit (ACL) by either the species sensitivity distribution (SSD) or assessment factor (AF) approach, depending on the toxicity data

- 5. normalising the toxicity data to an Australian reference soil (only done if the SSD approach is used to calculate the ACL)
- 6. accounting for secondary poisoning for those contaminants that are considered to biomagnify in the food web
- 7. calculating the ambient background concentration (ABC) of the contaminant in the soil
- 8. calculating the EIL by summing the ACL and ABC values

$$EIL = ABC + ACL (Eqn 2)$$

A key point to note in step 4 is that an 'added contaminant limit' is proposed to be developed, which is then added to background concentrations determined for the given contaminant (step 7) to derive EILs (step 8). The SSD method proposed to derive EILs (Burr Type III method) is the same as that used to derive the Australian and New Zealand water quality guidelines (ANZECC/ARMCANZ 2000) and is incorporated into the BurrliOZ programme (available from: http://www.cmis.csiro.au/Envir/burrlioz/Download1.htm). The rationale for using this method is that the Burr Type III has a family of distributions that enable a better fit of the data than do single distributions used by other methods. This method is guaranteed to fit a statistical distribution to the toxicity data at least as well as the Aldenberg and Slob method because the log-logistic distribution is a BT III distribution (Heemsbergen et al. 2009).

Canada

Federally-produced soil criteria in Canada are used as remediation goals, i.e. 'clean-down to' levels, not 'pollute up to' levels. These numeric values are based on comparison of calculated soil contaminant concentrations protective of human health to those calculated for protection of ecological receptors for designated land uses, and selection of the most protective as the final numeric value. For the different land uses, different ecological receptors are used. For agricultural land the main pathways considered are soil contact and ingestion (of soil, and food for grazing livestock and wildlife). Soil contact includes both microbial processes and toxicity to soil organisms. For residential, commercial and industrial land only the soil contact pathway is considered.

Details on the derivation methodology are provided in Appendix A. Briefly, where sufficient data are available, environmental soil quality criteria are derived using an adaptation of Long and Morgan's (1990, cited in CCME 1996) 'weight-of-evidence' approach. In this approach, at least 10 data points (which can include NOEC, LOEC, EC₅₀ and LC₅₀ values) from three studies are used to create a frequency distribution from which the 25th percentile is used to define the *no-potential-effects range* (NPER). Uncertainty factors (1–5) are applied to the calculated 25th percentile value depending on data availability.

Where insufficient data are available, uncertainty factors are applied to the lowest toxicity value available data.

For agricultural and residential/parkland land uses, NOEC data are used to calculate the soil quality criteria for soil contact, using the weight-of-evidence approach. For commercial and industrial land uses effect data only (e.g. LOEC, EC50) are used to calculate the soil quality criteria for soil contact. This is referred to as the effects concentration low (ECL) (CCME 1996).

Where soil quality criteria for microbial processes are lower than those for protection of soil organisms, the geometric mean of the two values is adopted. Otherwise the value for

protection of soil organisms is adopted. Where the derived SGV is lower than the acceptable geological background concentration, that concentration becomes the final SGV.

Cadmium soil guideline values

Derivation of the environmental soil guideline values for Cd is given in Environment Canada (1999). The soil quality guideline for soil contact (SQGsc) is based on toxicological data for vascular plants and soil invertebrates using the weight-of-evidence approach. Of the total 124 data points, the 25th percentile (no-potential-effects range) corresponds to 20 mg/kg, which corresponds to the concentration of Cd that resulted in reduction of dry weight of red oak. Due to the potential for Cd to bioaccumulate, an uncertainty factor of 2 was applied, and the threshold effects concentration was determined to be 10 mg/kg. This value was lower than that calculated for microbial processes of 54 mg/kg, which was calculated from the geometric mean of available LOECs. As such, an SQGsc of 10 mg/kg is used as the environmental soil quality criterion for residential/parkland land use.

For agricultural land, the soil contact value is compared to a soil quality guideline based on exposure via soil and food ingestion (SQGi). The SQGi was determined to be 3.8 mg/kg, which is lower than the SGQsc, so the environmental soil quality criterion for agricultural land is 3.8 mg/kg. A final SQG of 1.4 mg/kg was adopted for agricultural land, based on application of a 10-fold safety factor the residential SQGHH, because of higher plant uptake of Cd at low pH.

European Commission

The European Commission Technical Guidance Document on risk assessment (EC 2003) was developed to support European Commission directives regarding the risk assessment of new and existing substances. Part of this guidance relates to the derivation of predicted effect concentrations (PEC) and predicted no-effect concentrations (PNEC) for the terrestrial, aquatic and marine environments. The predicted effects concentration is the concentration of a substance that will occur in the environment as a result of release or use of a substance; essentially this provides the exposure concentration. The PNEC is regarded as a concentration below which unacceptable effects will most likely not occur.

For distribution-based extrapolations the level of protection is at the 95th percentile level. The PNEC can be derived in three ways:

- Where sufficient data are available, statistical extrapolation methods can be used. No minimum amount of data is specified for soil criteria although these data requirements are likely to be similar to those required for aquatic organisms: at least 10 NOECs for different species from at least eight taxonomic groups.
- When toxicity data are available for a plant, an invertebrate, and/or micro-organisms, the PNEC is determined using assessment factors.
- When only one test result for soil organisms is available, screening values derived using assessment factors are compared with those derived using equilibrium-partitioning methods, with the lowest PNEC selected.

No particular approach to statistical extrapolation is recommended in EC (2003).

Cadmium values

The derivation of a PNEC for Cd is described in EU (2007). NOEC data was used to derive a PNEC, using the statistical extrapolation of Aldenberg and Slob (1993). The HC5 for microbial processes (2.3 mg/kg) was slightly lower than the HC5 for species (plants and invertebrates) of 2.5 mg/kg (see Figure 2). An additional assessment factor of 1 or 2 can be applied, resulting in a final PNEC for soil of 1.5-2.3 mg/kg.

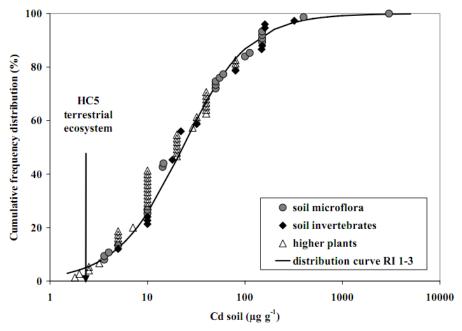


Figure 2 Species sensitivity distribution for cadmium in EU (2007).

Secondary poisoning was also considered for Cd as it is considered to biomagnify. Food chain approaches were evaluated but were considered too unreliable, and an alternative approach was adopted. This approach was based on kidney Cd concentrations in wildlife as an indicator of exposure and risk. A critical kidney Cd threshold of 400 mg/kg was used and statistical extrapolation determined that the HC5 for protecting mammals was 0.9 mg/kg. Thus, the final recommended PNEC for soil was 0.9 mg/kg.

United Kingdom

The approach to undertaking ecological risk assessment in the UK is outlined in Environment Agency (2008). This provides a comprehensive overview of the whole process, the first step of which is comparison of a PNEC with the predicted exposure concentration. The PNEC values used in the UK are those determined in the EU (EU (2007), discussed in previous section). In this case the adopted value was 1.5 mg/kg, with the note that 0.9 mg/kg could be included where secondary poisoning is suspected (Environment Agency 2008).

The Netherlands

The Netherlands has several tiers of SGVs. Intervention values (IV) indicate soil contaminant concentrations at which the urgency of remediation is required to be assessed. These values are determined by comparing serious risk concentrations determined from ecotoxicological data (SRC_{eco}) with those determined for human exposure (SRC_{human}) and selecting the lowest value as the intervention value. SRC_{eco} is defined as the concentration at which 50% of tested species or processes in an ecosystem experience adverse effects. SRC_{human} is based on the human-toxicological

maximum permissible risk (MPR) level, using back-calculation to determine the concentration at which the MPR is reached. The maximum permissible concentration (MPC) is the concentration at which 95% of species are protected and is based on ecotoxicological data. When MPCs have been calculated for each environmental compartment, a harmonisation procedure is used to adjust the MPC values (if required), which ensures that transfer of contaminants from one medium to another does not exceed the MPC in that medium (de Bruijn et al. 1999). Background concentrations of contaminants that also occur naturally (e.g. selected metals and metalloids) are taken into consideration using an added-risk approach (Crommentuijn et al. 1997). Further details on the Dutch methodology are provided in Appendix A.

