

Fertiliser-Derived Fluorine in Grazed Pasture Systems.

M.J. Hedley*, **P. Loganathan *** and **N. D. Grace****

**Fertilizer and Lime Research Centre, Institute of Natural Resources, Massey University, Palmerston North, New Zealand (email: m.hedley@massey.ac.nz)*

***AgResearch Limited, Grasslands Research Centre, Private Bag 11008, Palmerston North, New Zealand*

Summary

Phosphorus (P) fertilisers, which are the main fertiliser input for the economic production of legume-based pastures, are the largest source of F enrichment for pastoral soils. Excessive levels of soil fluorine (F) can result in adverse effects for soil quality, livestock health and food safety. The majority of fertiliser F applied to pastures continues to accumulate in the biologically active topsoil due to strong adsorption to soil constituents. Fluorine adsorption in soils increases with increased contents of iron and aluminium oxides, layer silicates and allophane in soils and increased soil pH. In most pastoral soils with near-neutral pH, the majority of F added in fertilisers remain in the topsoil and little moves below a depth of 20-30 cm and therefore is unlikely to contaminate ground waters. However, F may pose a risk to shallow ground waters in very acidic low P-fixing soils. Research is required both to test whether ground waters beneath farms (with long histories of P fertiliser use) are contaminated by F and also to examine the mechanisms of its movement.

Fluorine intake by grazing livestock is mostly by soil ingestion. Ingestion of soil F with elevated F concentrations can result in chronic fluorosis in sheep and cattle. Reducing soil ingestion by maintaining good pasture cover especially during winter periods can reduce F accumulation in livestock. In grazing livestock, F accumulates mainly in bones and horns and not in products that enter the human food chain. Thus the grazing animal filters out excess soil F leaving animal products, such as milk and meat, with low F concentrations and low impact on food safety.

Introduction

In Australia and New Zealand, pasture production has been increased through introduction of improved legume and grass species and regular application of phosphorus (P) and sulphur (S) fertilisers. P fertilisers (e.g. single and triple superphosphate, and diammonium phosphate) contain significant quantities of fluorine (F), present as fluoride (F⁻) derived from the phosphate rocks (PR) used in their manufacture.

Fluorine is one of 13 potentially toxic elements which have significantly higher concentrations in PR and P fertilisers than in the soils to which they are applied (Sauerbeck 1985; McLaughlin 2000). Considering the balance between current rates of F applied in P fertiliser to dry land wheat and irrigated potato in Southern Australia (Table 1) and the low rate of F removal in crops products and leaching, McLaughlin et al. (1996, 2000) concluded that it would take < 100 yrs to double F concentrations in topsoils. Similar calculations carried out for New Zealand pastoral soils showed the same time scale for doubling the concentrations of these elements in the topsoils (Table 2). This accumulation of soil F has raised concern that the dietary intake of F by grazing animals may steadily increase to reach unhealthy levels. Whereas trace amounts (~ 1 - 2 mg F/kg of dry matter consumed) of F are essential for tooth and bone development of livestock (Shupe, 1980), excessive intake of F can cause fluorosis. Chronic F toxicity in sheep and cattle can be induced by dietary F concentrations of 60 -170 mg/kg DM, over months or years, causing damage to teeth, jaw and bones (Clark and Stewart 1983). These dietary intake levels may be exceeded when sheep graze pastures containing 5- 11 mg F/kg dry matter also

incidentally ingest more than 100g topsoil per day containing 500 mgF/kg soil. Depending upon season and stocking rate, soil ingestion by sheep has been measured ranging from less than 30 to greater than 250g/day (Healy 1968a, 1973). Soil ingestion in the upper part of this range has the potential to cause chronic fluorosis. Soil ingestion, however, is unlikely to cause the type of acute fluorosis in grazing animals that has been caused by direct ingestion of freshly applied single superphosphate (SSP) fertiliser or basic slag (Clark et al. 1976; Cronin et al. 2000; Jones and Jones 1962; O'Hara and Cordes 1982). For example, O'Hara et al. (1982) noticed acute fluorosis in sheep with a short-term (few days) high F intake of >3000 mg/kg dry matter (DM) diet (lethal dose 50-100 mg F/kg live weight) resulting in kidney failure and death.

This paper reviews knowledge of the fate of fertiliser-derived F in soils and its influence on grazing livestock and animal products entering the human food chain..

Table 1. Estimated time taken for doubling the concentrations of F in top soils (0-100 mm depth) when P fertilisers are applied to wheat and potatoes in southern Australia (McLaughlin et al. 1996).

Crop	Input (g/ha)	Crop harvest (g/ha)	Net rate of addition (g/ha/yr)	Background soil conc. (mg/kg)	Years to double soil concentration
S. Australia					
Wheat	4000	3.0	3997	300	100
Potato	16000	10.0	15990	300	25

Table 2. Estimated time taken for doubling the concentrations of F in top soils (0-100 mm depth) when P fertilisers are annually applied to grazed pastures in New Zealand.

New Zealand	Input ¹ (g/ha)	Pasture uptake ² (g/ha)	Animal intake ³ (g/ha)	Animal removal ⁴ (g/ha)	Net rate of addition ⁵ (g/ha/yr)	Background soil conc. (mg/kg)	Years to double soil conc ⁶ .
Grazed pasture	6000	50	40	20	5880	300	51

¹30 kg P/ha/yr

²10000 kg dry matter/ha /yr., 5 mg F/kg dry matter.

³80% utilisation of pasture by animals

50% F permanent removal

⁵Column 2 minus column 5

⁶Bulk density of 1 g/cm³

Fluoride sources for grazing animals

Unless animals are fed P fortified supplements the main sources of F they are likely to encounter will be associated with the soil. This F will be derived from the soil parent material (rocks contain 180 to 1000 mg F/kg (Fleischer and Robinson 1963)). Atmospheric deposition (industrial pollution and volcanic activity) and P fertilisers are the main sources of F that serve to enrich agricultural topsoils. Ashfall from volcanic eruptions can also be an important source of F (e.g. Iceland, New Zealand (Coote et al. 1997; Cronin et al. 2003; Weinstein and Davison 2004)). Ground and surface waters associated with these sources can become major secondary sources and vectors of F to living organisms. In rural areas of New Zealand P fertilisers have been the main source enriching pastoral and arable topsoils above the F concentrations of the soil parent materials and unfertilised soils (Loganathan et al. 2003).

Fluorine Concentrations in Phosphatic Fertilisers

Common P fertilisers for pastoral soils, SSP, partially acidulated PR (PAPR), triple superphosphate (TSP), or diammonium phosphate (DAP) are manufactured by full or partial acidulation of phosphate rocks (PR). Small amounts of the more reactive phosphate rocks (RPR) are directly applied as low cost slow release P sources.

