Section 6

6. Issues with Contaminants in Fertilisers and By-Products

Key Learning Objectives

After studying this section you should be able to:

1. Describe the main groupings of fertilisers that contain contaminants.
2. Explain why Cd and F are of most concern as fertiliser contaminants.
3. Explain the major pathways grazing animals accumulate Cd and F.
4. Explain ways that Cd accumulation in plants and grazing animals can be minimised.
5. Explain ways that F accumulation in grazing animals can be minimised.

Fertiliser Contaminants

The Code of Practice for Nutrient Management aims to ensure that where fertilisers are applied, they are used safely, responsibly, and in a way that avoids, remedies or mitigates any adverse environmental effects. Applying fertilisers, and other amendments to soils is necessary to ensure the sustainability of food production. However, it is important to be aware that some fertilisers can pose a risk to the wider environment if they contain unwanted impurities.

Nitrogen, S and K fertilisers are relatively free of impurities, at least those that originate from sources that are not by-products of urban or industrial activity (i.e. manufactured fertilisers). Unfortunately, manufactured phosphatic fertilisers often contain several impurities that may have potentially harmful effects on soil quality, livestock health and food safety. Similarly, waste materials, which have potential as fertilisers (e.g. bio-solids), often contain potentially toxic elements. However, in New Zealand waste materials make a relatively small contribution because they are not as widely used as fertilisers.

In manufactured phosphatic fertilisers the main elements of concern are Cd and F, while in waste materials As, Cr, Cu, Hg, Ni, Pb and Zn may pose a threat to the soil resource. From a mass balance accumulation viewpoint Cd and F are the elements of most concern (McLaughlin, 2000) (Table 6.1). Therefore, impacts of the contaminants Cd and F will be discussed in more detail in this Section.

Cadmium presents a hazard to grazing animals and humans through accumulation via the food chain, whereas F is hazardous to grazing animals through accumulation in soils and potential ingestion by these animals.

Table 6.1. Estimated balance of potentially toxic elements for fertilised dryland wheat and irrigated potatoes in southern Australia (Source: McLaughlin, 2000).

Element	Input[a] (g/ha/yr)	Crop harvest[b] (g/ha/yr)	Net rate of addition (g/ha/y)	"Background" soil concentration c (mg/kg)	Years to double soil concentration in 0-100 mm[d]
Wheat					
As	1.0	0.30	0.70	4.0	7,500
Cd	6.0	0.12	5.88	0.2	45
Hg	0.1	0.03	0.07	<0.1	1,850[f]
Pb	4.0	0.30	3.70	21.0	7,500
F	4,000	3.0	3,997	300.0	100
Potatoes					
As	4.0	0.20	3.80	4	1,370
Cd	20.0	2.50	17.50	0.2	15
Hg	0.4	0.25	0.15	<0.1	870[f]
Pb	16.0	1.00	15.00	21.0	1,800
F	16,000	10.0	15,990	300.0	25

[a] assumes 20 kg P/ha applied per wheat crop and 80 kg P/ha per potato crop and fertiliser contains (per kg P) 50 mg As, 300 mg Cd (250 mg Cd for potatoes), 5 mg Hg, 200 mg Pb and 200 g F. Elements inputs in irrigation water assumed to be negligible, although F may be a significant impurity in some waters.

[b] assumes a 3 tonne grain and 50 tonne potatoes harvested per crop per ha, all stubble or haulms returned to the soil. Metal concentrations in wheat grain assumed to be (per kg) 100 µg As, 40 µg Cd, 10 µg Hg, 100 µg Pb and 1 mg F and in potatoes (per kg fresh weight) 4 µg As, 50 µg Cd, 5 µg Hg 20 µg Pb and 200 µg F. Data for element concentrations in crops taken from the AMBS (Stenhouse 1991), Tiller *et al.* (1976), Anon (1984) and Wiersma *et al.* (1986).

[c] data for "rural" soils uncontaminated from industrial or urban sources taken from mean data for Cd and Pb in rural soils from Merry and Tiller (1991), Oliver *et al.* (1993), data for As from Tiller (1992) and Olszowy *et al.* (1993), data for Hg from Olszowy *et al.* (1993) and data for F from McLaughlin *et al.* (unpublished data).

[d] assumes a soil bulk density of 1300 kg/m^3.

[e] Guideline threshold values above which investigation of the contamination should take place, from ANZECC/NHMRC (1992) and Moen *et al.* (1988).

[f] assumes "background' soil concentration equals 0.1 mg/kg· despite published analyses indicating values below this level (detection limit).

Cadmium (Cd)

Cd PROBLEM IN NEW ZEALAND

Cadmium in pastoral soils became an issue during the 1980's to 1990's, because of its accumulation in offal products of grazing animals. During 1988-1992, one in every five sheep and cattle kidneys tested in New Zealand, had a Cd concentration above the maximum permissible concentration (MPC) of 1 mg/kg fresh weight, set by the New Zealand Department of Health prior to 2000 (Figure 6.1).

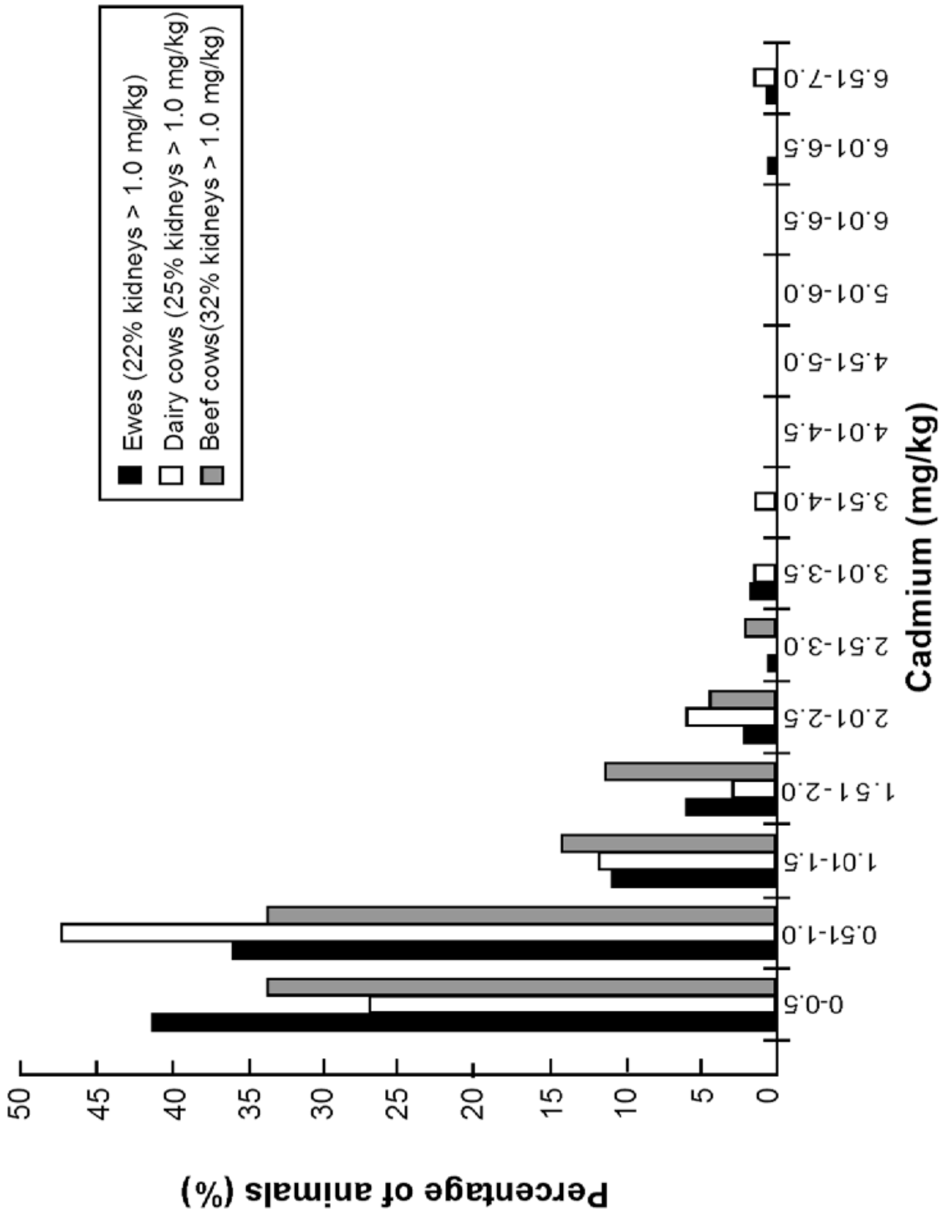


Figure 6.1 Cadmium residue levels in kidneys of grazing animals (<6 tooth) 1992/93 (Marshall, 1993)