Soil guideline values for cadmium

The added-risk approach is used to derive the MPC. In this case the available toxicity data are used to calculate the maximum permissible addition (MPA). The refined risk assessment approach was used to derive the MPA for species and processes (microbial and enzymatic). This gave rise to MPAs of 0.79 mg/kg for species and 15 mg/kg for processes. The lower of these is selected for the final MPA (0.79 mg/kg).

The background concentration of Cd in the Netherlands is considered to be 0.8 mg/kg (de Brujin et al. 1999), and the final MPC is 1.6 mg/kg, which is the sum of the background concentration and the MPC. The Negligible Concentration (NC) is 0.01 mg/kg, which gives rise to a target value equivalent to the background concentration of 0.8 mg/kg.

The SRC_{eco} of 12 mg/kg was cited by Lijzen et al. (2001) as being that derived by Swartjes (1999). However, no detailed information on the derivation of this value was found in Swartjes (1999). Verbruggen et al. (2001) used statistical extrapolation methods to derive an HC_{50} for species of 12 mg/kg, and an HC_{50} for microbial processes of 120 mg/kg. The lower of these (12 mg/kg) was selected as the SRA_{eco}, to derive an SRC_{eco} of 13 mg/kg, which is the sum of the background concentration of 0.8 mg/kg and the SRA_{eco}.

United States

Ecological soil screening levels (Eco-SSLs) are concentrations of contaminants in soil that are protective of ecological receptors that come into contact with soil. They are being developed for four receptor groups: plants, soil invertebrates, birds and mammals.

To derive Eco-SSLs, the available literature is first screened using various criteria to identify acceptable studies. Studies that pass all these criteria are then scored according to nine technical 'evaluation criteria' and the data from these studies are then grouped by toxicological endpoints and bioavailability score, and assigned a preference level from A to D, with level A being the highest. The bioavailability score is based on the qualitative assessment of bioavailability of the contaminant tested, with a value of two being assigned to studies conducted under conditions of high bioavailability. The toxicity endpoints used are either the concentrations at which effects are observed on 20% (EC20) or 10% (EC10) of the test population, or the maximum acceptable toxicant concentration (MATC). The MATC is typically defined as the geometric mean of the NOEC and LOEC.

The Eco-SSL is derived from the geometric mean of the toxicity values rated at the highest preference level for which there are sufficient data points. A minimum of three data points are required, with values taken from the next preference level down if

insufficient data are available at the highest preference level. No information is provided to indicate whether data from a minimum number of taxa were required.

Cadmium

Eco-SSLs of 32 mg/kg for plants, 140 mg/kg for soil invertebrates, 0.77 mg/kg for protection of avian wildlife, and 0.36 mg/kg for protection of mammalian wildlife have been derived (US EPA 2005). The Eco-SSL for plants is the geometric mean of the MATC values for 14 test species under different test conditions (pH and % organic matter). The Eco-SSL for soil invertebrates is the geometric mean of the MATC or EC10 values for three test species under six different test conditions (pH) from 10 studies. Eco-SSLs for birds and mammals are based on estimates of contaminants consumed by three trophic levels: insectivore, herbivore and carnivore. The final Eco-SSLs for birds and mammals were based on insectivores, with much higher values being determined for herbivores and carnivores.

Food safety standards and trade

Protection of food standards is another endpoint that could be used to develop New Zealand-specific SGVs for use in the TFMS. Food standards are typically expressed as Maximum Limits (ML) and represent the amount of a substance that is legally permitted to be present in that food. Maximum Limits for contaminants (including Cd) have been established by a number of sources, including Food Standards Australia and New Zealand (FSANZ), Codex, and the European Commission (Table 10).

In general MLs should be set only for those contaminants that present both a significant risk to public health and a known or expected problem in international trade, and for a food that is significant for the total exposure of the consumer to the contaminant (Codex 2010). Further, MLs are set **as low as reasonably achievable** and at levels necessary to protect the consumer.

This means that the ML may be lower than the level necessary to protect the consumer (i.e. human health), and in this context exceedance of the ML poses a trade, rather than a health, risk depending on the level of exceedance and the frequency of that event. Further, the MLs set in different jurisdictions reflect the difference between unavoidable environmental exposure and the tolerable exposure (the higher the background, the lower the MLs tend to be). This may explain some of the variation observed in MLs set in New Zealand and Australia and Europe (Table 10).

The Australian National Biosolids Research Program (NBRP) in Australia examined the uptake of Cd into wheat. This programme found that the soil concentration that causes Cd wheat grain concentrations to equal or exceed the Australian and New Zealand Cd food standard for wheat of 0.1 mg/kg (FSANZ 2011) varied as a function of soil pH and clay content (Warne 2011):

Using this equation resulted in suggested maximum permitted total Cd concentrations in soils receiving biosolids ranging from 0.3 mg/kg at pH 4.5 and 5% clay content, to 2.3 mg/kg at pH 7.5 and 50% clay content, to ensure wheat grain did not exceed the FSANZ limit (Warne 2011).

Cadmium accumulates in the liver, and particularly the kidneys, of livestock. Thus offal sold for food consumption may exceed Cd food standards if livestock have a high Cd intake. There are few examples of determining soil guideline values for food safety protection for kidneys and livers although using a food chain model, Rodrigues et al. (2012) found that protection of food safety standards in cow kidneys resulted in the lowest soil Cd concentrations (Table 11).

 Table 10
 Summary of cadmium maximum levels (MLs) set by various agencies for different foods.

FSANZ* Standard 1.4.1	ML (mg/kg)	CODEX Standard (193- 1995)	ML (mg/kg)	European Commission (Regulation 1661/2006)	ML (mg/kg
Leafy vegetables	0.1	Leafy vegetables	0.2	Leafy vegetables	0.2
Root and tuber	0.1	Potato (peeled)	0.1	Stem vegetables, root vegetables and potatoes,	0.1
vegetables		Root and tuber vegetables	0.1	excluding celeriac. For potatoes applies to peeled potatoes	
		Stalk and stem vegetables	0.1		
		Brassica vegetables	0.05	Vegetables and fruits (excluding leafy vegetables,	0.05
		Bulb vegetables	0.05	fresh herbs, all fungi, stem vegetables, root vegetables and potatoes)	
		Fruiting vegetables, cucurbits	0.05		
		Fruiting vegetables, other than cucurbits	0.05		
		Legume vegetables	0.1		
Rice	0.1	Rice	0.4		
Wheat	0.1	Wheat	0.2	Bran, germ, wheat grain and rice	0.2
		Cereal grains, except buckwheat, cañihua and quinoa	0.1		
Peanuts	0.5	Pulses	0.1	Soybeans	0.2
Meat of cattle, sheep	0.05			Meat of bovine animals, sheep, pig and poultry	0.05
and pig (excluding offal)				Horsemeat	0.2
Liver of cattle, sheep and pig	1.25			Liver of cattle, sheep, pig and poultry	0.5

Kidney of cattle,	2.5		Kidney of cattle, sheep, pig and poultry	1
sheep and pig				

^{*}Food Standards of Australia and New Zealand

Table 11 Soil cadmium threshold concentrations determined for the protection food or feed standards (Rodrigues et al. 2012).

Item	Soil threshold concentration (mg/kg)		
	рН 5	рН 6	
Green fodder	3.1	4.8	
Food safety (cow kidney)	0.7	1.0	
Food safety (cow liver)	2.4	3.6	
Animal health (cow kidney)	4.9	7.1	

Protection of groundwater

Protection of groundwater is another endpoint that may be relevant to consider for Cd management. Soil guideline values for the protection of groundwater are derived by back-calculation from desired groundwater quality, taking into account processes of leaching to groundwater and subsequent mixing. New Zealand (Petroleum hydrocarbons, MfE 2011c), Canada (CCME 1996, 2006) and the USA (US EPA 1996) are the only countries that have developed generic soil guideline values for the protection of groundwater. Further details are provided in Appendix B and in Cavanagh (2006). Briefly, derivation of soil guideline values by each agency is based on the conceptual models shown in Figure 3. The presence of an uncontaminated zone is the primary difference between the approach used in New Zealand guidance, versus that used in Canada and the USA. A number of different soil and groundwater parameters are required to develop SGVs protective of groundwater.