The range of F concentrations found in different PRs, especially in fluoroapatites, is relatively narrow (3-4%), with mean F:P ratios of 0.28 (Table 3). However, during the manufacture of phosphate fertilisers using PRs a significant quantity of the F is released as HF and SiF₄ gases and the level of F in the fertilisers is likely to depend on the recovery of these gases in flue scrubbers and whether scrubber fluids are re-blended with the fertiliser (Weinstein and Davison 2004). Typical F:P ratios in SSP range from 0.12 – 0.2 and in TSP and DAP from 0.06 – 0.15. Typical SSP applications of 10–30 kg P/ha/yr are likely to add at least 1–6 kg F/ha/yr to pasture soils.

Fluoride Accumulation in Pastoral Soils

A number of studies have shown that long-term use of P fertilisers has increased F concentrations in the topsoils (e.g. Cronin et al. 2000; McLaughlin et al. 1996; 2001; Loganathan et al. 2001; 2003, Figure 1).

Table 3. Fluorine and P concentrations of a range of phosphate rocks and fertilisers

Phosphate fertiliser	F (%)	P (%)
Kola PR		17.2
Chatham Rise PR	3.0	8.9
North Florida PR	4.0	13.3
Phalaborwa PR		17.2
Jordan PR	3.8	14.0
Egypt (Quseir) PR		12.7
Mexico PR	4.1	14.0
Makatea Island PR	3.2	13.0
Sechura PR	3.4	13.1
Arad PR	4.0	14.1
Khouribga PR*		13.8
Syria PR*		13.3
Algeria PR*		12.5
Nahal Zin PR*		13.3
Gafsa PR	4.1	13.4
Morocco (Boucraa) PR		15.7
Yousoufia PR*		14.2
Tunisia PR**		
North Carolina PR	3.5	13.0
Christmas Island PR	2.2	15.3
Togo PR*		15.9
Taiba PR*		15.9
Senegal PR**		
Ocean Island PR		
Nauru PR	3.0	15.6
SSP	1.08–1.84	9.0
TSP	1.3–2.4	21
DAP	1.2–3.0	20

PR - phosphate rock. Data from Loganathan et al. 2003.

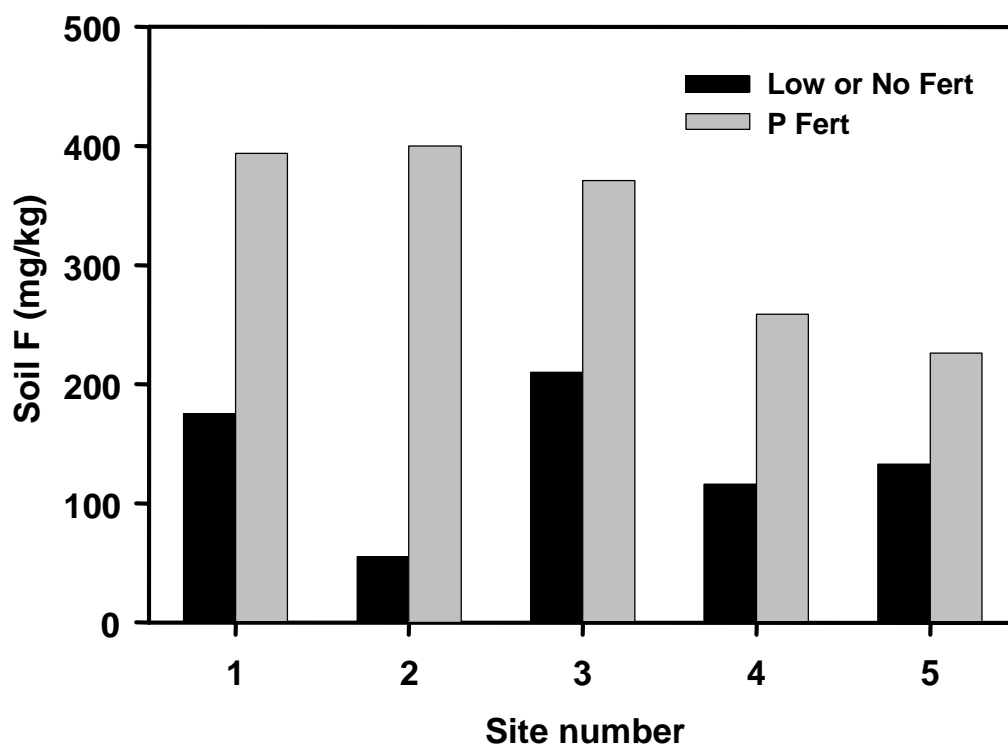


Figure 1. Mean F concentrations (0-75 mm depth) for native/pastoral sites topdressed with low rates of, or no, P compared to pastoral sites topdressed with high annual P rates (Site 1, Limestone Downs, Allophanic Soil; Site 2, Limestone Downs, Ultic Soil; Site 3, Normanby, Allophanic Soil; Site 4, Ballantrae, Pallic/Brown Soil; Site 5, Palmerston North, Pallic Soil (Loganathan et al. 2001, 2003; For soil classification descriptions see Hewitt 1998).

Agricultural soil P concentrations are a reflection of fertiliser history and in well fertilised soils current P concentrations can be double those of the native soil (Figure 2). Total F concentrations in regularly fertilised topsoils are often positively correlated with total P concentrations (Figure 2). The slopes of the regression lines in Figure 2 are numerically similar to the highest P: F ratio in SSP (Table 3) used in New Zealand prior to 1996. This again shows that there is a strong link between SSP use and accumulation of F in topsoils and P fertiliser application rate is the major factor influencing F accumulation rates in fertilised pastoral soils.