Cadmium concentration in kidneys increase with the age of the animal, so to meet the European Communities import requirements, kidneys from older animals (30 months of age) are currently excluded from shipments for human consumption. Although the loss of earnings from export of offal products is very small, the elevated Cd concentration in offal products could be used as an indirect tariff barrier preventing export sales to some countries. Also, it can be detrimental to the current image New Zealand has as a "safe food producer". In the Australian and New Zealand Food Authority (ANZFA) standards, adopted in December 2002, the MPC for kidneys is higher (2.5 mg/kg) and, therefore, the percentage of slaughtered animals having kidney Cd concentration exceeding the 2002 MPC is likely to be much lower (Table 6.2).

Table 6.2 Permitted levels of Cd in food (Furness, 2001)

	Cadmium content (ppm, fresh weight)	
	Prior to Dec. 2002	***Current***
Kidneys	1	2.50
Liver	1	1.25
Meat flesh	1	0.05
Leafy vegetables	1	0.10
Root and tuber vegetables	1	0.10
Wheat	1	0.10

Table 6.3 The levels of Cd found in selected New Zealand foods (Roberts et al, 1995)

	Cadmium Content (ppm, fresh weight)	
	Mean	***Range***
Lettuce	0.04	0.01-0.14
Potatoes	0.02	0.01-0.10
Onions	0.02	0.01-0.11
Wheat	0.07	0.02-0.19

Cadmium taken up by crops in excessive amounts and transferred to the food chain can potentially have harmful effects on human health. The levels of Cd found in New Zealand food items were generally much lower than the previous permissible levels of 1 ppm (Tables 6.1.2 and 6.1.3). However, with the lowering of the permissible levels for food crops in December 2002 it made it more difficult for some foods to comply with the levels set (Table 6.2).

A survey of wheat grain Cd concentration in the lower North Island, Canterbury and Southland showed that there was a considerable variation in wheat grain Cd concentration between different cultivars (Figure 6.2). The mean Cd concentration in this study was 0.05 ppm. Ten percent of the grain samples examined were non-compliant with the MPC of 0.10 ppm. The Monard cultivar stood out as a variety which accumulated significantly higher Cd concentration compared to any other cultivar. Therefore in areas where soil conditions are likely to enhance Cd absorption by grain (e.g. low pH, high total Cd) soil management practices (liming, organic matter addition) to reduce these adverse soil conditions should be practiced if high Cd accumulating cultivars such as Monard is to be cultivated

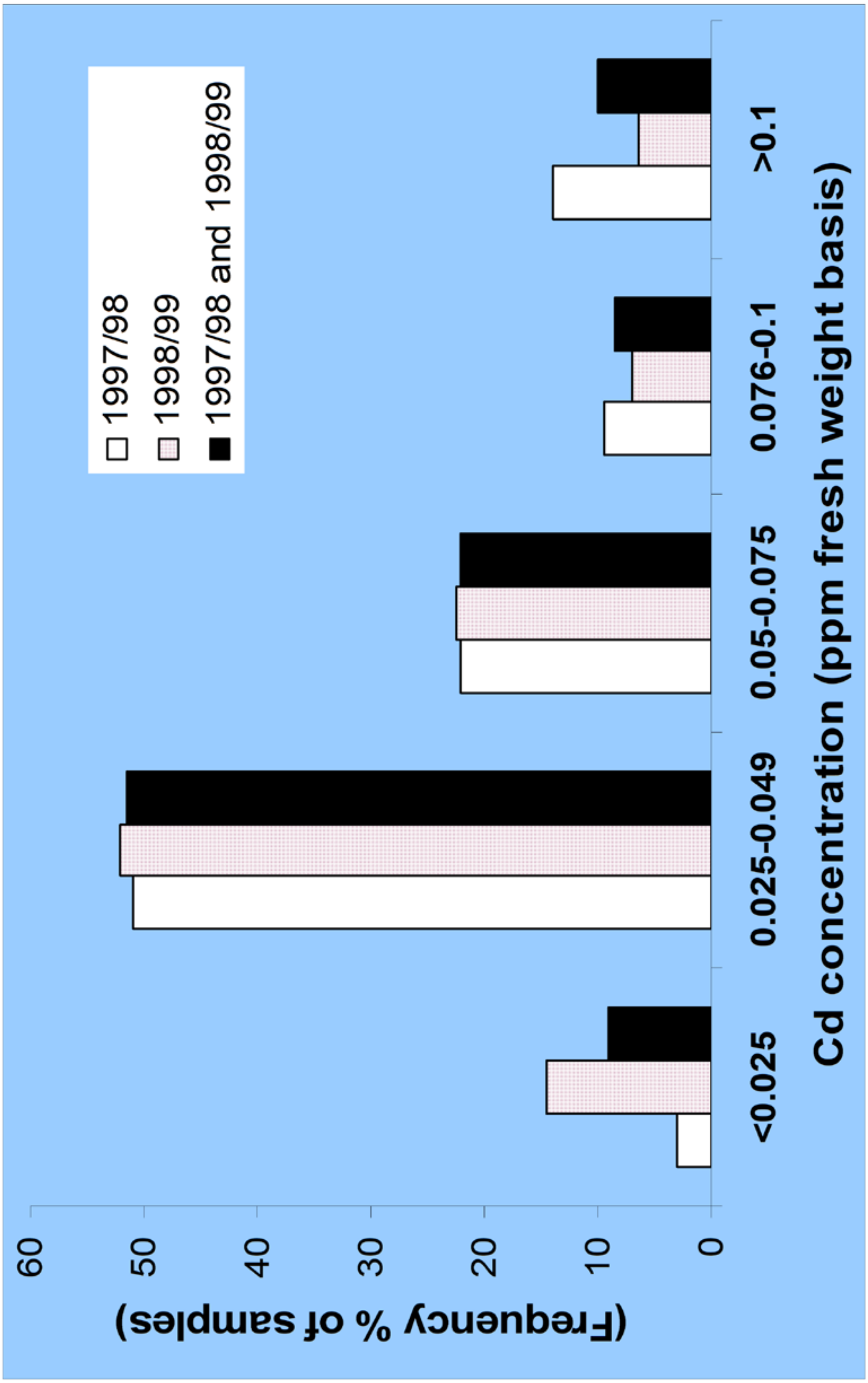


Figure 6.2 Frequency distribution of Cd concentrations in winter and spring wheat grain in New Zealand (Gray et al. 2001).

CADMIUM SOURCES

There are four major sources of Cd in agricultural soils. One source is the geogenic Cd coming from parent rock (0.1-2 mg Cd/kg), with igneous rocks having low Cd concentration and sedimentary rocks, like black shale, giving rise to high Cd concentrations. The other three sources are anthropogenic. They are the Cd:

1. from phosphate fertiliser use,
2. in the atmosphere arising from industries, and
3. from sewage sludge and industrial waste application to agricultural lands.