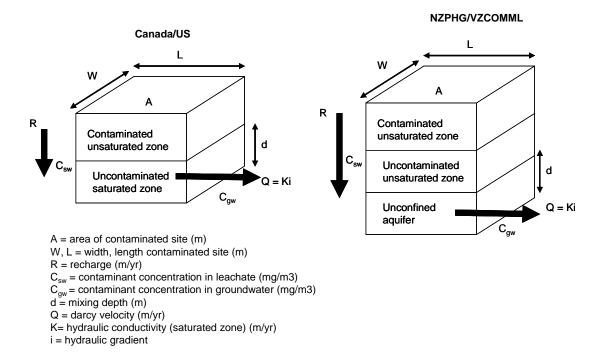


Figure 3 Conceptual models used by Canadian (CCME 1996) and US (US EPA 1996) regulatory authorities, and that used in the NZPHG (MfE 2011c).

Cavanagh (2006) concluded that a simple model to develop generic soil guideline values for the protection of groundwater would likely give rise to overly conservative soil guideline values (i.e. below background) for certain metals using any generic approach and that the likelihood of groundwater contamination should be considered on a site-specific basis. This was because metal-partitioning is highly site-specific and it is difficult to obtain appropriate partitioning coefficients.

While Cd was not included in the study, derivation of a generic Cd SGV for the protection of groundwater will also be difficult as a wide range of estimated partitioning coefficients currently exist for different soil pHs (Table 12). Gray et al. (1999a) and Gray and McLaren (2005) developed equations relating soil properties (pH, organic carbon, total soil Cd) to soluble Cd in New Zealand soils, which could be helpful in developing guidelines for the protection of groundwater. However, further research is needed.

 Table 12
 Partitioning coefficients of Cadmium at different soil pH (US EPA 1996).

Contaminant	Kd (L/kg)			
	pH 4.9	pH 6.8	pH 8	
Cadmium	15	75	4300	

4 Sensitivity of different endpoints and information required to develop NZ specific soil guideline values

The previous sections have outlined the range of endpoints that could be used to determine New Zealand-specific soil guideline values for Cd. For the TFMS, a set of increasing soil Cd concentrations are required to trigger different management options. This could be achieved using soil guideline values determined using the same endpoint, but different levels of protection, e.g. protection of 95% of species and 80% of species, or it could be achieved by using endpoints that have a different sensitivity. A further consideration is the relevance of certain endpoints in the context of applying the TFMS, i.e. whether soil guideline values that are likely to be highly site-specific are useful in the context of the TFMS, or whether it is more appropriate to use more broadly applicable endpoints.

As an indicator of the potential relative sensitivity of the different endpoints, a summary of the soil guideline values derived for the protection of various endpoints discussed in the previous section is shown in Table 13 and discussed in further detail below. However, for the most part, which endpoints are actually the most sensitive and relevant cannot be determined until some further research is undertaken (a summary of relevant research undertaken in New Zealand to date is provided in Appendix C). The following discussion highlights the relative sensitivity of the different endpoints, based on the available information, and the information required to develop New Zealand-specific soil guideline values.

 Table 13
 Collation of soil guideline values derived for all endpoints.

Endpoint	Range of values for derived soil guideline values (SGV)	Source
Human health	0.8 mg/kg (rural residenti al) (pH 5) 3 mg/kg (residenti al)	MfE (2011a)
Ecological receptors Microbial processes Soil species Secondar	1.5–86 mg/kg 1–140 mg/kg 0.6–0.9 mg/kg	Various (see Table 7)

poisoning		
Food safety	0.2-2.3 mg/kg (pH 4.5-7.5, wheat)	Warne 2011 Rodrigues 2012
	0.7-1.0 mg/kg (pH 5– pH6, offal (kidney))	
Groundwater	unknown	

Protection of human health

In the context of the TFMS, protection of human health is relevant to the extent that land may potentially be subdivided and used for residential purposes in the future. A National Environmental Standard has been established, with soil contaminant standards (SCS_{health}) for Cd developed. As such, in order to maintain flexibility of land use, soil Cd concentrations would need to comply with the relevant standards. As these standards have already been developed, there is no research required per se. However, it is noted that produce consumption is the most sensitive pathway for rural residential and residential land uses, and that limited New Zealand data were used to develop soil-plant uptake relationships. As such, further research on plant uptake under New Zealand conditions to refine this pathway would be beneficial—this information would also be applicable to developing soil guideline values for the protection of food safety standards (section 4.3).

Protection of ecological receptors

As highlighted in Table 13, a wide range of soil guideline values are available for the protection of ecological receptors. The key factors influencing the derived values for microbial processes and plant and soil invertebrate species are largely methodological and include:

- data used (including the influence of screening processes)
- derivation method (including general approach to derivation, choice of statistical extrapolation method)
- choice of protection level (e.g. 80% of species, 95% of species).

Thus, an agreed methodology needs to be developed first in order to determine the relative sensitivity of ecological receptors compared to other endpoints in a New Zealand context. Based on a review of the methodologies (section 3.2), and

consideration of the general trend towards harmonisation of Australian and New Zealand approaches (e.g ANZECC/ARMCANZ 2001; Biosolids review) it is recommended the proposed Australian methodology for deriving ecological investigation levels as it applies to agricultural land (Heemsbergen et al. 2009, outlined in section 3.2.2) is adopted (a summary of the methodology is provided in Appendix D, with further details in Heemsbergen et al. 2009). However, the relevance of the biomagnification pathway, and the nature of that pathway (e.g. what animals should be considered, how important is the pathway) in a New Zealand context needs further consideration. Consensus from the Cadmium Management Group on this approach is required.

While there is a reasonable amount of data on the toxicity of Cd to microbes, plants and invertebrates internationally, no New Zealand data on the toxicity to these groups of organisms in New Zealand soils were found (see Appendix C). Generation of such data is necessary to ensure greater relevance of derived values to New Zealand.

Protection of food safety standards

In addition to the SGVs shown in Table 13, the plant uptake equations developed for the NES (section 3.1) can be used to indicate soil Cd concentrations which might lead to exceedance of a food standard for produce of 0.1 mg/kg. Table 14 shows the estimated Cd concentrations in spinach and potatoes at a range of soil Cd concentrations at pH 5.5, assuming dry weight of 7.3% for spinach and 21% for potatoes. These calculations suggested exceedance of the food standards might not arise until soil Cd concentrations reach 1.5 mg/kg. However, only limited data from New Zealand were used to derive these relationships. Data presented by Warne (2011) indicates that exceedance of food standards may occur at lower soil Cd concentrations. Previous data collected in New Zealand also indicate some wheat cultivars exceed food standards at low soil Cd concentrations (Gray et al. 2001), highlighting the importance of having New Zealand data.

Table 14 Estimated plant cadmium concentrations at different soil cadmium concentrations using the plant uptake relationship determined in the National Environmental Standard for assessing and managing contaminants in soil.

	Soil concentration (mg/kg) (pH 5.5)				
Produce	0.46 ^a	1	1.5	2	
	Plant concentration (mg/kg) (wet)				
Spinach	0.04	0.083	0.11	0.12	
Potatoes	-	0.025	0.076	0.11	

^aMean concentration in cropping areas (CWG 2008)

It seems logical that exceedance of food standards occurs before toxicity effects are observed, thus protection of food safety standards for produce should be a more sensitive endpoint than toxicity—for plants anyway. Plant species and cultivar will also have a significant influence on plant uptake, thus plant uptake relationships should be determined for the most relevant species and cultivars, using factors such as sensitivity to Cd uptake, or area used for growing.