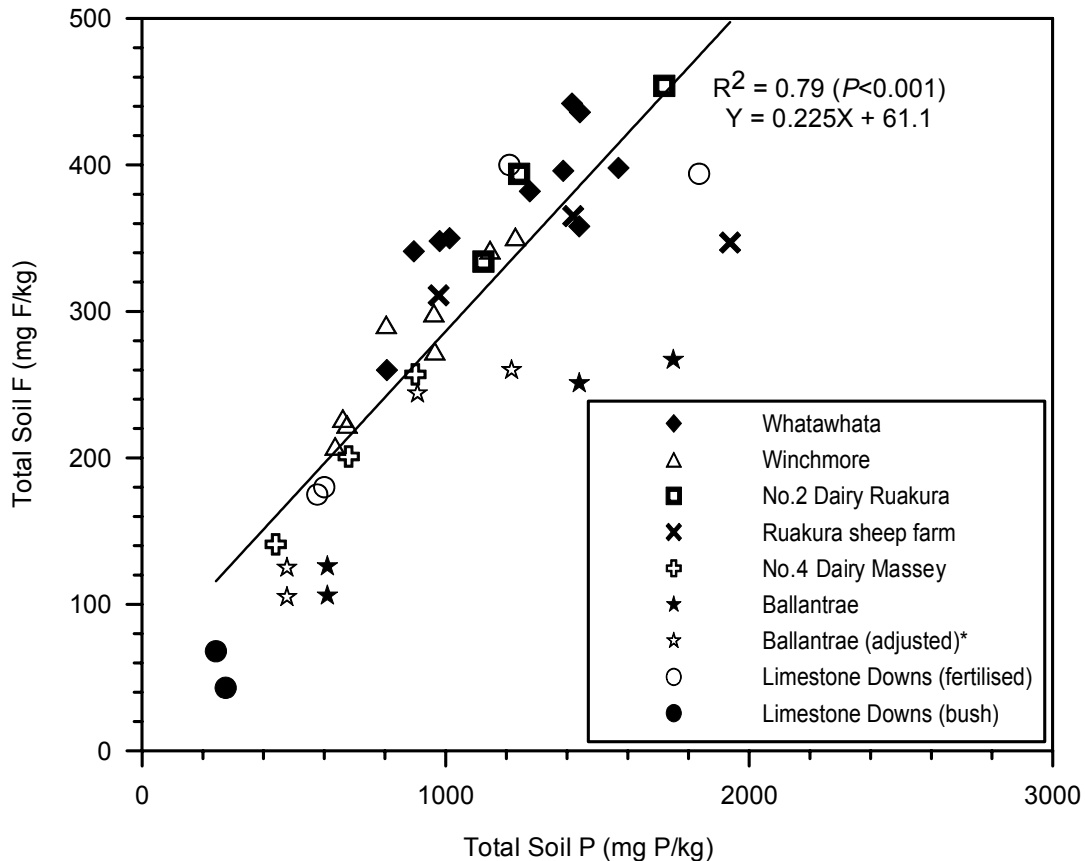


Figure 2. Relationship between total P and total F in the 0-75 mm soil depth in New Zealand pastoral soils (Loganathan et al. 2003).

The F added to soils in fertiliser undergoes similar reactions to P (Figure 3). F and P anions are mostly specifically adsorbed to soil components. The common soil properties that influence the partitioning of F between soil solid and solution phases are listed in Table 4. In New Zealand pastoral soils, the quantity of F in soil solution represents <1% of the total soil F content (Loganathan et al. 2006). In soil solution, F occurs both as free ionic forms and complexed with other ions (Figure 3). The greatest proportion of the F in pastoral soils is associated with Fe and Al oxides and a residual non-acid soluble fraction. The proportion of F associated with organic fractions appears to be very low (Loganathan et al. AJSR, in press).

Soil pH has often been found to be the most important single soil property that determines F mobility and bioavailability in soils. Fluorine solubility is lowest between 5.5 and 6.5 (Figure 4) and it increases dramatically at lower and higher pH (Larsen and Widdowson 1971, Omuetti and Jones 1977) (Figure 4). Increased solubility at low pH is due to F-forming complexes with Al in the soil solution leaving little free F (F⁻) ions in soil solution for sorption. In slightly acidic New Zealand pastoral soils (pH in water 5.4-5.9), only up to 55% of the F in soil solutions were estimated to be complexed to Al and the remaining F in soil solution was in the uncomplexed F⁻ form (Manoharan et al. 1996, 2006). In acidic (pH in 0.01 M CaCl₂ 4.7-4.8) Australian pastoral topsoils (0-100 mm depth), 95-98% of the F was estimated to be complexed with Al (McLaughlin et al. 2001) but at lower soil depths (200-300 mm depth) the pH was higher (pH in 0.01 M CaCl₂ > 5.2) and F⁻ was the dominant form of F in soil solutions. At higher pH, the negative electrostatic potential of the oxide coatings on soil particles increases, resulting in decreases in the retention of F on the soil. Increases in F⁻ concentration in

soil solution also result from the displacement of adsorbed F^- by increased concentration of OH^- in soil solution at higher pH (Larsen and Widdowson 1971).

The laboratory studies of Omueti and Jones (1977) provide evidence of the effect of soil pH on the sorption of F (Figure 4).

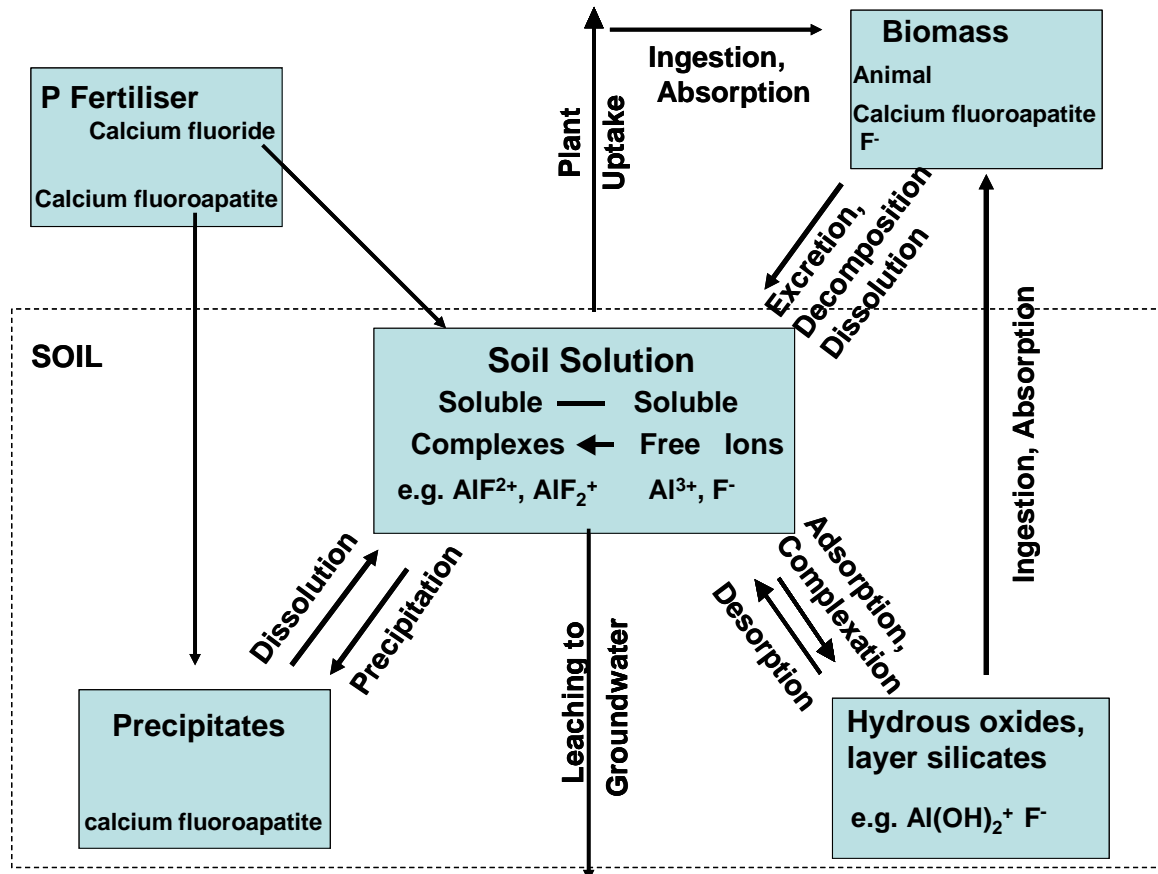


Figure 3. Biological, chemical and physical reactions influencing the fate of fertiliser F in soil.