All of these last three sources are major contributors to the Cd burden in agricultural soils in Europe and North America (Figure 6.3). Sewage sludges and industrial wastes applied to lands in USA have a wide range of Cd concentration (1-4000 mg Cd/kg, median 10 mg Cd/kg). In New Zealand phosphate fertilisers are considered to be the major source of Cd. Atmospheric deposition and sewage sludges are important only in certain localities. For example, Fergusson and Stewart (1992) reported that within a 20 km distance around Christchurch the Cd input to land from atmosphere was 1-2 g Cd/ha/yr, which is equivalent to 10-20% of normal Cd input from fertilisers. But at 30-80 km from the city the Cd addition from the atmosphere was 0.02-0.05 g/ha/yr, which is <1% of Cd addition in fertilisers.

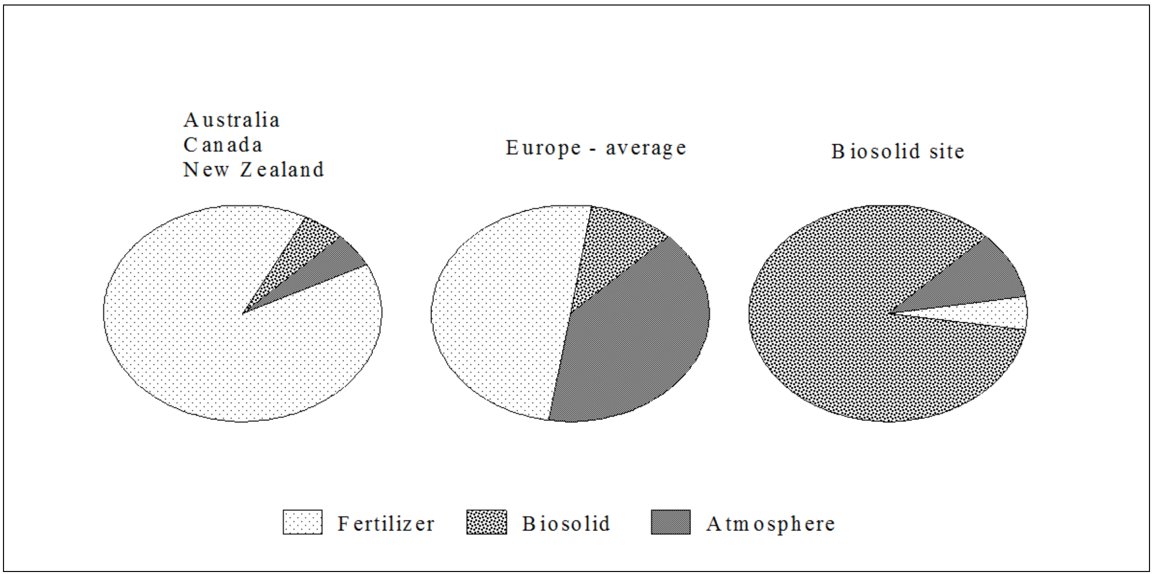


Figure 6.3 Diagrammatic representation of relative contribution of Cd from fertiliser, atmospheric and biosolid sources to agricultural land in various countries (Source: McLaughlin, 2000)

The concentration of Cd in phosphate fertilisers, depends on the Cd concentration of the phosphate rock (PR) used to manufacture the fertilisers. The Cd concentration of PRs vary widely with the PRs of sedimentary origin (e.g. Christmas Island, Nauru, North Carolina) having high Cd concentration (5-300 mg Cd/kg) and those of igneous origin (e.g. Phalaborwa, Kola) having low Cd concentration (1-5 mg Cd/kg) (Table 6.4).

Table 6.4 Cd and P concentrations in some phosphate rocks.

Phosphate Rock	Cd (mg kg^{-1})	P (%)	Reference
Kola	0.2	17.2	McLaughlin *et al*. (1996)
Chatham Rise	2	8.9	Syers *et al.* (1986)
North Florida	3	13.3	Syers *et al.* (1986)
Phalaborwa	4	17.2	Williams (1974)
Jordan	5	14.0	Loganathan *et al*. (1996)
Egypt (Quseir)	8	12.7	McLaughlin *et al*. (1996)
Mexico	8	14.0	Syers *et al.* (1986)
Makatea Island	10	13.0	Syers *et al.* (1986)
Sechura	11	13.1	Syers *et al.* (1986)
Arad	12	14.1	Syers *et al.* (1986)
Gafsa	38	13.4	Syers *et al.* (1986)
Morocco (Boucraa)	38	15.7	McLaughlin *et al*. (1996)
North Carolina	41	13.0	Loganathan *et al.* (1996)
Christmas Island	43	15.3	David *et al* (1978)
Ocean Island	99		Williams (1974)
Nauru	100	15.6	Syers *et al.* (1986)

The single superphosphates (SSP) used in New Zealand and Australia until the early 1990's were made from the high Cd containing Nauru and Christmas Island PRs and therefore the SSPs had a high Cd concentration of 27-48 mg/kg. DAP is another common P fertiliser extensively used in many countries including New Zealand. This fertiliser is made from PR as one of the starting materials. The Cd concentration in DAP can vary from 7 to 70 mg/kg depending on the PR used to make the phosphate acid which is a raw material used in the manufacture of DAP.

SOIL Cd

A National Survey of Cd in New Zealand soils carried out in the early 1990's by AgResearch, Ruakura, showed that in most soil types the Cd concentrations of fertilised soils were significantly higher than those of the adjacent unfertilised soils, implicating P fertiliser as the major source of Cd in these soils (Table 6.5). The average for fertilised soils was 0.44 mg total Cd/kg soil and for unfertilised soils it was 0.20 mg/kg. These levels are, however, lower than the world average of 0.66 mg/kg and 1 mg/kg in Germany and Japan, and much lower than the New Zealand maximum Cd concentration guideline of 1 mg/kg.

Table 6.5 Total Cd (mg/kg) in soils (0-75 mm depth) in New Zealand (Roberts et al., 1994)

Soil Group	Fertilised	Unfertilised
Alluvial	0.16	0.13
Brown grey loam	0.49	0.19
Gley	0.42	0.24
Peat	0.69	0.22
Yellow brown earth	0.22	0.16
Yellow brown loam	0.70	0.23
Yellow brown pumice	0.75	0.31
Yellow grey earth	0.12	0.13
Mean of 312 fertilised sites and 86 unfertilised sites	0.44 (range 0.04-1.53)	0.20 (range 0.02-0.77)

A study carried out on a yellow brown/yellow grey earth integrade soil at the AgResearch Ballantrae Hill Research Station, near Woodville, also showed that increased rates of P fertiliser application over 20 years (1973-1992) markedly increased soil Cd levels (Table 6.6).

Table 6.6 Total Cd in low slope, east aspect farmlets (Yellow brown/Yellow grey earth integrades) at Ballantrae (Loganathan et al., 1995)

P and Cd applied in P fertilisers 1973-1992		Cd in soils (0-75 mm depth) 1993
P (kg/ha)	Cd (g/ha)	Cd (mg/kg)
0	0	0.10
113	42	0.12
765	284	0.55

The majority of applied Cd in fertilisers remains in the top 10 cm of the soils due to adsorption by soil organic matter (see Figure 6.11 in the section on Fluoride).

PLANT-AVAILABILITY OF SOIL Cd

Plant-availability of soil Cd depends on several soil and crop factors (Table 6.7).

Table 6.7 Factors affecting Cd uptake from soil (from Chaney and Hornick, 1978; McLaughlin et al., 1996)

Description	Factor affecting Cd uptake
Soil Factors	pH (increase pH decrease Cd uptake); Amount of Cd present in soils Metal sorption capacity of soil (increase sorption decrease Cd uptake): organic matter, cation exchange capacity, clay, Fe and Mn oxides; Other micronutrients: Zn, Cu, Mn; Macronutrients: NH_4, PO4, K Temperature, moisture content, compaction Aeration: flooding = CdS; Recurrent v. single application Salinity (CdCl complexes) increase Cd uptake
Crop Factors	Species and cultivar; weeds > grass > clover Plant tissue: leaf>grain fruit and edible root; Potato – roots>stems, leaves>tuber Leaf age: older >younger Metal interactions

Cd Intake, Distribution and Retention in Grazing Animals

Grazing animals accumulate Cd in their organs by soil ingestion and herbage intake. Under lax grazing situations, Cd intake by sheep and cattle through soil ingestion is low – approximately 15% and 2% of total Cd uptake during winter and summer months, respectively. These percentages can double or treble with increased stocking rates on soils with weak structure (Healy, 1967, 1968).