Exceedance of food standards in offal is a challenging area to examine as there are a number of factors that will influence uptake. For example, Loganathan et al. (1999) found Cd concentrations in fertiliser to be the most significant factor influencing Cd accumulation in kidney and livers. More recent studies found soil Cd concentrations (as a source of Cd in feed) is an important component (Phillips & Tudoreanu 2011; Rodrigues et al. 2012). Soil ingestion is typically not found to be a significant factor influencing Cd accumulation. A meta-analysis of sheep feeding trials (Prankel et al. 2011) found that the product of the Cd concentration in the feed and the duration of exposure to that feed were significant predictors of the Cd concentration in livers and kidneys, and that the predominantly organic rather than inorganic form of Cd in the feed further increased accumulation. Other variables (dry matter intake, the vehicle of the elevated Cd in the diet, animal age, weight, and sex) were not significant. Food chain models have typically been used to describe Cd accumulation, and seem to indicate that low soil Cd concentrations are needed to ensure that food safety standards in offal are not exceeded. Further research is required to develop robust relationships for New Zealand systems.

Protection of groundwater

Few studies of Cd leaching have been conducted in New Zealand, particularly across the wide range of soil types under intensive land use, thus it is difficult to judge the relative sensitivity of this endpoint. Research undertaken to date shows that what little Cd leached would, at least in the short term, pose little risk to groundwater concentrations (Gray et al. 2003a; McLaren et al. 2004; McLaren et al. 2005). Gray et al. (2003a) provides one of the more comprehensive attempts to understand Cd leaching. They found a wide range in Cd leached, spanning 0.27 to 0.86 g/ha per year, although with no statistical relationships between the amounts of Cd leached and major soil attributes. However, 51% of the variation in Cd leaching was explained by a regression model with drainage volume and leachate pH parameters. Other studies have shown that total soil Cd concentrations, soil pH and organic matter all influence soluble Cd concentrations (e.g. Gray et al. 1999a; Gray & McLaren 2006).

There appears to be a higher risk of leaching in certain soils, for example high mobility of Cd has been observed in sandy soils (Mann & Ritchie 1995; McLaughlin et al. 1996), and very acidic soils with low organic matter (Zanders et al. 1999). However, no New Zealand studies were found that investigated Cd loss through soils most susceptible to preferential flow. Similarly there are no reported data on Cd dynamics across the range of stony soils which are now being intensively developed and managed with irrigation and high P fertiliser application rates.

Further research on Cd leaching in New Zealand soils is required to better understand the risk of leaching to groundwater, in particular for soils that may be considered the most susceptible (e.g. stony soils). It seems likely that it will be highly soil-specific, and in this regard, it is probably not a useful endpoint to consider in the development of soil guideline values for use in the TFMS.



5 Summary and conclusions

A set of increasing soil Cd concentrations is required to trigger different management options in the Tiered Fertiliser Management System. This could be achieved using soil guideline values determined using the same endpoint, but different levels of protection, e.g. protection of 95% of species and 80% of species, or it could be achieved by using endpoints that have a different sensitivity. Four key endpoints were considered:

- protection of human health
- protection of ecological receptors
- protection of food standards
- protection of groundwater.

Of these, protection of food standards and ecological receptors are the most relevant to agricultural land although there are limited data available to develop New Zealand-specific values. Research is required to better understand the pathway of Cd accumulation in animal agricultural systems in New Zealand and to establish the relationship between plant uptake and species, cultivar, and soil properties. This would enable the development of New Zealand-specific SGVs and determination if these SGV are lower than those developed for the protection of ecological receptors.

A two-stage process is proposed for developing New Zealand-specific SGVs for the protection of ecological receptors. In the first stage, a methodology based on the proposed Australian methodology is recommended for use in developing preliminary SGVs using international toxicity data. This would enable an initial assessment of the relative sensitivity of the protection of ecological receptors endpoint. The second stage would be to validate the preliminary SGVs by generating toxicity data under New Zealand conditions (species, soils), and recalculation of SGVs if needed.

Protection of human health is considered in the Resource Management (National Environmental Standard for assessing and managing contaminants in soil to protect human health) Regulations 2011, and is relevant for the consideration of future land use flexibility of agricultural soil. Soil contaminant standards have been developed for Cd and incorporated by reference in the NES, thus there is limited need for further research in this area. Further research on plant uptake under New Zealand conditions would be beneficial, and would provide a more robust basis for assessing exposure via produce consumption.

Protection of groundwater is most relevant to consider on a site-specific basis. The risk of Cd leaching to groundwater will be higher for soils prone to leaching, e.g. stony soils, and further research is required to determine the extent of this risk.



6 Recommendations

To develop New Zealand-specific soil guideline values for use in the Tiered Fertiliser Management System it is recommended, in order of priority, that:

- Further research is undertaken to better understand the pathway of Cd accumulation in animal agricultural systems in New Zealand.
- Further research is undertaken to establish the relationship between plant uptake and species, cultivar, and soil properties for relevant species. This research requires industry input to determine what species and cultivars are most economically important and widely grown, and should include crop species that are high and low in Cd.
- The methodology for deriving SGVs for ecological receptors proposed in this report is agreed by all members of the Cadmium Management Group, and is used to generate preliminary SGVs using currently available toxicity data. New Zealand data on the toxicity of Cd under New Zealand conditions (species, soils) are generated to determine whether the preliminary SGVs are sufficiently protective.
- Further research is required to better establish the risk of leaching to groundwater, in particular for vulnerable soils, such as stony soils.

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Acronyms and glossary

ABC Ambient background concentration. The background concentration of

chemicals which is the sum of naturally derived concentrations and those due to long-distance atmospheric transport. Using the ABC rather than the background concentration is an acknowledgement that long distance transport has effectively increased the natural background concentrations.

ACL Added contaminant limit (ACL)*: An ACL is the added concentration of a

contaminant above which further appropriate investigation and evaluation of

the impact on ecological values will be required.

Biomagnification The accumulation and transfer of chemicals via the food web due to

ingestion, resulting in an increase of the internal concentration in organisms

at the succeeding trophic levels.

CCME Canadian Council of Ministers of the Environment
CONTAM Panel on contaminants in the food chain (EFSA)

ECx Effective concentration: the concentration which affects X% of a test

population after a specified exposure time.

ECL Effects concentration low (Canada)

Eco-SSL Ecological soil screening level (United States)

FSANZ Food Standards Australia and New Zealand

IV Intervention value (The Netherlands)

HC_x Hazardous concentration at which x% of the exposed population is

affected.

Lethal concentration at which 50% of the exposed population dies.

LOAEC Lowest observed effect concentration. The lowest concentration of a test

substance that caused a statistically significant adverse effects on the

organisms compared to the controls.

MATC Maximum acceptable toxicant concentration. The range or geometric mean

of concentrations spanning the NOEC and LOEC.

ML Maximum (legal) limit of a contaminant in food (Food Standards)

MPA Maximum permissible addition (The Netherlands)

MPC Maximum permissible concentrations (The Netherlands)

NOEC No observable effect concentration. The highest concentration of a test

substance to which organisms are exposed that does not cause any observed and statistically significant adverse effects on the organisms

compared to the controls.

NPER No-potential-effects range (Canada)

PNEC Predicted no effect concentrations (European Union)

RV Remediation values (The Netherlands)

Secondary poisoning

The product of biomagnification and toxicity

SQG Soil quality guideline (Canada)

SRA Serious-risk addition, a nominal amount of a metal that can be added to the

background concentration to derive an SRC_{eco} (The Netherlands)

SRC_{eco} Serious-risk concentration for ecological systems (The Netherlands)

Species sensitivity distribution (SSD)

A suite of methods that are the main method used to derive quality guidelines for contaminants in different compartments of the environment (e.g. soil, water, sediment). Basically these plot toxicity data (one value per species) as a cumulative frequency distribution against the concentration at which the toxic effect occurs.

Soil guideline value

A collective term used to describe any quantitative or qualitative limit that controls the concentration of contaminants in soils.

Appendix A – Detailed description of method used to derive soil guideline values for the protection of ecological receptors

A1 New Zealand: Auckland Regional Council

In 2006, the Auckland Regional Council contracted Landcare Research to develop soil guideline values protective of on-site and off-site ecological receptors for a range of contaminants, including Cd, to assist in the management of contaminated land. This appendix provides a detailed description of the methodology.