Increases in F concentration in soil solution leads to increases in their mobility and bioavailability.

Table 4. Soil properties influencing the dynamics of F in soils

Soil property	F	References
pH	Decrease of pH below 5.5 and increase above 6.5 increase solution conc.	Larsen and Widdowson (1971); Loganathan et al. (2006)
Fe and Al oxides and allophane	Decrease of solution conc. due to sorption	Bower and Hatcher (1967); McLaughlin et al. (1996); Omuetti and Jones (1977); Pickering (1985)
Mn oxides	No significant influence	Pickering (1985)
Layer silicates	Decrease of solution conc. due to sorption	Kau et al. (1998); McLaughlin et al. (1996); Pickering (1985)
Organic matter	Indirect effect (see text)	Loganathan et al. (2006); Pickering (1985)
Other ions in solution	Increase of solution F conc. due to increase Al conc. High rates of Ca application reduce solution F conc.	Fung and Wong (2004); Manoharan et al. (1996) ; McLaughlin et al. (1996) ; McLaughlin et al. (2001)
Eh (redox potential)	Increased redox potential likely to reduce F ⁻ sorption but no published data	

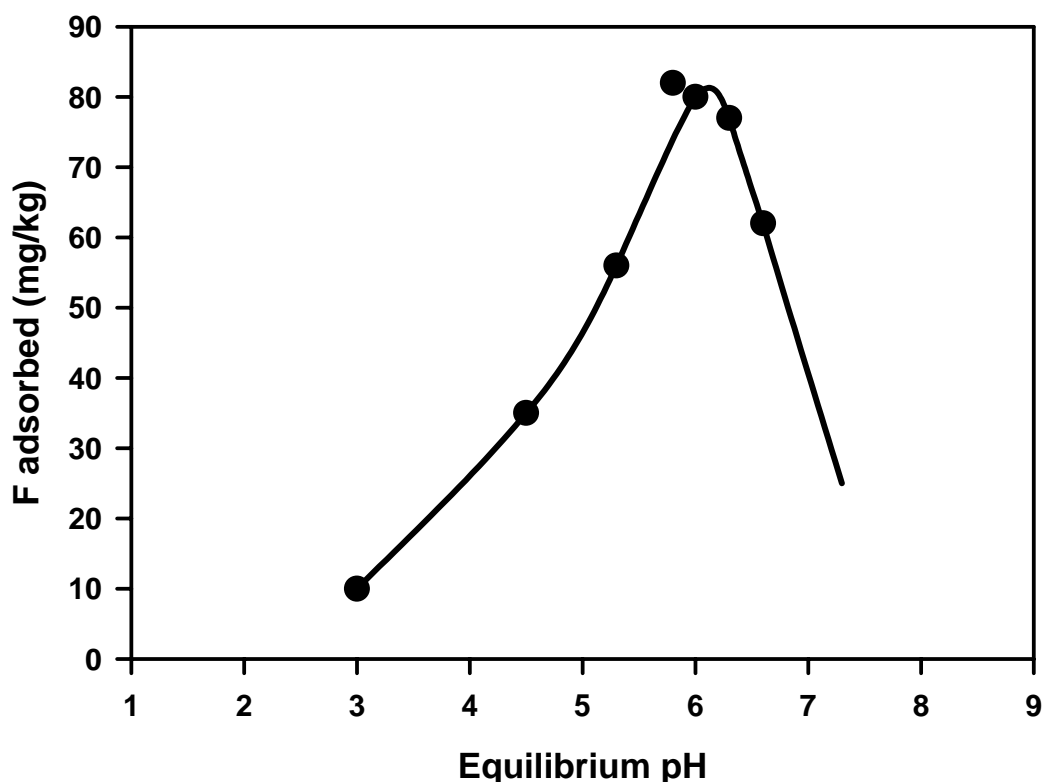
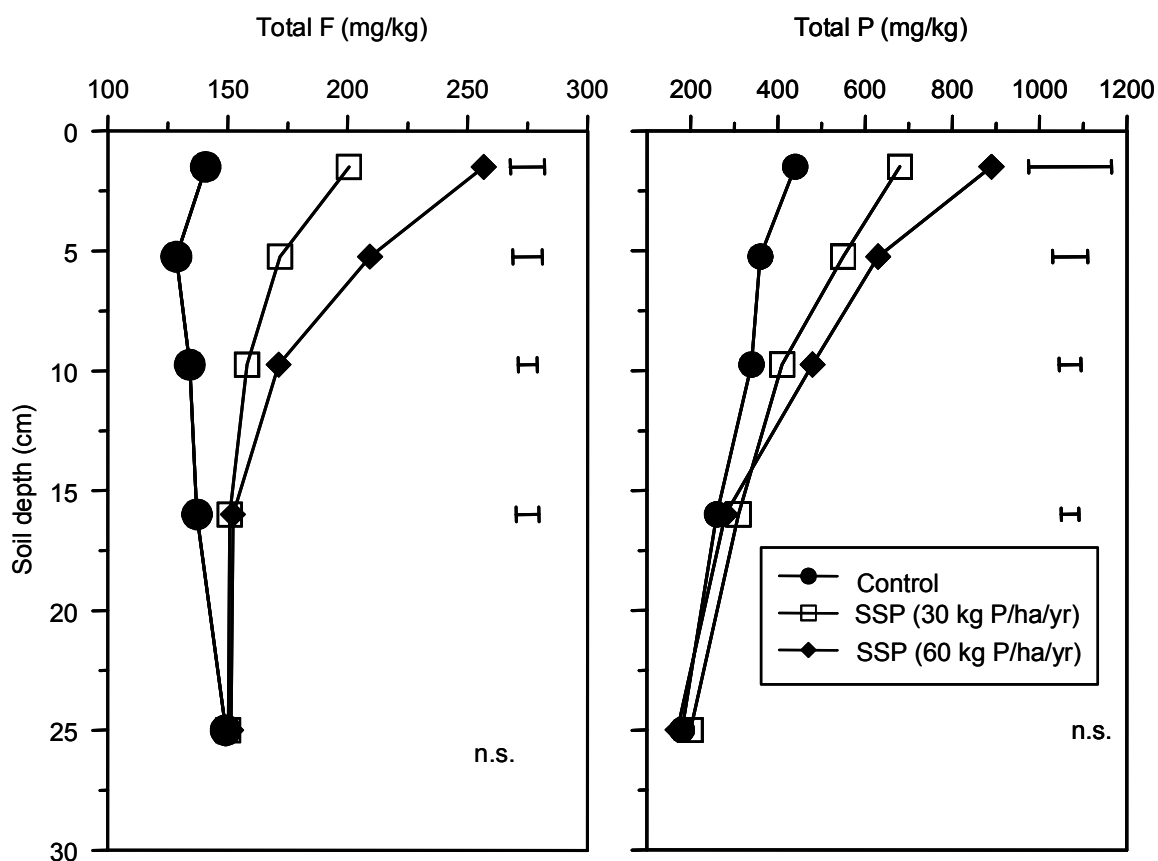


Figure 4. Effect of pH on F⁻ adsorption by an A horizon of Cisne soil (Mollic Albaqualf) from Illinois, USA. Initial F concentration was 4 mg/litre (Omueti and Jones 1977).