More than 99% of an animal's daily Cd intake is returned back to the soil in faeces and as a result, daily net absorption is small (Figure 6.4). Cd concentrations in kidneys and liver are high and those in milk and muscle are very low. The levels of Cd measured in carcass meat are significantly lower than the "permitted levels". The Cd concentration in sheep liver and kidneys increases with the age of the animal, but the rate of increase decreases with the age (Figure 6.5).

At 6 months of age, the sheep retains about 0.1% of the Cd intake in the kidneys whereas in later years this figure decreases to 0.04% or less. This suggests that the strategies aiming at reducing Cd in animals should focus more on their young age (1st 100 days after weaning). One way to do this is to allow the animals to graze low Cd areas when they are young. However, this poses a practical problem as young animals have fast growth rates, and these are achieved on pastures that have been heavily fertilised

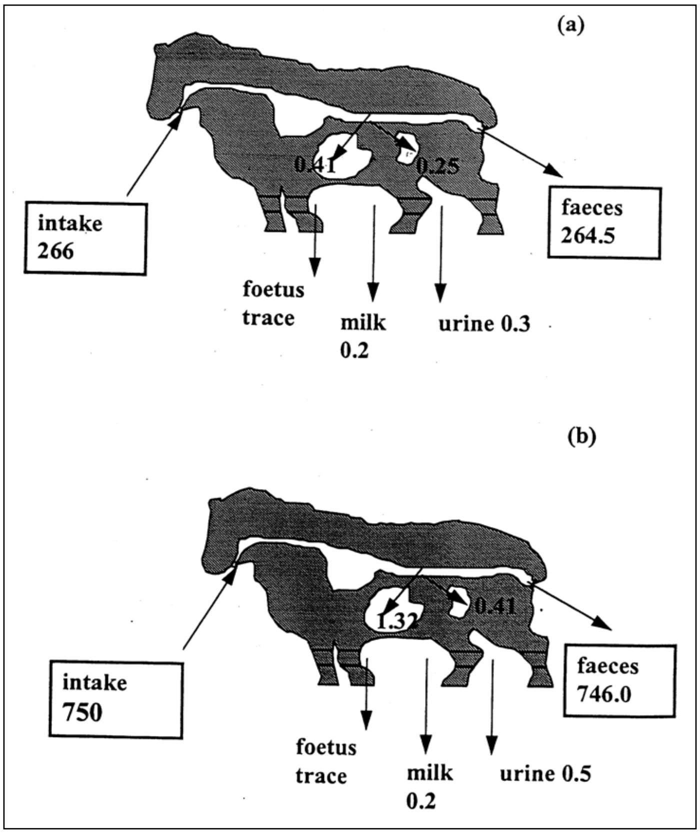


Figure 6.4 Cadmium movement (ug Cd/day) in typical Romney sheep grazing ryegrass/white clover pasture containing either (a) 0.2 ug Cd/gDM or (b) 0.5 ug Cd/gDM. Net absorption of daily Cd is approximately (a) 1.5 ug/day and (b) 4 ug Cd/day respectively (Lee et al., 1994).

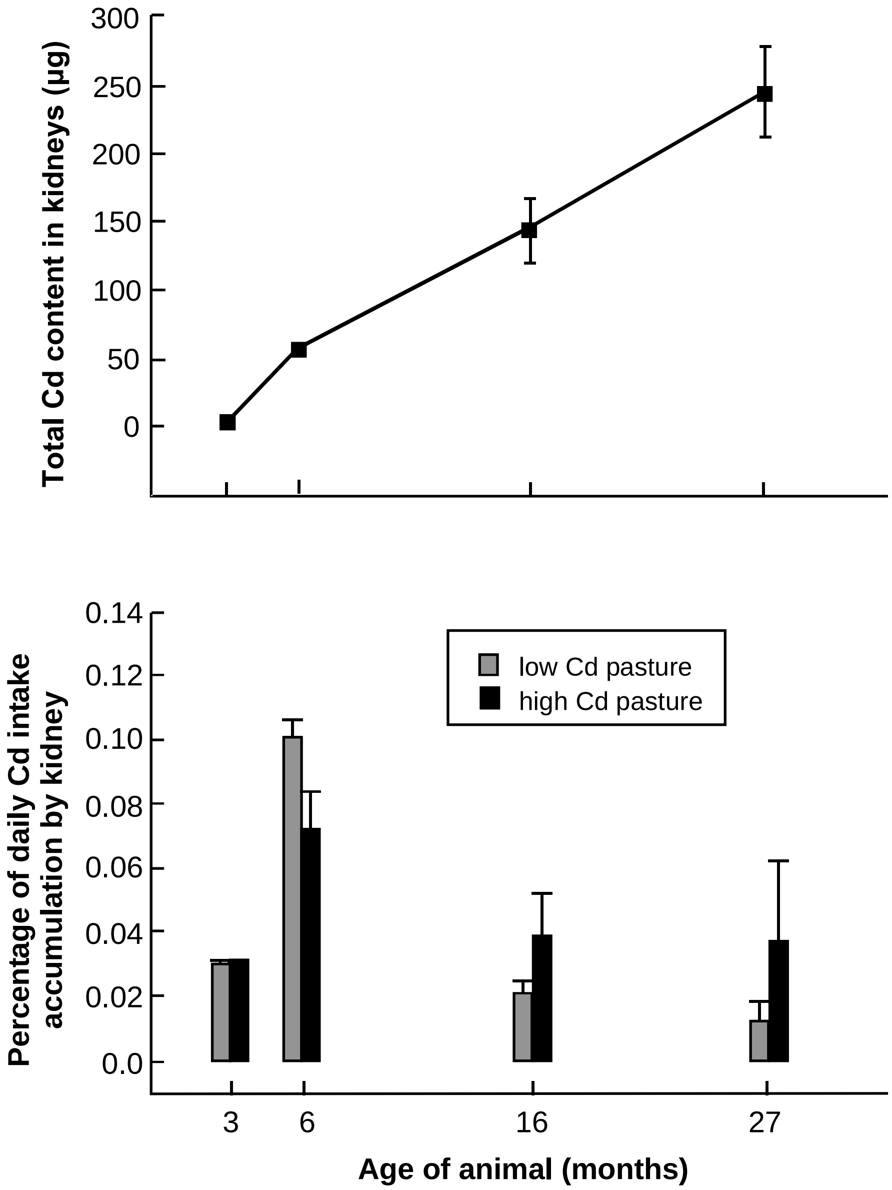


Figure 6.5 *Total and daily accumulation of Cd in kidney from grazing Sheep (Lee et al., 1994)*

MEASURES TO CONTROL Cd ACCUMULATION

National Cadmium Management Strategy

The Cadmium Management Strategy (MPI, 2011; Rys et al., 2011) was developed by the Cadmium Working Group (CWG), a group established in 2006 of representatives from industry, food safety, environment, regional councils and local communities to assess any potential risks of Cd in New Zealand's agricultural and food systems. This management strategy was reported in 2011 by the Ministry of Primary Industry and outlines a combination of governance, research, monitoring and management activity for food, soils and fertiliser. It includes a Tiered Fertiliser Management System (TFMS), linked to soil Cd levels, to manage the gradual Cd build-up in New Zealand's agricultural soils.