The statistical extrapolation method used in the report was based on that used by Dutch agencies, specifically by Verbruggen et al. (2001). The work of Verbruggen and co-authors was based on the methods of Lijzen et al. (2001) (who derived Dutch Intervention Values), except that the statistical extrapolation method of Aldenberg and Jaworska (2000) was used. This approach assumes a log-normal distribution, as opposed to a log-logistic distribution, of toxicity data. The concentration at which a certain proportion of species are affected can be determined as:

$$logHC_x = x - (k \times s)$$

where HC_x = hazardous concentration at which x proportion of species is affected

 $x = \text{mean of } \log^{10}\text{-transformed toxicity data}$

s =standard deviation of transformed data

k = extrapolation factor from Aldenberg and Jaworska (2000) based on quantity of data.

Aldenberg and Jaworska (2000) provided extrapolation factors to estimate different levels of confidence (lower, median, upper) in the estimated hazardous concentration. In our work for the ARC we used a median confidence level (i.e. there is a 50% chance that the hazardous concentration is over or under estimated).

The minimum data required to use the statistical extrapolation method (based on Verbruggen et al. (2001)) are four NOECs from four taxonomic groups. Microbial and enzymatic processes are considered separately to species effects, as the process in question may be performed by more than one species and, under toxic stress, the functioning of the process may be taken over by less sensitive species. More than one value per process may be included as it is considered that NOECs derived from different soils comprise different populations of bacteria. If the same soil is used, one value is selected or calculated (Verbruggen et al. 2001).

A2 Canada

Where sufficient data are available, environmental soil quality criteria are derived using an adaptation of Long & Morgan's 'weight-of-evidence' approach, described in CCME (1996). At least 10 data points from three studies, including a minimum of two soil invertebrate and two plant data points, are required, and data can include NOEC, LOEC, EC₅₀ and LC₅₀

(E

values. These data are used to create a frequency distribution from which the 25^{th} percentile is used to define the *no-potential-effects range* (NPER). Expert judgment is required to prevent values being calculated from biased data; e.g. bias can be created if more than 50% of the effects data are LC_{50} or EC_{50} values, or if more than 75% of the data are NOEC values. In addition, uncertainty factors (1–5) are applied to the calculated 25^{th} percentile value depending on data availability (e.g. whether only the minimum data are available, or whether more than 25% of data below the 25^{th} percentile are definitive effects data).

A lowest-observable-effect method or a median-effects method is used if insufficient data are available (CCME 1996). For both methods, at least three studies must be available, including at least one plant and one invertebrate study. Uncertainty factors are applied to the lowest EC_{50} or LC_{50} values and may also be applied to the lowest LOEC value (Table A1). Alternatively they may be applied to the EC_{50} and LC_{50} values, depending on data availability (i.e. whether fewer than three taxonomic groups were available, and whether the LOEC was taken from an acute or a sublethal study).

For agricultural and residential/parkland land uses, NOEC data are used to calculate the soil quality criteria for soil contact, using the weight-of-evidence approach. For commercial and industrial land uses, effect data only are used to calculate the soil quality criteria for soil contact—this is referred to as the effects concentration low (ECL) (CCME 1996).

Table A1	Magnitude of un	certainty factors f	for deriving soil c	riteria in Canada.

Data type	Factor
Lowest LOEC	1–5
Lowest EC ₅₀	5
Lowest LC ₅₀	10

Where soil quality criteria for microbial processes are lower than those for protection of soil organisms, the geometric mean of the two values is adopted. Otherwise the value for protection of soil organisms is adopted. The final derived value is also compared to plant nutritional guidelines (for essential elements for plant growth—agricultural, residential and parkland only), and acceptable geological background concentrations. Where the derived soil quality criterion is lower than the acceptable geological background concentration, that concentration becomes the final soil quality criterion.

A3 Netherlands

The Netherlands has several tiers of numeric values. Intervention values (IV) indicate soil contaminant concentrations at which the urgency of remediation is required to be assessed, while target values indicate long-term sustainable soil quality. Intervention values are used to determine remediation urgency of individual sites under the Soil Protection Act (1994). These values are determined by comparing serious risk concentrations determined from ecotoxicological data (SRC $_{\rm eco}$) with those determined for human exposure (SRC $_{\rm human}$) and selecting the lowest value as the intervention value. SRC $_{\rm eco}$ is defined as the concentration at which 50% of tested species or processes in an ecosystem experience adverse effects. SRC $_{\rm human}$ is based on the human-toxicological maximum permissible risk (MPR) level, using back-calculation to obtain the concentration at which the MPR is reached.

Remediation values (RVs) are set either based on the quality of agricultural and horticultural produce (Lijzen et al. 1999) or the SRC_{eco}. Target values are based on negligible concentrations (NC), which are defined as 1% of the maximum permissible concentration (MPC). The MPC is the concentration at which 95% of species are protected and is based on ecotoxicological data. When MPCs have been calculated for each environmental compartment, a harmonisation procedure is used to adjust the MPC values (if required), which ensures that transfer of contaminants from one medium to another does not exceed the MPC in that medium (de Bruijn et al. 1999). Background concentrations of contaminants that also occur naturally (e.g. selected metals and metalloids) are taken into consideration using an added-risk approach (Crommentujin et al. 1997).

A3.1 Derivation of MPC and SRCeco

Available soil toxicity data are separated into chronic and acute data, and microbial processes and enzymatic activity (e.g. nitrogen-mineralisaion, phosphatase inhibition, urease inhibition). If available, data from up to 13 taxonomic groups (bacteria, protozoa, macrophyta, fungi, platyhelminths, nematodes, gastropods, annelids, arachnids, insects, diplopods, isopods, chilopods) are used. All collated ecotoxicological data are recalculated to a standardised soil (25% clay, 10% organic matter, pH 6). For metals, this recalculation is based on regression equations developed from analysis of Dutch soil.

A3.2 Data selection

Only one value per species is used, and where there are several studies using the same species and endpoint, the geometric mean value of all studies is used. Where there are several studies on the same species but different endpoints, the lowest value is used. Data are collated, and where chronic data for four or more species of at least four taxonomic groups are available, standardised environmental risk limits (ERLs) are calculated using a statistical extrapolation method, or if fewer data are available, assessment factor methods are used to calculate ERLs. ERLs for microbial processes and species are compared and the lowest is adopted as the final value.

Refined risk assessment: Statistical extrapolation procedures are used to derive both the SRC $_{\rm eco}$ and MPC, provided that at least four NOECs for four different taxonomic groups are available. Ecotoxicological data to derive the NOEC values are studies based on growth, reproduction, or microbial processes. From these data, the concentrations at which 50% (SRC $_{\rm eco}$) and 5% (MPC) of NOEC values are exceeded are determined. These concentrations represent those hazardous to 50% (HC50) and 5% (HC5) of the species present in an ecosystem. The procedure described by Aldenberg and Slob (1993) has been used to derive MPCs and NCs given in Crommentujin et al. (1997). Verbruggen et al. (2001) revised the MPCs and SRC $_{\rm eco}$ using the method of Aldenberg and Jaworska (2000). The primary difference between these two methods is that Aldenberg and Slob (1993) assumed a log-logistic distribution of data while Aldenberg and Jaworska (2000) assumed a log-normal distribution.

Assessment factor method: If data for fewer than four taxonomic groups are available, the lowest value of the geometric mean of NOEC values and the geometric mean of $L(E)C_{50}/10$ is used to calculate SRC_{eco} (Lijzen et al. 2001). Verbruggen et al. (2001) used the uncertainty factors shown in Table A2 to derive SRC_{eco} and MPC for a range of contaminants.

These factors are those used in the European Commission Technical Guidance Document (EC 2003, and differ slightly from that used by de Bruijn et al. (1999) and Crommentujin et al. (1997). No minimum data requirements for either method are given.

Table A2 Magnitude of uncertainty factors for deriving environmental risk limits (ERLs) in the Netherlands.