Distribution of fertiliser-derived fluorine in the soil profile

Fluorine originating from P fertilisers accumulates in topsoil either as insoluble fertiliser residues or strongly bound to Fe and Al oxides coatings of soil particles. The relative mobilities of F and P following 10 years annual application of SSP (30 and 60 kg P/ha/yr) in a pastoral soil were similar (Figure 5). More than 50% of the total quantity of the elements accumulated in the profile remained within the top 75 mm soil. Likewise, in six other New Zealand pastoral soils with long-term P fertiliser application histories, 33-66% of fertiliser-derived F was recovered in the top 75 mm soil (Loganathan et al. 2001). The slow rate of downward movement of F and P is due to their relatively strong adsorption on to clay minerals and oxides of Fe and Al (Bower and Hatcher 1967). Because of the strong retention of F in surface soil layers the leaching potential of these elements to contaminate ground water is expected to be low, however, the strong retention may lead to increased intake of these elements by grazing livestock if they ingest large amounts of soil (see later section).

In highly acidic soils, high rates of F additions in gypsum and fertiliser can lead to ground water contamination, especially for coarse-textured soils with shallow water tables (Specht and McIntire, 1961) and in Australian soils receiving gypsum neutralised-red mud (Summers et al. 1996) .



(Horizontal bars represent l.s.d. ($p=0.05$). n.s., treatment effects not significant.)

Figure 5. Effect of 10 years annual applications of SSP to sheep grazed pasture on the downward movement of F, and P in a Pallic Soil (an Aeris Fragiaqualf in New Zealand, redrawn from Loganathan et al. 2001).

Fluorine uptake by Pasture

Phosphate fertiliser application to pastures increases topsoil F concentration but seldom increases the F concentration in the herbage (Loganathan et al. 2001). For example, McLaughlin et al. (1996) reported that, on a highly fertilized Australian soil, F concentrations in pasture herbage were not significantly greater than in pasture growing on adjacent unfertilized soil. The low plant availability of F in most soils is consistent with low soil solution F concentrations because F is strongly bound to Fe and Al oxide surfaces and layer silicates (Figure 3, Table 4). The combination of low soil pH and high soil F concentration is more likely to raise pasture F concentrations. For example, in an Australian pasture soil of $pH_{(CaCl_2)}$ 4.6, it was reported that the mean pasture herbage F concentration (22 mg F/kg DM) in P fertilised plots (annually topdressed with 125 kg SSP/ha for 36 years) was significantly higher than that (11 mg F/kg DM) in the unfertilised plots (McLaughlin et al. 2001). Similarly, out of 12 soils around aluminium smelters in Norway, in 11 soils having pH of 4.1–5.8 and water soluble F of 1–6 mg/kg the F concentration in ryegrass shoots was 3–9 mg F/kg DM, but in a highly F-contaminated soil having a pH of 4.9 and water-soluble F concentration of 33 mg/kg the F concentration in ryegrass shoots reached levels of 15 to 18 mg F/kg DM (Arnesen 1997). These pasture F concentrations are lower than the dietary F tolerance concentration limit of 30–150 mg/kg reported for grazing livestock (Cronin et al. 2000)

High rates of F (80–160 mg/kg soil, Manoharan et al. (2006)) in strongly acidic soil conditions (pH (water) 4.3–4.6) will reduce the root growth of sensitive species like barley due to the toxicity of high concentrations of Al-F complexes (100–300 μM) formed in soil solution. Stevens et al. (1997) have shown that the toxicity depends on the proportion and concentration of the different types of Al-F species in nutrient solutions (AlF^{2+} , AlF_2^{1+} , AlF_3^0). These results appear to contradict those of Cameron et al. (1986), who demonstrated that addition of F to nutrient solution decreased Al phytotoxicity but the behaviour of F in soils is more complex. The addition of F to acid soils will dissolve soil solid-phase causing more Al to be released to the soil solution (Moore and Richie 1988). At current recommended rates of P fertiliser application to moderately acidic pastoral soils (pH (water) 5.5–6.0), it is unlikely that the concentrations of Al-F complexes (10–30 μM) will be sufficiently high to cause phytotoxicity (Manoharan et al., 2006). Continued application of high rates of P fertilisers to increasingly acidic soils, is expected to eventually create an F risk to plants (Stevens et al. 1997) and grazing livestock (Stevens et al. 2000).

Fluorine intake and retention in grazing livestock

Fluorine intake by grazing animals via pasture herbage intake is much lower than through soil ingestion because of the very low F concentration in pasture herbage (generally < 5 mg/kg dry matter, Loganathan et al. (2001); McLaughlin et al. (1997)) compared to topsoil F concentration (217–454 mg/kg soil, Loganathan et al. (2001)). Soil adheres to grazed pastures and forage crops and soil ingestion is an incidental part of forage intake by grazing and foraging animals (Table 5).

Table 5. Soil ingestion per unit of forage dry matter consumed by grazing and foraging animals. (modified from Sheppard, 1995)

Animal environment	Soil ingested g/kgDM	Reference
Cattle grazing pasture	56-230	Fries et al. (1982a, b), Healy (1968a,b)
Cattle fed cut forage	3.2-27	Kirby and Stuth (1980), Mayland et al. (1975, 1977)
Pigs grazing root crop	150-260	Fries et al. (1982a, b),
Sheep grazing swedes	25-85	Healy and Drew (1970)
Sheep grazing pasture, > 6 ha ⁻¹	35-190	Beresford and Howard (1991), Healey (1973)
Sheep grazing pasture, < 6 ha ⁻¹	4-39	Healy (1968b), Healy and Ludwig (1965), McGrath et al. (1982)

Although the amount of soil ingestion is much less than pasture consumption, many factors including season and stocking rate may influence the magnitude of the ingestion of soil. The amount of soil ingested can increase several fold during the wetter winter/early spring when more soil adheres to herbage and the grazing pressures on the pastures are high (Figure 6). In New Zealand, the cooler, and

wetter, winter/early spring months result in more soil adhering to the leaves of pasture plants, while higher stocking rates cause pastures to be grazed low, thereby increasing soil intakes (Figure 6, Healy 1973).