The TFMS utilises four soil Cd trigger values to signal increasing levels of phosphate fertiliser management. Phosphate fertiliser recommendations will be managed so that it will be at least 100 years before soils at the lower trigger value of 0.6 mg Cd/kg soil accumulate to the upper trigger value of 1.8 mg Cd/kg soil. :

- **Tier 0 (within natural background levels)** - there are no limits on the application of phosphate fertiliser other than a five yearly screening soil test for Cd status.
  (The trigger value to move to Tier 1 is 0.6 mg Cd/kg soil).
- **Tier 1 -** phosphate fertilisers are restricted to a set of products and application rates to manage Cd accumulation, and landholders are required to test for Cd every five years using approved programmes.
  (The trigger value to move to Tier 2 is 1.0 mg Cd/kg soil).
- **Tier 2** - phosphate fertilisers are further managed to ensure that Cd does not exceed the agreed accumulation rate.
  (The trigger value to move to Tier 3 is 1.4 mg Cd/kg soil).
- **Tier** 3 – the choice of phosphate fertiliser product and rates are restricted yet further to manage the soil accumulation rate.
  (The trigger value to move to Tier 4 is 1.8 mg Cd/kg soil)
- **Tier 4** - no further net accumulation above the trigger value of 1.8 mg Cd/kg soil is to occur unless there is a detailed site-specific investigation to identify risks and pathways for potential harm

Farmers should always consider Cd loading levels, regardless of soil Tier levels.

At Tiers 1- 4 landholders will be encouraged to use a set of management practices to limit the risks posed by Cd to the food chain and environment.

Use of low Cd fertilisers

The major dietary load of Cd for the grazing animal is through direct pasture intake, not soil ingestion, as is the case for F (see F section for detail).

An obvious method of reducing Cd accumulation in soils, pastures, crops and grazing animals is to use fertilisers containing low Cd concentration. In 1994, fertiliser companies in New Zealand agreed on a timetable for reduction of Cd in fertiliser (Table 6.8). The companies complied with this timetable and currently the Cd content in fertilisers made in New Zealand is not greater than 280 mg/kg P or 26 mg/kg fertiliser. This reduction is achieved by blending phosphate rocks with different Cd concentrations. From March 2002, this Cd limit in fertilisers was incorporated into the New Zealand Fertmark Quality Assurance Scheme. Fertmark will, within its audit procedures, check Cd levels to ensure farmers comply with this Cd limit (NZFMRA 2002).

The current Cd concentration limits for fertilisers of 280 mg/kg in New Zealand are slightly lower than those proposed or in effect in Australia and Japan but higher than those in many other countries especially the Scandinavian countries (Table 6.8).

Table 6.8 Cadmium limits for P fertilisers in several countries (Mortvedt, 1996)

Country	Cd limit, mg/kg P**	Effective year
Australia	450	1994
	350	1995
	300	2000
Austria	120	1994
Belgium	200	Voluntary
Denmark	150	1994
	110	1995
Finland	50	1994
Germany	200	Voluntary
Japan	343	1994
Norway	100	1994
	50	1995
Sweden	100	1994
Switzerland	50	1994
The Netherlands	35	
New Zealand*	420	July 1995-Dec 1996
	340	Jan 1997-Dec 1999
	280	Jan 2000 onwards

**Voluntary standards – Wood (1996), MAF Quality Management*
***(mg Cd/kg P) x (%P in fertiliser) ÷ 100 = mg Cd/kg fertiliser*

Another method of reducing Cd in fertilisers is by volatilising most of the Cd by calcination of the PRs since Cd has a low boiling point (BP = 765^{0}C). The manufacture of most phosphoric acid used in the food industry is through this method. However calcination of PRs may not be a practical option in the fertiliser industry because it is expensive and calcination decreases the reactivity of PRs, making them unsuitable for direct application as a source of P.

In some PRs, a significant quantity of Cd is associated with the organic carbon present in the PRs (Loganathan and Hedley 1997). Therefore another means of removal of Cd may be through the removal of organic matter using caustic solvents since these can remove the associated Cd without removal of P.

Soil Management

Soil management practices that can reduce Cd accumulation in crops and animals include reduction in soil acidity by lime application, maintaining high levels of soil organic matter, alleviating Zn deficiency (Zn reduces Cd uptake by plants) and reducing weeds, which are known to have much higher Cd concentration than grass and clover (Figure 6.6; Table 6.9)

Cultivation and resowing of permanent pasture will reduce the soil surface concentration of Cd.

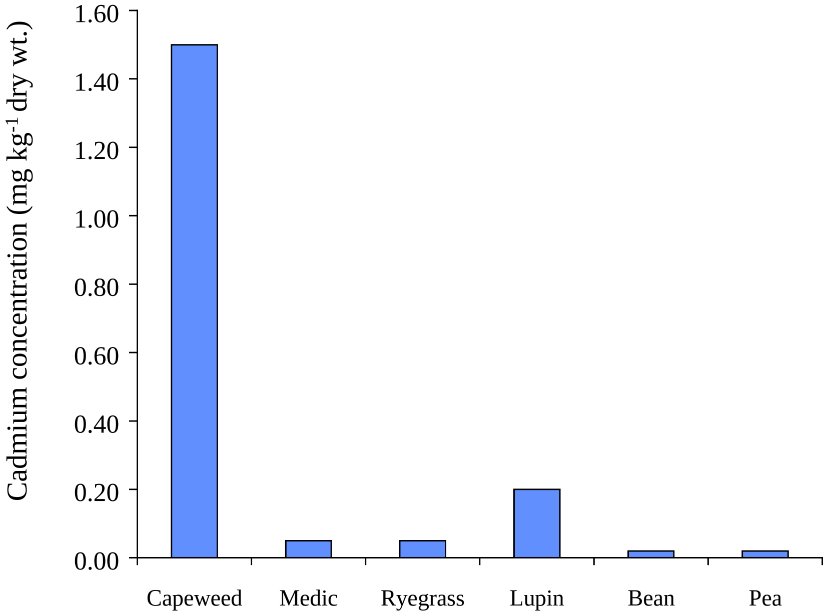


Figure 6.6 *Concentrations of Cd in pasture species and grain legumes grown at Tarlee, South Australia (from Merry, 1992; source: McLaughlin, 2000)*

Table 6.9 *Mean herbage Cd contents for native and pastoral sites (Roberts et al., 1994)*

Plant	Site	Mean Cd content (µg/g)
Grass species	Native	0.08
	Pastoral	0.10
Legume species	Native	0.07
	Pastoral	0.06
Weed species	Native	0.14
	Pastoral	0.28

The implication of forage (weed) crops on Cd intake

'Weed' in the context of Table 6.9 is defined as any pasture plant that is not grass or clover. Under this definition, the diet of many livestock has a high proportion of weeds when the integration of forage species (e.g. chicory and plantain) within New Zealand grazing systems is considered. Chicory has a reputation as a good accumulator species for many heavy metals, and research by Stafford et al. (2016) has highlighted the Cd accumulation potential of this and other forage species (Table 6.10). This research, conducted under controlled pot conditions, has subsequently been verified with field survey and trial work. However, the relationship between high Cd concentrations in forage crops and the rate of Cd accumulation in animals has yet to be determined, so caution must be exercised in extrapolating any direct meaning of the reported concentrations.