ERL	Available data	Factor
MPC	NOECs from three taxonomic groupings	10
	NOECs from two taxonomic groupings	50
	1 NOEC, > 1 L(E)C ₅₀	100
	1 NOEC, no L(E)C ₅₀	100
	$> 1 L(E)C_{50}$, lowest L(E)C ₅₀	1000
SRC_{eco}	Geometric mean of NOECs	1*
	Geometric mean of L(E)C ₅₀	10

^{*} this value is compared with the extrapolated value based on acute $L(E)C_{50}$ values. The lowest is selected. See Acronyms and glossary section of this report for abbreviations.

Additional information: Background concentrations of contaminants that also occur naturally (e.g. metals) are taken into consideration in derivation of the environmental risk limits, using an added-risk approach (Crommentuijn et al. 1997). This approach assumes that background metal concentrations are not bioavailable, while metals added in toxicity tests are fully bioavailable. A nominal amount that can be added (SRA_{eco}, MPA, NA instead of SRC_{eco}, MPC, NC) to the background concentration (bc) is derived using methods described above. The specific environmental risk limits are given by:

$$SRC = cb + SRA, MPC = cb + MPA, while NC = cb + MPA/100$$
 (Eqn A2)

Appendix B – Details for methodology to protect groundwater

Adapted from Cavanagh (2006)

New Zealand (MfE 2011c), Canada (CCME 1996, 2006) and the USA (US EPA 1996) are the only countries that have explicitly considered protection of groundwater in the development of generic soil guideline values. (Dutch agencies provide an intervention value for groundwater (in $\mu g/L$), but the purpose of this value is to signal serious contamination in soil as opposed to providing protection of groundwater per se.) The way in which protection of groundwater is taken into account differs slightly between countries.

In Canada, a groundwater 'check' has been used to date (CCME 1996). This 'check' ensures that the soil quality guideline derived for the protection of human health does not result in contamination of groundwater (used for drinking water). If this value is less than the preliminary human health guideline value then the guideline 'check' value becomes the final human health guideline value. This approach has changed in a recent revision of the Canadian protocol (CCME 2006), and protection of groundwater is now routinely considered in the derivation of guidelines. Further, protection of freshwater life in nearby water bodies, livestock watering, and irrigation water are considered in addition to potable water. CCME (1996) uses parameters that are most representative of groundwater systems in Canada, while CCME (2006) considers both coarse (sand) and fine-grained (silt/clay) aquifers. Groundwater is assumed to lie directly below the contaminated zone.

In New Zealand and the United States generic guideline values for the protection of groundwater quality have been developed, where desired groundwater quality is typically drinking water standard. US EPA methodology uses parameters that are most representative of groundwater systems in the United States and assumes groundwater lies directly below the contaminated zone. In contrast, the NZPHG derives soil guideline values for six different soil types, and includes separation of the contaminated zone and the groundwater.

The simple model (Eqn B1) was used to investigate whether a simple approach could be used to derive generic soil guideline values for the protection of groundwater. The generic parameters used in Cavanagh (2006) are shown in Table B1.

$$C_s = DF \times C_{gw}(Kd + \frac{\theta_w}{\rho_b})$$
 (Eqn B1)

Where C_s = contaminant concentration in soil (mg/kg)

 C_{gw} = concentration in groundwater (mg/L)

 $Kd = \text{distribution coefficient, contaminant specific (cm}^3/\text{g})$

 θ_{w} = water-filled porosity (unitless)

 ρ_b = soil bulk density (g/cm³)

The dilution factor (DF) is given by:

$$DF = \frac{C_{sw}}{C_{ew}} = \frac{Kid}{RL} + 1 = \frac{KiD + RL}{RL}$$
 (Eqn B2)

Where C_{sw} = soil water concentration (mg/L)

 C_{gw} = groundwater concentration (mg/L)

 \vec{K} = saturated hydraulic conductivity (m/yr)

i = hydraulic gradient (unitless)

d = mixing depth (m)

R = recharge (m/yr)

L =length of contaminated site parallel to groundwater flow (m)

Table B1 Summary of soil and groundwater parameters used in Cavanagh (2006).

Parameter		Sand	Loam	Clay	Gravel
Aquifer parameters					
	mixing depth (d, m)	2	2	2	2
	hydraulic conductivity (K, m/c	d)10	1	0.001	10
	hydraulic gradient (I, m/m)	0.001	0.001	0.001	0.001
	recharge (R, m/yr) ¹	0.25	0.25	0.25	0.25
Generic <i>DF</i>		2.95	1.19	1.0	2.95
Soil parameters					
	Water-filled porosity (θ_w)	0.243	0.337	0.46	0.085
	Bulk density (ρ_b)	1.5	1.66	1.4	2
	Organic carbon fraction (foc)	0.005	0.005	0.005	0.005
Site length ²		15	15	15	15

Soil type was considered to make a negligible difference to recharge, and so is constant for all soil types.

² In the first instance the length of the contaminated site was considered to be the same as that used in the NZPHG, but this could be modified as required.

Appendix C - New Zealand studies on cadmium

To assist in deteriming, identified literature relating, and shows the relevant studies on Cd in New Zealand soils that provide some inforantion relelvant to the development of New Zelaand-specific SGVs for use in the TFMS.

Table C1 Summary of New Zealand studies on cadmium relevant to Cd management in agricultural systems (Adapted from Cavanagh et al. 2012).

Grouping	Title	Study
Cd concentration/accumulation	Cadmium in New Zealand agriculture	Bramley 1990
Cd concentration/accumulation	Trace element and Sigma DDT concentrations in horticultural soils from the Tasman, Waikato and Auckland regions of New Zealand	Gaw et al. 2006
Cd concentration/accumulation	Soil factors affecting heavy metal solubility in some New Zealand soils.	Gray and McLaren 2006
Cd concentration/accumulation	The effect of long-term phosphatic fertiliser applications on the amounts and forms of cadmium in soils under pasture in New Zealand	Gray et al. 1999c
Cd concentration/accumulation	Fractionation of soil cadmium from some New Zealand soils	Gray et al. 2000
Cd concentration/accumulation	Atmospheric accessions of heavy metals to some New Zealand pastoral soils	Gray et al. 2003b
Cd concentration/accumulation	Cadmium distribution in hill pastures as influenced by 20 years of phosphate fertilizer application and sheep grazing	Loganathan et al. 1995
Cd concentration/accumulation	Effect of phosphate fertiliser type on the accumulation and plant availability of cadmium in grassland soils.	Loganathan et al. 1996
Cd concentration/accumulation	Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine: a review.	Loganathan et al. 2003
Cd concentration/accumulation	Concentrations of arsenic, cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage.	Longhurst et al. 2004
Cd concentration/accumulation	Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge. 3. Distribution of residual metals.	McLaren et al. 2005
Cd concentration/accumulation	Cadmium status of soils, plants, and grazing animals in New-Zealand	Roberts et al. 1994

Grouping	Title	Study
Cd concentration/accumulation	Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer.	Schipper et al. 2011
Cd concentration/accumulation	Concentrations of cadmium, copper, selenium, zinc, and lead in tissues of New-Zealand cattle, pigs, and sheep	Solly et al. 1981
Cd concentration/accumulation	Changes in phosphorus availability and nutrient status of indigenous forest fragments in pastoral New Zealand Hill country	Stevenson 2004
Cd concentration/accumulation	Cadmium in soil solutions from a transect of soils away from a fertiliser bin	Taylor and Percival 2001
Cd concentration/accumulation	Accumulation of cadmium derived from fertilisers in New Zealand soils.	Taylor 1997
Cd concentration/accumulation	The source and distribution of cadmium in soils on a regularly fertilised hill-country farm	Zanders et al. 1999
Cd concentration/accumulation	Cadmium accumulation in Waikato Soils	Kim 2005
Cd concentration/accumulation	Cadmium in Taranaki soils	Taranaki Regional Council 2005
Cd concentration/accumulation	Envirolink 73 – HBRC 9 – soil cadmium	Longhurst 2006
Cd concentration/accumulation	The rate of accumulation of cadmium and uranium in a long-term grazed pasture: implications for soil quality	McDowell In press
Cd fate	Is Cadmium loss in surface runoff significant for soil and surface water quality: a study of flood-irrigated pastures?	McDowell 2010
Cd sorption/leaching	Adsorption of cadmium by an aquent New-Zealand soil and its components	Kim and Fergusson 1992
Cd sorption/leaching	Sorption of cadmium by complexes of kaolinite with humic-acid.	Taylor & Theng 1995
Cd sorption/leaching	Sorption of copper and cadmium by allophane-humic complexes.	Yuan et al. 2002
Cd sorpion/leaching	Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge. 2. Leaching of metals	McLaren et al. 2004
Cd sorption/leaching	Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time.	Gray et al. 1998

