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## Fluoride: A review of its fate, bioavailability, and risks of fluorosis in grazed-pasture systems in New Zealand

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**Abstract** Fluoride (F) is an essential element for animal growth, not readily taken up by plants from soils, yet cases of acute fluorosis in grazing animals caused by ingestion of phosphatic fertilisers, volcanic ash, and industrial wastes remind us of its potential hazard. Fluoride concentrations in topsoils slowly increase where annual inputs through atmospheric pollution and phosphatic fertilisers exceed losses. This paper reviews information on the fate of F in grazed pasture systems with the aim of assessing the potential toxicity of accumulating soil F. A preliminary F-cycling model for grazed pastures, based on the review of international literature and F concentrations in selected New Zealand pasture soils, indicated that grazing sheep and cattle obtain over 50% of their dietary F (and this may be >80% during winter) from soil ingestion. The model suggests that at the extremes of the ranges of the measured winter soil ingestion ( $143\text{--}300\text{ g d}^{-1}$  for sheep and  $900\text{--}1600\text{ g d}^{-1}$  for cattle) and dietary F absorptivity (bioavailability) of soil F (20–38%), total topsoil F concentrations in the range of  $372\text{--}1461\text{ }\mu\text{g F g}^{-1}$  could cause chronic fluorosis in sheep and  $326\text{--}1085\text{ }\mu\text{g F g}^{-1}$

in cattle. We recommend that research is undertaken to measure F accumulation rates and soil F dietary absorptivity for a range of intensively managed New Zealand pasture soils.

**Keywords** cattle; fluoride; pasture; fluoride bioavailability; fluorosis; phosphate fertilisers; sheep; soil ingestion; volcanic ash

### INTRODUCTION

Fluorine is widely dispersed in nature and is estimated to be the 13th most abundant element on our planet (Mason & Moore 1982). While being distributed universally throughout soils, plants, and animals, F is assumed to be an essential element in animals. However, no environment has been described where F is limiting (National Research Council 1980). By contrast, the effects of excess F are only too well known in many parts of the world, where endemic fluorosis affects grazing animals and humans alike. In parts of India, Australia, and Africa, groundwater with high F concentrations causes fluorosis in grazing animals, while in parts of North Africa chronic fluorosis is caused by contamination of plant foliage and water by F-rich phosphatic dust blown from phosphate rock deposits (Underwood 1981). Chronic and acute fluorosis is also common in Iceland during and following volcanic eruptions, where F-rich gases and ashes contaminate surrounding pastures (Roholm 1937).

Human activities have extended the areas affected by fluorosis. Factories producing fertiliser, aluminium, steel, bricks, and glass, as well as coal-fired power stations, produce F-rich emissions that can seriously affect surrounding plants and animals (Roholm 1937). Supplements containing phosphate rock materials are fed out to ruminants in amounts that have sometimes also produced chronic and acute fluorosis (Suttie 1969; Jubb et al. 1993; Schultheiss & Godley 1995). Also, the extraction of deep F-rich groundwaters to maintain production

during droughts and summer periods has caused numerous cases of fluorosis (Botha et al. 1993).

In addition to these point-source F polluters, vast areas of land around the world have F added on a yearly basis with the application of phosphatic fertilisers (Robinson & Edgington 1946). Fluoride added in this way persists in most soils and has slowly accumulated over the last century. In New Zealand for the year ended 30 June 1994, 1.4 million tonnes of single superphosphate (SSP) was applied to c. 13.5 million ha of land (Registrar-General 1996). With an average 1.5% F in the SSP (Evans et al. 1971; P. Loganathan et al. unpubl. data), this equates to c. 21 000 tonnes of F added in only one year (c. 1.6 kg ha<sup>-1</sup>). Assuming similar rates of SSP application over the last 50 or more years, there has probably been >1 000 000 tonnes of F added to pastoral soils in New Zealand. What does not appear to be known, is just what are the likely repercussions of this continual addition of F to our food-producing soils. How will it affect our crops, grazing animals, water supplies, and soil organisms? How long will it take before signs of excess F in our pastoral and crop systems show?

In this review we compile the information currently known and identify what needs to be researched, in order to answer these questions. The answers are drawn from many fields of research, including geochemistry, soil science, plant science, animal science, and veterinary science. Our review is an attempt at integrating published work from these diverse areas and from this to develop models for predicting the effects of accumulating F on New Zealand pastoral systems.