Thus high F intakes associated with the ingestion of soil occur only for 2–3 months of the year. For example a rising 1year old lamb on winter (June-August) pasture rations of 1 kg DM/day (11 mg F/kg DM) may ingest 0.2 kg soil (450 mg F/kg) resulting a short term intake of 101 mgF/kg DM. If only 50% of the soil F is adsorbed, effects on lamb growth rates are unlikely. Hobbs et al., (1954) found that the growth rate of 8 - 12 months old sheep was significantly reduced when fed a concentrate containing 200 mgF/kg for 140 days. Sheep of the same age fed a concentrate containing 100 mg/kg feed over a period of 3 years, went on to record normal growth rates, lambing percentages and lamb weight gains.

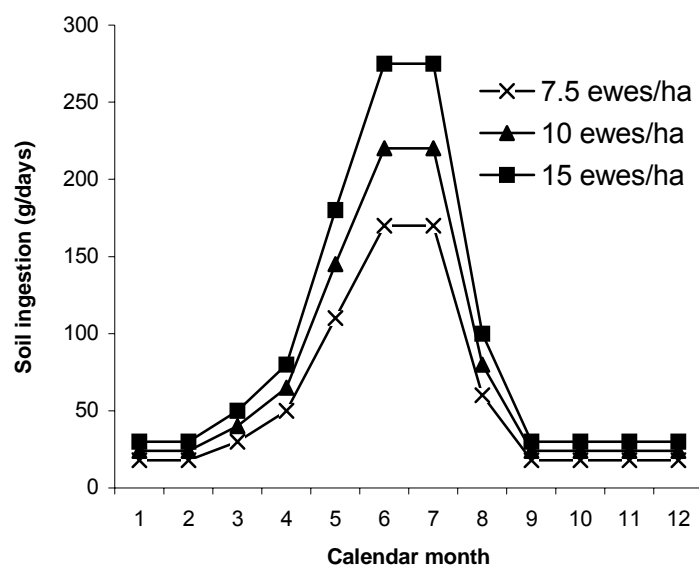


Figure 6. Soil ingestion by grazing sheep as a function of calendar month and stocking rate in New Zealand (Summer months 12, 1, 2; Autumn 3, 4, 5; Winter 6, 7, 8; Spring 9, 10, 11) (data from Healy 1968a, 1973).

Assuming a stocking rate of 2.9 dairy cows/ha and an annual herbage dry matter production of 15000 kg/ha and using a herbage F concentration of 3 mg F/kg the rate of F intake by dairy cows through pasture ingestion (85% dry matter utilisation) is calculated to be <13 g F/ cow /year. This rate of total F intake is less than 0.7% of F added annually in fertilisers to soil (assuming a rate of fertiliser addition of 30 kg P/ha/year, and F and P contents of fertiliser of 1.5 and 9% respectively). In comparison, the rate of F intake by a dairy cow through soil ingestion is 87-181 g F/cow/year assuming an annual average soil ingestion rate of 1095 g/cow/day (Cronin et al. 2000) and soil F concentration of 217 to 454 mg F/kg soil (Loganathan et al. 2001). This annual rate of total F intake is equivalent to 1.8-3.6% of F applied in P fertiliser per year. Thus F ingestion by grazing animals is increased 3–6 times if the animal has the opportunity to ingest soil.

Weinstein and Davison (2004) reported that the proportion of ingested F that is absorbed and retained by an animal depends on the acidity of the digestive system, concentrations of chemical species such as Ca and Al in the digestive system and the presence of calcified tissues in the body. They illustrated this by citing several examples on F absorption in humans, cattle, rabbit, voles and insects. The values

reported for F absorption and retention in sheep and cattle feeding on different types of diet are presented in Table 6. The values are lower for ingestion of soil compared to those for pasture and the soluble salt, NaF. The difference in the absorption values reported for soils is probably due to the difference in the chemical form of F in the soils, which is dictated by soil properties such as pH, mineralogy, texture, and the period allowed for F added in fertilisers to react with the soils. It could also be due to differences in the design and conduct of the trials.

Retention of fluorine in grazing animals

Grazing livestock accumulate F in bones and teeth as calcium fluoroapatites (typical F concentration of enamel and dentine is 250–700 mg/kg; and bones is 250–900 mg/kg) (Clark and Stewart 1983; Milhaud et al. 1992). Fluorine does not accumulate in the soft tissues (Grace et al. 2003). Typical F concentrations of sheep and cattle liver, kidney, thyroid, heart and pancreas are < 3 mg/kg dry tissue. On the basis of cattle studies, the following bone F criteria have been established to describe fluorosis. Bone F concentrations of <2400, 2400–3200, 3200-4800 and 4800-7000 mg/kg DM reflect an innocuous, threshold, moderate and severe fluorosis, respectively (Shupe 1980; Wheeler and Fell 1983). Bones with F concentrations of >4800 mg/kg DM appear mottled but are normal on X-ray examination, while bone with F concentrations between 5000-7000 mg/kg DM are abnormal as they are more porous, chalky white, enlarged with irregular surfaces and have altered mechanical properties. The F not sequestered into bone is excreted in the urine. For sheep, urinary losses are 10-23% of the ingested F, leaving 27-40% of the absorbed F to be retained in the bone (Grace et al. 2003). High bone F concentrations are indicative of animals being on a high F intake for an extended period.

Table 6. Apparent absorption (% of intake) and retention (% of intake) of F by livestock

Animal	F source	Trial design	Absorption	Retention	Reference
Sheep (14 months old)	Lucerne	63-day feeding/8-day F balance trial	75–77	34–35	Grace et al. (2003)
	NaF + lucerne		69	27–31	
	Soil (10% by wt in lucerne feed, 600 and 1751 mg F/kg soil) + lucerne		44–53	28–42	
Dairy cattle (>7 years old)	Soil (10% by wt in lucerne feed, 1452 mg F/kg soil)	63-day feeding/10-day F balance trial	43–44		Grace et al. (2005)
Sheep (2-5 year old)	Seven soils (30% by wt. in forage feed, 235–1030 mg F/kg soil, close to an Al smelter)	28-day feeding/5-day F balance trial	5-25		Milhaud et al. (1989)
Lambs (at weaning)	Dicalcic phosphate + grain meal Defluorinated phosphate Phosphate rock	70-day feeding/bones analysed		50-53** 18-21** 61-72**	Clay and Suttie 1985)
Bulls (5 years old)	Soil (6% by wt in hay + grain feed, 718 mg F/kg soil, close to an Al smelter)	10-months feeding/5 balance studies	30-41		Wöhlbier et al. (1968)

** F retention relative to NaF

Continuous exposure to soil F ingestion

An indoor sheep feeding trial was conducted in New Zealand to simulate high soil ingestion during one winter season. In this trial, young sheep (14 months old) were fed daily with lucerne (7 mg F/kg dry matter) or lucerne plus soil (184 mg F/kg dry matter) daily for 63 days. The blood F concentration in sheep fed with soil increased significantly within 23 days and then remained constant up to 55 days (Figure 7). The F intake had little or no effect on the F concentrations of the kidney or liver but bone F concentrations were significantly increased by the end of the trial at 63 days (Table 7).