Grouping	Title	Study
Cd sorption/leaching	Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand	Gray et al. 1999a
Cd sorption/leaching	Cadmium leaching from some New Zealand pasture soils	Gray et al. 2003a
Cd sorption/leaching	The effects of anion sorption on sorption and leaching of cadmium	Bolan et al. 1999
Cd sorption/leaching	Cadmium sorption and desorption in soils: a review.	Loganathan et al. 2012
Livestock	A model to predict kidney and liver cadmium concentrations in grazing animals	Loganathan et al. 1999
Livestock	Pasture soils contaminated with fertilizer-derived cadmium and fluorine: livestock effects.	Loganathan et al. 2008
Cd concentration/livestock	Cadmium cycling in sheep-grazed hill-country pastures	Roberts and Longhurst 2002
Cd concentration/livestock	Cadmium in soil and plants and its cycling in sheep-grazed hill country pastures	Roberts et al. 1997
Misc	The determination of labile cadmium in some biosolids-amended soils by isotope dilution plasma mass spectrometry	Gray et al. 2003c
Misc	Is soil acidification the cause of biochemical responses when soils are amended with heavy metal salts?	Speir et al. 1999
Plant uptake	Measurement of plant-available cadmium in New Zealand soils.	Andrewes et al. 1996
Plant uptake	Changes in Cd bioavailability in metal spiked soils amended with biosolids: results from a wheat seedling bioassay	Black et al. 2010
Plant uptake	Evaluation of soil metal bioavailability estimates using two plant species (<i>L. perenne</i> and <i>T. aestivum</i>) grown in a range of agricultural soils treated with biosolids and metal salts.	Black et al. 2011
Plant uptake	Examining the integrity of soil metal bioavailability assays in the presence of organic amendments to metal-spiked soils.	Black et al. 2012
Plant uptake	Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies.	Bolan and Duraisamy 2003
Plant uptake	Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability.	Bolan et al. 2003a

Grouping	Title	Study
Plant uptake	Immobilization and phytoavailability of cadmium in variable charge soils. I. Effect of phosphate addition	Bolan et al. 2003b
Plant uptake	Immobilization and phytoavailability of cadmium in variable charge soils. II. Effect of lime addition.	Bolan et al. 2003c
Plant uptake	Uptake of Sigma DDT, arsenic, cadmium, copper, and lead by lettuce and radish grown in contaminated horticultural soils	Gaw et al. 2008
Plant uptake	The effect of ryegrass variety on trace metal uptake	Gray and McLaren 2005
Plant uptake	Cadmium phytoavailability in some New Zealand soils	Gray et al. 1999b
Plant uptake	Effect of soil pH on cadmium phytoavailability in some New Zealand soils	Gray et al. 1999d
Plant uptake	Cadmium concentrations in some New Zealand wheat grain	Gray et al. 2001
Plant uptake	Effect of nitrogen fertiliser applications on cadmium concentrations in durum wheat (<i>Triticum turgidum</i>) grain	Gray et al. 2002
Plant uptake	An assessment of cadmium availability in cadmium-contaminated soils using isotope exchange kinetics	Gray et al. 2004
Plant uptake	Cadmium adsorption by rhizobacteria: implications for New Zealand pastureland	Robinson et al. 2001

Appendix D – Proposed methodology for the derivation of cadmium soil guideline values for the protection of ecological receptors in production land

The proposed methodology for deriving Cd soil guideline values for the protection of ecological receptors to assist in the management of Cd in New Zealand is adapted from that outlined in Heemsbergen et al. (2009). This has been accepted as the Australian methodology for derivation of Ecological Investigation Levels (EILs), although the official methodology is yet to be released (pers.comm M. Warne, Department of Environment and Resource Management, Queensland). The Australian methodology derives land-use specific EILs, and the methodology proposed for deriving Cd soil guideline values for productive land in New Zealand is an adaptation of the Australian methodology for agricultural land. An outline of the proposed methodology, highlighting any points of difference from the Australian methodology, is provided below. Full details of the methodology, including rationale, are provided in Heemsbergen et al. (2009).

The main steps in the methodology are:

- collation and screening the data
- standardisation of the toxicity data
- incorporation of an ageing/leaching factor for aged contaminants
- calculation of an added contaminant limit (ACL) by either the species sensitivity distribution (SSD) or assessment factor (AF) approach, depending on the toxicity data
- normalisation of the toxicity data to a reference soil (only if the SSD approach is used to calculate the ACL)
- accounting for secondary poisoning
- calculation of the ambient background concentration (ABC) of the contaminant in the soil
- calculation of the SGV by summing the ACL and ABC values: SGV = ABC + ACL.

The separation of naturally occurring concentrations of a contaminant and the added contaminant is based on the 'added risk approach' (Crommentuijn et al. 1997) and is used by Dutch agencies. This approach assumes that the availability of the ABC of a contaminant is zero or sufficiently close that it makes no practical difference. This approach is recommended for use in New Zealand as a good starting point, although the practicalities of using such an approach, particularly in terms of determining ambient background concentrations for Cd, needs to be evaluated when SGVs are derived.

D1 Toxicity data collation, and screening and selection of toxicity data

Toxicity data is collated through literature review and/or searching databases for available toxicity data, such as the USEPA ECOTOX database (US EPA 2012). The suitability of the

available toxicity data should be determined using the criteria set out in Heemsbergen et al. (2009), specifically that toxicity data are considered acceptable when the:

- difference between tested concentrations was not greater than five-fold
- exposure duration was greater than or equal to 24 hours
- toxicity endpoint measured was growth, seedling emergence, lethality, immobilisation, reproduction, population growth or the equivalent
- measured toxic effect was a given percentage effect concentration (e.g. LC10, EC50) or were NOEC, LOEC or MATC values.

The quality of the remaining data is to be assessed using a modification of data quality assessment procedures outlined in Table 7 of Heemsbergen et al. (2009).

For productive land use, the only plant toxicity data used are those for agricultural crops, although all available data for soil invertebrates and microbial processes are used.

D2 Standardisation of the toxicity data

It is recommended that standardisation of the toxicity data is undertaken as outlined in Heemsbergen et al. (2009) and as summarised below.

D2.1 Measures of toxicity

For the purposes of this methodology, toxicity data that cause less than a 20% effect (e.g. EC0 to EC19) and NOEC data are considered equivalent and for brevity are referred to as NOEC and EC10 data. Toxicity data that cause a 20% to 40% effect and LOEC data are considered equivalent are referred to as LOEC and EC30 data. Toxicity data that cause >40% to 60% effect are considered equivalent to EC50 data and are referred to as EC50 data.

Chronic NOEC, LOEC, EC/LC50 and maximum acceptable toxicant concentrations (MATC) values can be converted to NOEC values using a series of default conversion factors (Table D1).

Table D1. Default conversion factors used to convert different chronic measures of toxicity to chronic no observed effect concentrations (NOECs) in the Australian and New Zealand water quality guidelines (ANZECC and ARMCANZ, 2000) (From Heemsbergen et al. 2009).

Toxicity data ^a	Conversion factor
EC50 to NOEC or EC10	5
LOEC or EC30 to NOEC or EC10	2.5
MATC* to NOEC or EC10	2

^a EC50, EC30 and EC10 values are the concentrations that cause a 50, 30 or 10% effect, NOEC = the no observed effect concentration, LOEC = lowest observed effect concentration, MATC = the maximum acceptable toxicant concentration and is the geometric mean of the NOEC and LOEC.

In the Australian methodology, a policy decision was made that the most appropriate type of toxicity data to be used in deriving the EILs was a combination of lowest observed effect concentration (LOEC) and 30% effect concentration data (EC30).