## FLUORIDE IN SOILS

### Natural abundance of F in soils

Native F in soils is generally contained within the minerals apatite (specifically fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F)), fluorite (CaF<sub>2</sub>), cryolite (Na<sub>3</sub>AlF<sub>6</sub>), forms of topaz (Al<sub>2</sub>(SiO<sub>4</sub>)F<sub>2</sub>), and within micaceous clay minerals. Fluoride can also be present in soil as specifically and non-specifically adsorbed ions and compounds (Bowen 1966; Robinson 1978; Pickering 1985). Native soil F content is highly dependent on soil parent material. It can be very high in phosphate-derived soils in North Africa, USA, and Russia, and on some Pacific and Caribbean Islands, where values of 35 000–42 000 µg g<sup>-1</sup> soil are reported (Manley et al. 1975). Soil F can also be high in some volcanic areas that have

regular inputs of fresh F-rich volcanic ash; the best example of this is in Iceland (Roholm 1937; Óskarsson 1980). However, in most areas, where soils are developed in quartzo-feldspathic rocks and sediments, phosphate-free carbonate rocks, and older igneous rocks, native soil F contents are substantially lower (Table 1).

In almost all studies of total soil F, high variability is reported between soils that are apparently uncontaminated (Table 1). Many authors correlate this variability with particle size of the soil; in particular, increasing total F is associated with increasing clay content (Robinson & Edgington 1946; Eysinga 1974; Manley et al. 1975; Omueti & Jones 1977a). Under natural conditions it is also common for total soil F to increase with depth in the profile (Robinson & Edgington 1946). This may be due to low affinity of F for organic matter (Omueti & Jones 1977a), increasing clay content with increasing soil depth, and the long-term downward movement of F through the profile.

Labile forms of soil F are variously estimated by water soluble, acid-extractable, and resin-extractable F concentrations. The most common method of estimating water soluble F is by shaking soil with a 0.01 M CaCl<sub>2</sub> solution (Larsen & Widdowson 1971). Labile soil F estimated by any one of these methods is often one to three orders of magnitude lower than the total soil F (Table 1).

Fluoride forms its most stable bonds with Fe, Al, and Ca, and labile F is held by soil components that contain these elements, including clay minerals, calcium and magnesium compounds, and iron and aluminium compounds (Bower & Hatcher 1967; Omueti & Jones 1977b; Häni 1978). At low concentrations, iron and aluminium oxides and hydroxides have the greatest ability to adsorb F and, among the layer-lattice clay minerals, kaolinite and halloysite have the greatest capacity for adsorption (Bower & Hatcher 1967; Omueti & Jones 1977b; Morshina & Fanaskova 1987). The degree of F adsorption is also controlled by soil pH and is greatest in non-calcareous soils, which generally contain higher Al levels (Larsen & Widdowson 1971; Omueti & Jones 1977b; Pickering 1985; Barrow & Ellis 1986).

Natural soil solution F concentrations are normally a small proportion of labile soil F, and are normally <1 µg ml<sup>-1</sup>. Almost all soils hold F strongly, and only in coarse, clay and Fe/Al oxide-poor soils is F weakly held (Pickering 1985). Measured normal ranges of soil solution F in the USA were 0–1.5 µg ml<sup>-1</sup> (Fleischer & Robinson

1963), and in Sweden 0.3–0.4  $\mu\text{g ml}^{-1}$  (Noemmik 1953). In a suite of industrially polluted soils, total soil F was 616–2700  $\mu\text{g g}^{-1}$ , the distilled-water extractable fraction was 10–292  $\mu\text{g g}^{-1}$ , and the soil solution F was 0.3–8.2  $\mu\text{g ml}^{-1}$  (Polomski et al. 1982a). Manoharan et al. (1996) reported soil solution F concentrations ranging from 0.23 to 0.49  $\mu\text{g ml}^{-1}$  in New Zealand pasture topsoils fertilised for 8 years with superphosphate at a rate of 30–60  $\text{kg P ha}^{-1} \text{yr}^{-1}$ .

In most developed and developing countries native soil F contents are strongly affected by application of fertilisers and by deposition of industrial air-borne pollutants. Labile and water-soluble F concentrations appear to be affected most by industrial pollution (Polomski et al. 1982a; Haidouti 1991) and superphosphate application (Larsen & Widdowson 1971; Manoharan et al. 1996). However, prolonged application of superphosphate can have marked effects on total soil F (e.g., Kudzin & Pashova 1970; P. Loganathan et al. unpubl. data).