Table 6.10 Mean herbage Cd concentration in 12 forage species grown under controlled pot conditions on soil collected from a South Otago dairy farm, and amended with superphosphate fertiliser (Stafford et al., 2016). Mean concentrations with the same letter are not significantly different

Plant species	Cultivar	Mean Cd concentration (µg/g)
Perennial ryegrass	Trojan	0.103 (abc)
White clover	Huia	0.035 (a)
Red clover	Hamua	0.059 (ab)
Lucerne	Wairau	0.332 (de)
Crimson clover	Blaza	0.045 (a)
Strawberry clover	Palestine	0.152 (abc)
Haresfoot trefoil	Increase	0.076 (abc)
Sheep’s burnet	-	0.188 (bc)
Chicory	Puna II	1.639 (g)
Plantain	Tonic	0.734 (f)
Kale leaf	Gruner	0.123 (abcd)
Kale stem		0.138 (abcd)
Turnip leaf	Barkant	0.526 (e)
Turnip bulb		0.281 (cde)

Crop management

Different cultivars of the same crop type can vary in their tendency to accumulate Cd. Studies in the main wheat growing regions of Manawatu, Canterbury and Southland indicated significant differences in Cd concentrations for various cultivars of wheat (Gray et al., 2001). As part of their ongoing research programmes, seed suppliers have the ability to combine low Cd traits with other quality traits such as high yields and disease resistance. Growers can therefore check with seed suppliers as to the Cd accumulation properties of different cultivars. If cultivars are selected that accumulate more than 0.05 mg Cd/kg grain, appropriate options should be implemented to minimise Cd accumulation (Gray et al., 2001). However, it should be realised that selecting cultivars based on Cd accumulation is likely to be a lower priority for growers than selecting for yield or disease resistance and it is unlikely that selecting based on cultivar will be practiced by the majority of farmers.

Grazing Management

The rates of Cd accumulation in young animals are much higher than those in older animals. Therefore, young animals should not be allowed to graze high Cd-containing pastures. Reducing stocking rates and avoidance of hard grazing in winter can reduce Cd uptake by soil ingestion.

Fluoride (F)

- Essential element for animals but not for plants.
- High F concentration in diet can cause fluorosis in animals.

SOURCES

Apart from soil parent material, P fertilisers are the major source of F input in many agricultural soils although factories producing fertilisers, aluminium, bricks, steel and glass can be point sources of F pollution (Figure 6.7). In New Zealand, fresh volcanic ash deposits on soils and pasture are another important source of F presenting a major risk to grazing animals in the Central North Island.

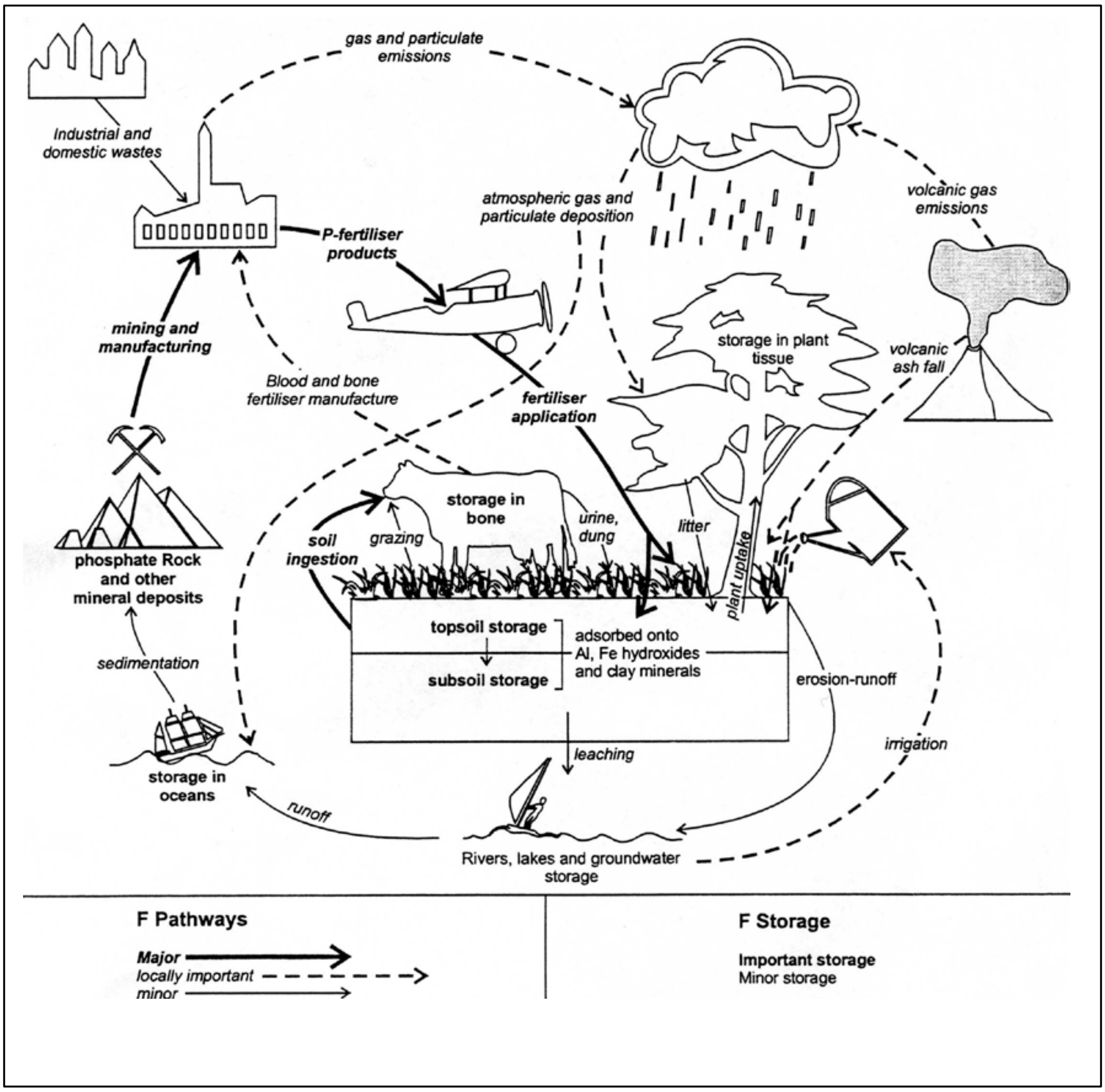


Figure 6.7 The F Cycle (Cronin et al., 2000)

F concentration in P fertilisers, volcanic ash, soils and pasture

- phosphate rock 1.5 – 4% (Table 6.11)
- Christmas and Nauru rocks low F
- superphosphate 1.5 – 2%
- volcanic ash 300 – 900 ppm
- New Zealand top soils (0-75 cm) 200 – 500 ppm (Figure 6.8)
- pasture (mixed herbage) < 2 – 10 pp

TOXICITY

F concentrations in herbage rarely exceed 10 ppm irrespective of the soil concentration. The major contributors to F intake by grazing animals are through direct ingestion of soil, volcanic ash and P fertiliser.

Acute Fluorosis

Short-term (1-2 days) P fertiliser ingestion – animals grazing pasture recently top-dressed with P fertilisers can suffer from acute fluorosis (kidney failure leading to death). (Clark et al., 1976; O'Hara and Cordes, 1982). Acute toxicity is associated with F intake of > 3000 mg/kg diet.

Volcanic ash ingestion can also cause acute fluorosis in grazing animals (1783 eruption of Lakagigar in Iceland – tens of thousands of animals died. The 1995 eruption of Ruapehu, New Zealand – caused many sheep deaths from ingestion of high F (350-800 ppm F) 2-3 mm thick ash layer deposited on short pasture.

Chronic Fluorosis

Long-term (months-years) ingestion of soil high in F concentration can cause chronic fluorosis (tooth and bone deformities). Associated with F intake of > 60 mg F/kg diet.

F ACCUMULATION IN SOILS

Farmers apply between 2 and 15 kg F/ha/yr in P fertilisers applied at rates of approximately between 10 and 75 kg P/ha. Fifty years of P application at these rates can increase topsoil (0-7.5 cm) F concentration by 84 to 625 ppm (B.D. 800 kg/m^3 assumed) if approximately 50% of added F moves below 7.5 cm. In a YGE soil, at a site in the Manawatu, the levels of total soil F (0-7.5 cm) increased from 133 ppm to 226 ppm after 10 years annual application of 60 kg P/ha (12 kg F/ha) as SSP (Figure 6.9). The majority of accumulated F in these topsoils was adsorbed to Fe/Al oxides associated with clay minerals.