Table 7. Effect of 63 days of soil F ingestion on the F concentrations (mg F/kg DM) of ribs and radius bones, kidney and liver of young sheep. (Grace et al. 2003)

Treatment	Lucerne basal diet 7 mg F/kgDM	Lucerne + soil F 184 mg F/kgDM
Rib	739 ± 42.0	1388 ± 45.9
Radius	726 ± 40.4	1271 ± 76.5
Kidney	1.1 ± 0.4	2.9 ± 0.7
Liver	<0.08	<0.08

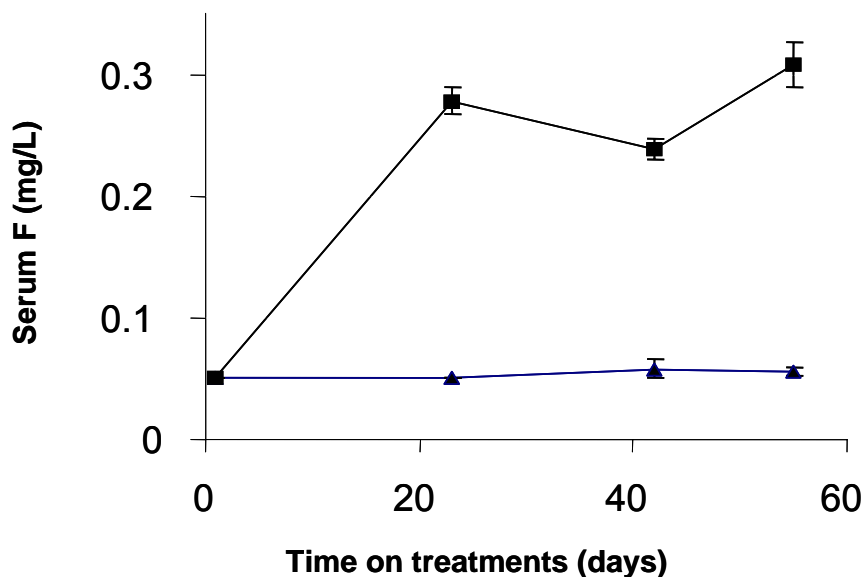


Figure 7. Changes in blood serum F concentrations of young sheep ingesting a diets contaminated with soil F at ■ 184 mg F/kg dry matter and ▲ 7 mg F/kg dry matter .(redrawn from Grace et al. 2003).

The bone F concentrations, however, were below a threshold bone F concentration of 2400 mg F/kg dry matter, at which minor bone abnormalities may be observed. This suggests that young sheep exposed to an increase in F intake, as a result of soil ingestion, for one winter season under New Zealand conditions are unlikely to develop chronic fluorosis (Grace et al. 2003).

Temporal change in exposure to soil F ingestion

Suttie et al. (1972) found that as F intake to dairy cows was reduced so bone F concentrations decreased. Grace et al. (2007) have shown that some bone F, which accumulated during periods of increased soil ingestion may be re-mobilized and bone F concentrations decreased when soil F ingestion rates were lower during summer and autumn (Figure 8). This work involved a 345-day soil feeding trial (Grace et al. 2007), in which lambs were daily fed for 94 days with lucerne/grain pellets containing soil having very high F concentration (224 mg F/kg DM containing 10% soil by weight) showed that the bone F concentration increased from approximately 200 mg F/kg dry matter (DM) at Day 1 to 1800–2700 mg/kg DM at Day 94 (Figure 8b). When the F intake was decreased at Day 94 (12 mg F/kg DM containing only lucerne/grain) the bone F concentrations then decreased to 1069–1075 mg/kg DM after 59 days (at Day 153) and remained at not more than 1200–1500 mg/kg DM for up to Day 345. These results confirm those of Suttie et al. (1972), that changes in soil F intakes by sheep are immediately reflected by change in blood F concentrations (Figure 8a). Increased F ingestion, however, causes a slower rate of increase in bone F concentrations (Figure 8b) and a subsequent decreased in soil F intake is reflected in a slow decline in bone F. (Grace et al. 2007). In these young growing sheep only part of the F accumulated in the bones during winter/early spring months can be remobilized when the F intake becomes low once again during summer and autumn (Figure 8b). Phillips et al. (1963) also found a slow reduction in bone F once cows were removed from a high F diet. Whereas, Grace et al. (2007) and Suttie et al. (1972) observed an immediate reduction in serum F concentration when sheep and cows were removed from high F diets, urinary F may continue to be excreted at higher levels (Phillips et al., 1963) allowing the skeletal F burden to be slowly reduced., (Further studies are required to investigate this seasonal effect on bone F accumulation and re-mobilisation as animal age varies).