For use in New Zealand it is recommended that SGVs are derived using both NOEC/EC10 and LOEC/EC30 in the first instance, and the suitability of the derived values for use in the TFMS determined.

D2.2 Added concentrations

The Australian methodology uses the added concentration as the basis for determining toxicity values. If the toxicity data are not expressed in terms of added contaminant then they should be converted to that form, if possible. This can be achieved by:

- subtracting the ambient background concentration (ABC) if it is known
- or subtracting the average concentration in the control soil (i.e. the test soil with no addition of the test contaminant) from the total concentrations and then recalculating the toxicity.

D2.3 Duration of exposure

Following Heemsbergen et al. (2009), the conversion of acute toxicity data to chronic toxicity is recommended only for short term exposure tests. Acute to chronic ratios should be used if available, otherwise an assessment factor of 10 should be used.

D-2.4 The use of toxicity data for endemic or overseas species

While there is debate over the relevance of using toxicity data for overseas species to protect endemic species, derived SGVs become increasingly reliable as the number of species for which there is toxicity data increases. Therefore, Heemsbergen et al. (2009) recommends toxicity data for both endemic and overseas species should be used to derive SGVs, unless there is sufficient [Australian] data, which then can be used preferentially. A similar approach is recommended here but with New Zealand data given preference.

Further, because the cadmium SGVs are proposed for use in production land, the only plant toxicity data that should be used are those for agricultural crops, although all available data for soil invertebrates and soil microbial processes should be used.

D3 Incorporation of an ageing and leaching factor

The toxicity of metals that have been present in soils for a period of time (aged soils) is generally expected to be lower than that for freshly-spiked soils. Heemsbergen et al. (2009) recommends the use of ageing leaching factors (ALF) determined by Smolders et al. (2009), based on toxicity measures in a variety of European field and freshly spiked soils. These ALFs were developed based on a maximum of 18 months ageing and leaching and were developed for a range of metals including cadmium (Smolders et al. 2009).

The ALF determined by Smolders et al. (2009) for Cd2⁺ was 1, i.e. ageing did not significantly reduce the toxicity compared to toxicity arising from freshly spiked soils. It is recommended that an ageing/leaching factor of 1 is used for deriving Cd SGVs, unless data showing an influence of ageing in New Zealand soils become available.

D4 Calculation of added contaminant limit (ACL)

As discussed in the main text, the methods suitable for the derivation of SGVs is dependent on the amount of data available. Where sufficient data is available, statistical extrapolation using species-sensitivity distributions is used, while assessment factors are used where insufficient data is available. Table D2 shows minimum data requirements specified in Heemsbergen et al. (2009) and recommended for deriving New Zealand cadmium SGVs.

Table D2 Minimum data requirements for the species sensitivity distribution (SSD) and assessment factor (AF) approaches (Heemsbergen et al, 2010).

Number of specie s or functio nal proces ses	Number of taxono mic or nutrient groups	Methodology to derive SGVs
≥9	≤3	SSD Burr III
5 to 8	≤3	SSD Burr III
3 to 5	<3	AF

The SSD approach recommended for use is Burr Type III method available in the BurrliOZ program (available from: http://www.cmis.csiro.au/Envir/burrlioz/Download1.htm). This approach was also used to derive the Australian and New Zealand WQGs (ANZECC/ARMCANZ 2000).

All SSD methods use a single numerical value to describe each species or soil process for which toxicity data are available. Following Heemsbergen et al. (2009), the means by which a single value is obtained for each species or soil process are set out below:

- 1. If there was only one toxicity datum, that was taken to represent the species or process.
- 2. If there were several toxicity values for the same endpoint, the geometric mean of the values was calculated and was taken to represent the species or process.
- 3. If there were several toxicity values for different endpoints (e.g. mortality or reproduction), the endpoint with the lowest geometric mean was taken to represent the species or process.

Species sensitivity distribution methods require the toxicity data to have a uni-modal distribution. If the dataset is not uni-modal (e.g. insecticides are more toxic to insects than mammals) then the toxicity data belonging to the most sensitive distribution should be used for ACL derivation.

If the minimum data requirements for the SSD approach cannot be met, the AF approach should be used to derive SGVs. In this approach the lowest toxicity value for a contaminant (i.e. the most sensitive data point) is divided by an AF in order to derive an ACL (Eqn D1):

$$ACL = (lowest \ NOEC \ or \ EC10)/10$$
 (Eqn D1)

Table D3 Assessment factors to be used to derive added contaminant limits (Heemsbergen et al. 2010).

Number of species or function al process es	Number of taxono mic or nutrient groups	Assessment factor
<3	NA	500
≥3	1	100
≥3	2	50
< 5	3	10
Field data/da ta of model ecosyst em		10

D5 Normalisation of toxicity data to a reference soil

Heemsbergen et al. (2009) recommends normalisation of toxicity data to an Australian reference soil (Table D4) prior to the data being used in the SSD, if normalisation relationships exist. This may include the use of international normalisation relationships that have been validated for Australian soils or for soils that have characteristics similar to Australian soils. The use of normalisation relationships is an attempt to minimise the effect of soil characteristics on the toxicity data so the resulting toxicity data will reflect more closely the inherent sensitivity of the test species to the contaminant. This step is not used if there are no valid normalisation relationships available or if the available toxicity data are only sufficient to meet the minimum data requirements of the AF approach.

This step should be considered in the development Cd SGVs for New Zealand, although there are currently limited data that would enable normalisation relationships to be developed. The soil properties that define a New Zealand reference soil need to be developed first.

Table D4 Values of soil properties for the Australian reference soil used to normalise toxicity data.

Soil prop erty	Value
рН	6
Clay	10%
CEC	10 cmol/k g
Organic carb on	1% or equival ent OM

D6 Accounting for secondary poisoning and biomagnification

Cadmium is known to biomagnify in the food chain. Following Heemsbergen et al. (2009), this is taken into account by increasing the level of protection (percentage of species or microbial processes protected) where an SSD approach is used. Table D5 outlines the level of protection proposed for the development of New Zealand Cd SGVs.

Table D5 Percentage of species and soil processes to be protected for Cd in agricultural soils.

Land use	Biomagnification protection %
Agricultural	98 ^{a,b} and 85 ^{a,c}

^aif surface area exceeds 1000 m², ^bagricultural crops, ^cfor soil processes and terrestrial fauna

D7 Calculation of the ambient background concentrations

In the Australian methodology, ambient background concentrations (ABCs) for soils are required to enable derivation of EILs. This may be through direct measurement at a clean reference site with a comparable soil type to the site being examined, or by using the estimation method of Hamon et al. (2004) or collations of ABC values such as Olszowy et al. (1995 cited in Heemsbergen et al. 2009). However, the estimations of Hamon et al. (2004) do not include Cd, and the data of Olszowy et al. (1995) is for Australian soils and thus of little relevance to ambient background concentrations in New Zealand.

There are limited sources of data on ambient background concentrations of Cd in soils in New Zealand (Auckland Regional Council 2001, Tonkin and Taylor 2007). Evaluation of the existing data is required to determine its suitability for use for deriving SGVs.

D8 Calculation of the SGV

The SGV is calculated by adding the added contaminant limit to the ambient background concentration as follows:

$$SGV = ABC + ACL$$
 (Eqn D2)

The appropriateness of the derived values should determined by comparison of the derived Cd SGV with available field-, mesocosm- or microcosm-based toxicity data, and with background concentrations.

D9 Summary

The proposed methodology for deriving Cd SGVs for the protection of ecological receptors in agricultural soils in New Zealand is adapted from the Australian methodology for deriving soil ecological investigation levels as outlined in Heemsbergen et al. (2009). This ensures consistency between Australian and New Zealand approaches for deriving soil guideline values for the protection of ecological receptors, and also with the Australian and New Zealand Water Quality guidelines (ANZECC/ARMCANZ 2000). The proposed methodology should be evaluated against the official Australian methodology when it is released in case changes from Heemsbergen et al. (2009) have been made. Also, the process of deriving SGVs for Cd also might result in some changes to the methodology proposed here, e.g. difficulties in adequate determination of ambient backgound concentrations.