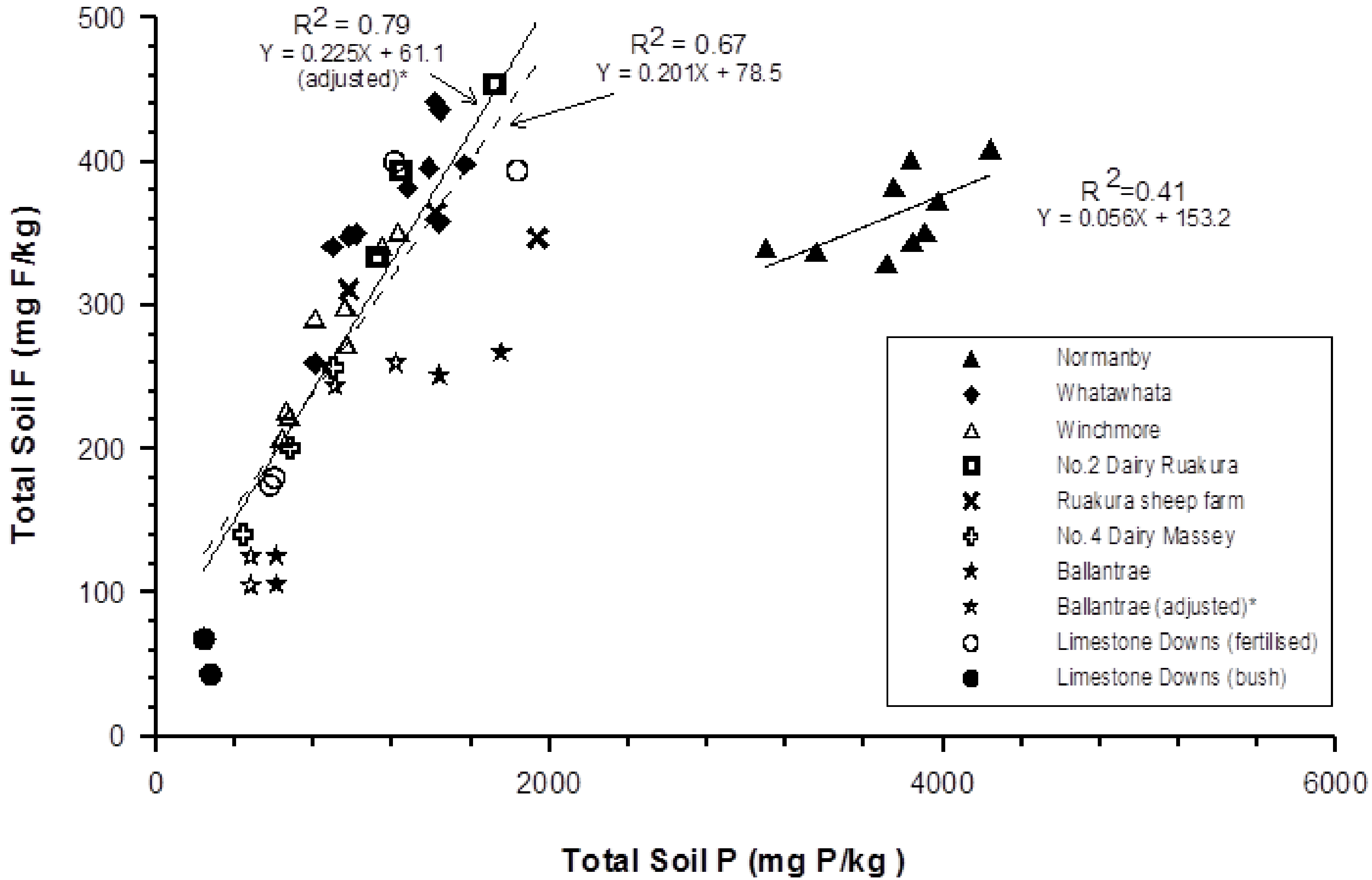
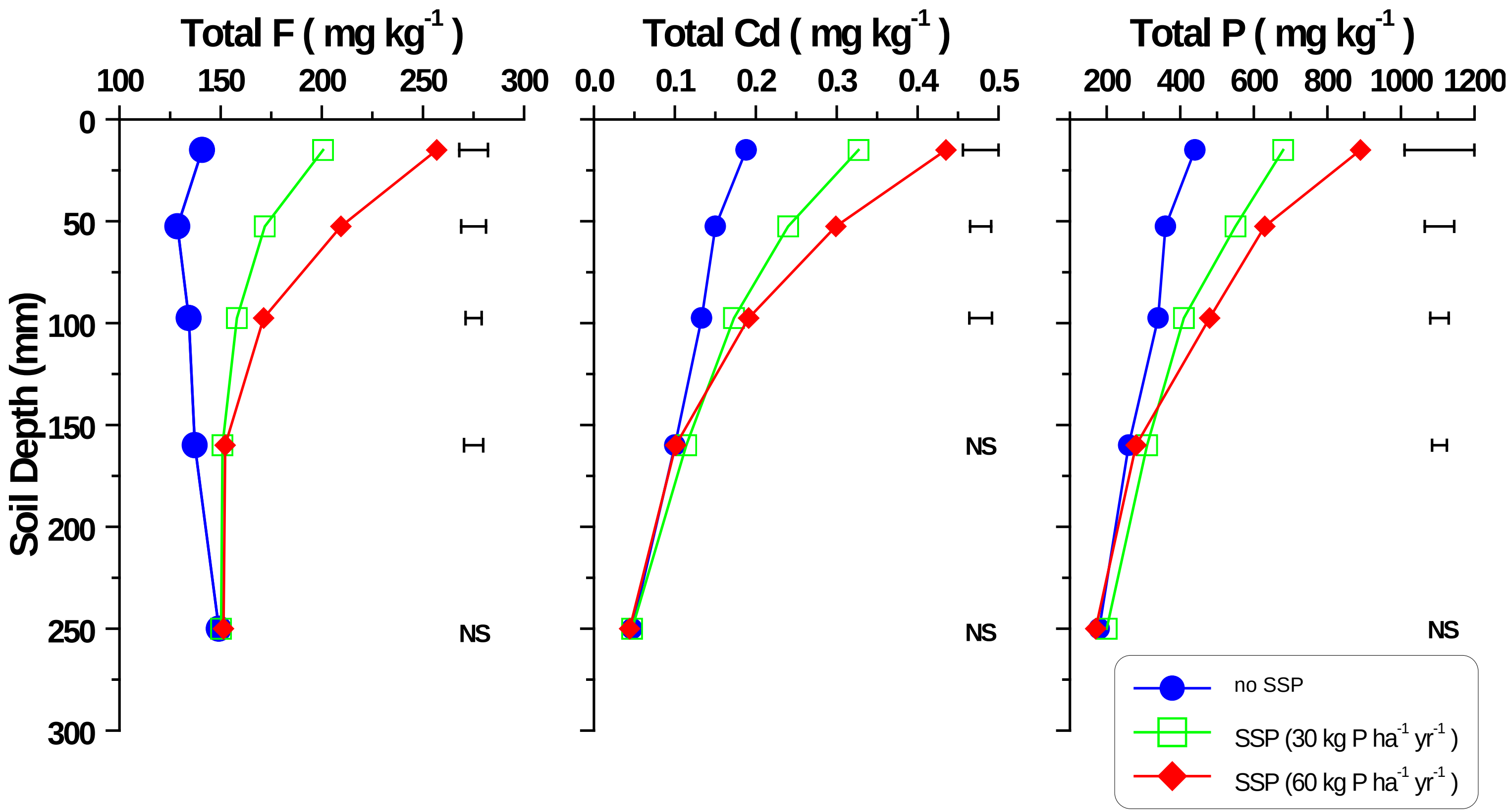


Figure 6.8 *Relationship between total soil P and total soil F in topsoils (0-7.5 cm) at various sites in New Zealand that have received regular applications of P fertilisers (P fertiliser form: TSP at Normanby, SSP mainly at all the other sites) (Loganathan et al., 2001).*



(Horizontal bars represent LSD values [5% significance]. 'NS' denotes treatment effects were not significant.)