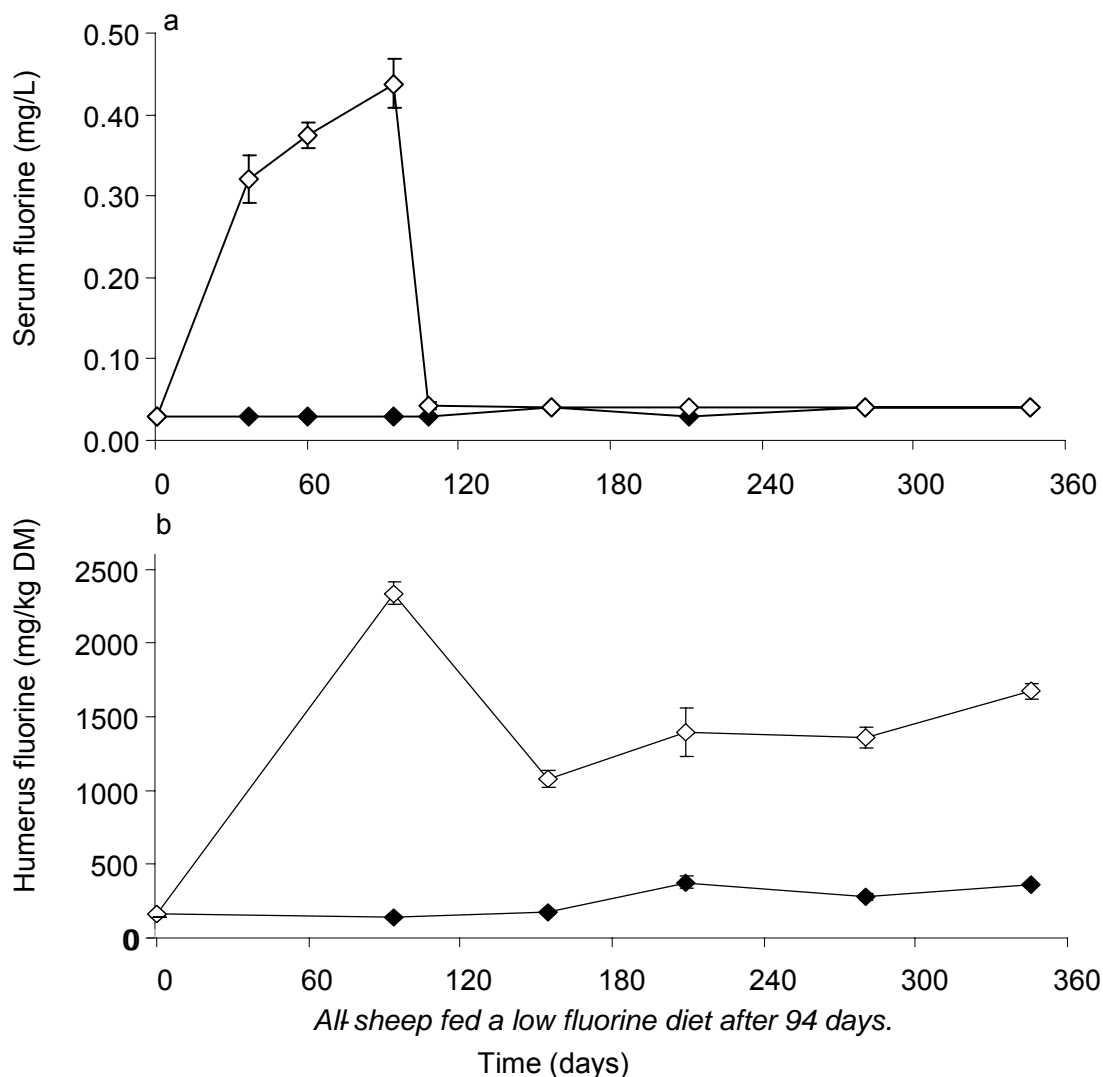


Figure 8. A comparison of feeding a high soil fluorine (F) diet (224 mg F/kg dry matter; DM; ◇) for 94 days followed by a low-F diet (12 mg F/kg DM) for 251 days, with feeding a low-F diet (12 mg F/kg DM; ◆) for 345 days on the mean (\pm standard error) concentrations of (a) serum F and (b) humerus bone in the young sheep. (redrawn from Grace et al.2007).

Grazing Livestock products and food chain considerations

When rising 1year sheep ingest superphosphate enriched soil for a period of 60days, 47 - 66% of the F is excreted in dung and 11-16% in urine (Grace et al.2003). Most animal feeding studies indicate that of the F retained in the animal virtually all is present in bone, teeth or horn (Table 8). Even when the dietary F intake of cattle and sheep is potentially toxic, 99% of the F retained in the body will be sequestered in bone and antler (Table 8). Even in sheep with fluorosis, F concentrations found in brain and kidneys were 7.9 and 2.6 mgF/kg respectively, whereas in muscle, and liver the levels remained below 0.5 mgF/kg (Milhaud et al., 1983). Similarly milk F concentrations remained low (0.06, 0.10, 0.14 and 0.20 mg/L) even when Holstein cows were fed diets with elevated F content (10, 29, 55 and 109 mg F/kg DM, respective) over a life time of 7 years (Greenwood et al. 1964). The ability of animals to sequester dietary F in bone, teeth or horn and excrete excess in urine results in the animals being an effective filter removing F from the human food chain. The

exception being if bone or horn products enter the human food chain. One example of this is the medicinal use of deer velvet. At the recommended dose of 2.5 g velvet powder per day the daily recommended human adult F intake of 1mg is likely to be exceeded if antlers were harvested from deer in medium to high F environments (Walton and Ackroyd, 1988).

We can conclude therefore that if left to farmers and dairy cows, they will not deliver F concentrations in their milk that will exceed the daily recommended F dose for children (0.06 mg F/kg body wt./day, Ahokas et al.,1999) and adults . If, however, milk powder is reconstituted with F enriched water (Ahokas et al.,1999) or politicians legislate to add F to milk (O'Mullane 1994) then who can blame the farmer and the cow!

Table 8. The range of F concentrations in products from grazing animals.

	Low dietary F	High dietary F	Reference and feed F contents.
	(mgF/kg)		
Bone (cattle)	700	2000	Anon 1974. low = ~10 mg F/kgDM; high = 20-30 mgF/kgDM
Bone (sheep)	700	1500	Grace et al.2003. low = 5mg F/kgDM; high = 50mgF/kgDM
Deer (antlers)	600	2000	Suttie et al.1985. low = 25mg F/kgDM; high = 50mgF/kgDM
Deer (antlers)	300	2000	Walton and Ackroyd 1988, wild deer uk.
Liver (sheep)	<1	<1	Grace et al.2003. low = 5mg F/kgDM; high = 50mgF/kgDM
Kidney (sheep)	1	2	Grace et al.2003. low = 5mg F/kgDM; high = 50mgF/kgDM
Milk	0.06	0.2	Greenwood et al.1964. low = 10mg F/kgDM; high = 109 mgF/kgDM
Beef steak	0.3		Taves,1983,

Mitigation strategies to reduce F risk to grazing animals

Currently there is no cost-effective method to reduce the F concentration of P fertilisers and therefore is not an option for decreasing the rate of F accumulation in soils and its subsequent intake by animals. During the manufacture of P fertilisers by acidulation of phosphate rocks, the gaseous F compounds released are removed by scrubbing with water and the resulting scrubber liquor is then often used in the fertiliser manufacturing process (acid dilution and fertiliser granulation). If the scrubber liquor is not recycled the F concentration in the final fertiliser product can be reduced slightly.

Reducing P fertiliser application rates will reduce F input to soils. Increases in soil test values (Olsen P) are strongly correlated with increased total soil F concentration (Loganathan et al. 2003). Therefore by not exceeding the optimum Olsen P value, farmers can avoid applying excess P and this will slow the rate of F input to soils. Furthermore, available organic manures with low F/P ratio can also be used to reduce the F input.

Withholding stock from pastures recently top-dressed with P fertilisers until at least 25 mm of rain has fallen to wash away the F in the pasture can prevent acute F poisoning from fertiliser ingestion. This requires a planned fertiliser application programme so that some unfertilized paddocks are always available for grazing or animals can be fed forage crops until rain washes down the fertilisers adhering to the pasture. Under rotational grazing, fertiliser can be spread on paddocks that have been most recently grazed to maximise the interval between application and grazing.

As soil ingestion is the main source of F intake by grazing animals, it can be minimised by maintaining good pasture cover and reducing stocking rates of grazing animals especially during winter. Grazing animals ingest topsoils (0-30 mm depth) that generally have a higher F concentration than the subsoil horizons. Therefore deep-ploughing lands high in topsoil F concentration during pasture renovation can reduce the topsoil F concentration and hence F intake by animals. A recent study by Loganathan et al. (2007) showed that cultivation of soil by ploughing to a depth of 150 mm using a mouldboard plough once in six to nine years decreased F concentration in the top 30 mm soil depth by approximately 20%.

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