Figure 6.9 Effect of ten years annual applications of SSP on the downward movement of F, Cd and P in a Pallic (YGE) soil at a site in the Manawatu.

Table 6.11 F levels in P fertiliser materials

Fertiliser Material	F concentration (%)
Phosphate rocks	**4.0**
Arad (Israel)	2.2
Charismas Island-A	3.0
Gafsa (Tunisia)	4.1
Jordan	3.8
Makatea Island	3.2
Mexican	4.1
Khouribga	4.0
Nauru Island	3.0
North Carolina	3.5
North Florida	4.0
Sechura (Peru)	3.4
Fertilisers	
SSP	1.1-1.8
TSP	1.3-2.4
MAP	1.6-2.2
DAP	1.2-3.0

PATHWAYS OF F INTAKE BY GRAZING ANIMALS

F intake by grazing animals through pasture consumption is much lower than through soil ingestion (soil F/pasture F~ 100. soil Cd/pasture Cd~ 1). F risk to grazing animals depends on soil F concentration, soil ingestion rate and soil F bioavailability (Figure 6.10).

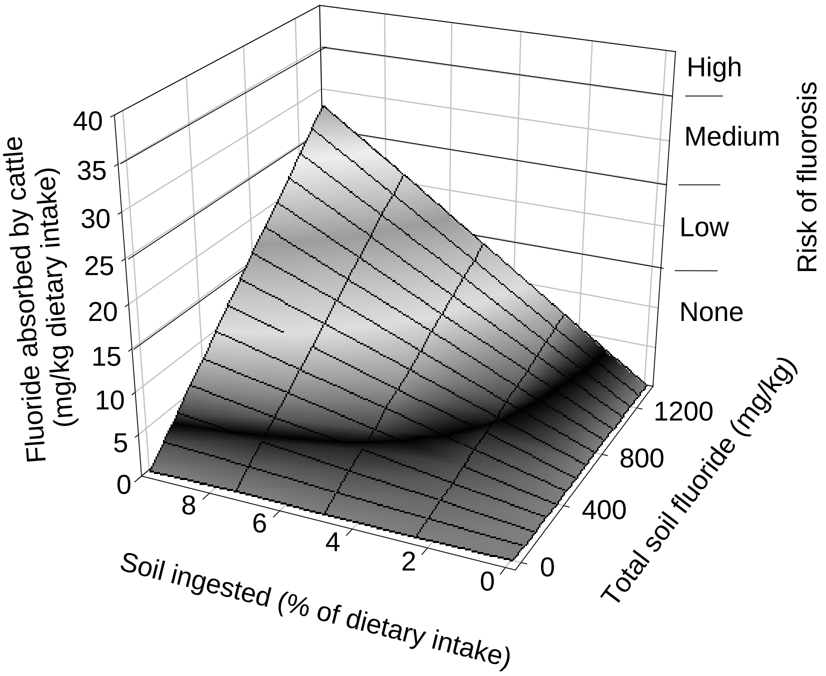


Figure 6.10 Effect of total F concentrations in soil and quantity of soil ingested on F absorbed by cattle and risk of fluorosis (from McLaughlin et al. 2000).

Horticulture tends to use much higher P rates, compared to pastoral farming, and can be up to 10 times higher. If these lands are returned to pastoral agriculture there can be potential F risk to grazing animals through soil ingestion.

F MOBILITY IN SOILS

- F is relatively immobile in soils like P and Cd (Figure 6.9). In high P fixing soils 70-80% of F added is expected to reside in the top 7.5 cm soil depth. Therefore, grazing animals may take-up large quantities of F through soil ingestion.

- In low P-fixing acidic soils, high rates of F additions can lead to more rapid F movement to ground water in the form of soluble Al F complexes.

REDUCING F RISK TO GRAZING ANIMALS

- Superphosphate poisoning can be prevented by withholding stock from recently top-dressed pastures until at least 25 mm of rain has fallen. This requires staggered fertiliser application so that some unfertilised paddocks are always available for grazing. Under rotational grazing, fertiliser can be spread on paddocks that have been most recently grazed to maximise the interval between application and grazing. If staggered fertiliser application is not possible, stock can be put on effluent paddocks or fed with silage or hay during the short period after top-dressing.

- Reduce soil ingestion by maintaining good pasture cover especially during winter (Consult Table 6.12).

- Deep-plough lands high in topsoil P concentration during pasture renovation to reduce topsoil F concentration.

- Reduce the F concentration of fertiliser by not using the stack scrubber liquor (approx. 20% F in the final superphosphate product) for granualtion or dilution of sulphuric acid.

Summary

- P fertiliser is the main source of contaminants applied to agricultural lands in New Zealand.

- Cd and F are the contaminants of most concern because their levels in P fertiliser are relatively high compared to soil and plant levels and there are many recorded cases of Cd toxicity to humans and F toxicity to grazing ruminants.

- Cd and F mainly accumulate in the topsoil; Cd by adsorption to organic matter and F by adsorption to Fe/Al oxides and clay minerals.

- Cd intake by grazing ruminants is mostly by pasture ingestion.

- F intake by grazing ruminants is mostly by soil ingestion (also by direct ingestion of volcanic ash or P fertiliser).

- Cd accumulates mostly in kidneys and liver of grazing ruminants.

- F accumulates mostly in bones of grazing ruminants.

- New changes to the MPC for Cd in kidneys and liver means that in the future:
  - compliance is less of a concern for kidneys and liver;
  - but compliance is more difficult for some vegetables and wheat grains.

- F accumulation in soils is potentially a problem for animal health only, not human health. However, there is currently no evidence to support that the levels of F ingested by livestock in New Zealand are a problem under normal conditions.

Test Your Knowledge

1. You have a wheat grower on land with a history of high fertiliser use and potentially high levels of soil Cd. What are his/her options to ensure that Cd levels in grain don't exceed the 0.1 ppm Cd maximum permissible concentration (MPC)?

2. Compare and contrast the pathways by which the majority of Cd and F are ingested by grazing animals.

3. Describe the relevance of soil organic matter and hydrous oxides of iron and aluminium to the retention of Cd and F in soils.

4. You have a sheep farmer with relatively high soil fertility. What are some measures he/she can take to reduce F accumulation in the livestock?

5. What is the total soil Cd concentration value that would trigger a change in fertiliser policy?

RESEARCH FINDINGS IN NEW ZEALAND:

Table 6.12 Threshold rate of soil ingestion for chronic fluorosis risk in sheep and cattle.

Animal	Soil type	Farm type	Fertiliser rates (kg SSP/ha/yr)	Native soil F (µg F/g soil)	Estimated top soils (0-7.5cm) F after 30 yrs* (µg F/g soil)	Threshold % of soil in diet for chronic fluorosis**	Total dry matter intake*** (g/day)	Threshold soil ingestion rate for chronic fluorosis risk (g/day)
Sheep	Sedimentary	Low Fert	100	150	210	41	1000	410
	Sedimentary	High Fert	200-300	150	300	28	1000	280
Cattle	Sedimentary	Beef – Low Fert	100	150	210	30	6400	1920
	Sedimentary	Beef – High Fert Dairy – Low Fert	200-300	150	300	21	6400	1344
	Volcanic ash	Dairy - High Fert	450-550	250	550	11	6400	704

* Assumptions: bulk density 800 kg/m^3, 40% of fertiliser F has moved below the 7.5 cm soil depth.

** Calculated from the formula: [% soil in diet x soil F concentration x soil F absorptivity in animal (0.5) + % pasture in diet x pasture F concentration (5 µg/g) x pasture F absorptivity in animal (0.75)] 1/100 = Risk limit (µg F absorbed / g diet) in sheep (45) or cattle (34)

*** Cronin et al. (2000).

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