#### Mobility and adsorption of F in soils

Many of the common F compounds are only sparingly soluble, e.g.,  $\text{CaF}_2$  (0.016  $\text{g l}^{-1}$ ),  $\text{MgF}_2$

(0.13  $\text{g l}^{-1}$ ), and  $\text{Na}_3\text{AlF}_6$  (0.42  $\text{g l}^{-1}$ ), although some others are quite soluble, e.g., HF,  $\text{SiF}_4$  (hydrates), and NaF (40  $\text{g l}^{-1}$ ) (Pickering 1985). Many investigations (detailed below) have been made to gauge the F adsorption of soils and to determine which soil components are responsible for this.

Early studies concluded that F is retained by finer textured soils, particularly those with a significant clay component (Robinson & Edgington 1946; Brewer 1966). Later work revealed that the sorption of F also depended strongly on soil pH. At a pH of 6, F sorption was at a maximum and it decreased dramatically (by a factor of 2) at one unit higher or lower pH (Larsen & Widdowson 1971; Gilpin & Johnson 1980). This behaviour was parallel with that of the solubility of natural fluorapatite under changing pH. Barrow & Ellis (1986) later predicted that at low pH, complexes between Al and F formed in soil solution and that little was present as free  $\text{F}^-$  ions. At high pH an increasingly unfavourable electrostatic potential decreases retention of F on the soil and increases the  $\text{F}^-$  concentration in soil solution. It is also due to displacement of adsorbed  $\text{F}^-$  by the increased concentration of  $\text{OH}^-$  in soil solution at the higher pH (Larsen & Widdowson 1971).

**Table 1** The total and labile native F concentrations (range, and mean within parenthesis;  $\mu\text{g g}^{-1}$  soil) of various soils. Water soluble F is measured by extraction with differing concentrations of  $\text{CaCl}_2$  as well as with water.

Location and number of samples	Total F concentration	Water-soluble F	Resin extractable F	Source
Argentina – La Pampa	24–1220	0.53–8.33		Lavado & Reinaudi (1979)
Canada – New Foundland		1.0–2.7		Sidhu (1979)
China	186–388	0.8–2.7		Fung et al. (1999)
England	110, 230			Agate et al. (1949)
England (100)	(300)	0–1.6 (0.25)	0–50 (20)	Larsen & Widdowson (1971)
France		0.1–8		Bertrand & Wolf (1970)
Greece	95–108			Haidouti (1991)
Netherlands (102)	39–679			Eysinga (1974)
New Zealand			20–30	Stewart et al. (1974)
New Zealand – Bluff (25)	22–230 (134)			Manley et al. (1975)
New Zealand (28)	68–540 (200)			Gemmell (1946)
New Zealand (3)	116, 133, 214			P. Loganathan et al. (unpubl. data)
Russia (46)	30–320 (200)			Vinogradov (1954)
Scotland	8, 13, 15, 82			Agate et al. (1949)
Sweden		5.3–20.3		Noemmik (1953)
Switzerland	166–288	11–12		Polomski et al. (1982a)
USA – Illinois (201)	70–618 (271)			Omueti & Jones (1977a)
USA – Pennsylvania (55)	136–990 (377)	0.05–1.5 (0.4)	7.7–66.8 (21.7)	Gilpin & Johnson (1980)
USA – Tennessee	80–3650			MacIntire (1952)
USA (30)	20–590 (290)			Robinson & Edgington (1946)
USA (clay subsoil)	45, 83, 411			McHargue & Hodgkiss (1939)
Various tropical areas (37)	68–216 (131)			Hall & Cain (1972)

Bower & Hatcher (1967) investigated the retention of F by alkaline soils, an acid soil, common hydroxyl-containing soil minerals, freshly precipitated  $\text{Al}(\text{OH})_3$ , and  $\text{Al}(\text{OH})_3$  precipitated onto bentonite. Adsorption of F over a range of 2–16  $\text{mg l}^{-1}$  was well described by Langmuir isotherms and pH of the solution phase increased, although the increase in  $\text{OH}^-$  was only a small fraction of F adsorbed. The order in the ability of the various materials to adsorb F was:  $\text{Al}(\text{OH})_3$  precipitate on bentonite >  $\text{Al}(\text{OH})_3$  >> hydrated halloysite and dehydrated halloysite > a weakly acidic soil >> kaolinite > gibbsite > alkaline soils > goethite > bentonite and vermiculite. Their main findings were that (1) adsorption of F on hydrated halloysite was not higher than on its dehydrated form (with much less lattice OH exposed), and (2) that  $\text{Al}(\text{OH})_3$  had an extremely high F adsorption capacity. From this, Bower & Hatcher (1967) concluded that F adsorption occurs primarily by exchange with OH groups from  $\text{Al}(\text{OH})_3$  and basic Al polymers adsorbed on mineral surfaces, rather than by exchange with crystal lattice OH groups of clay minerals.

Later, Flühler et al. (1982), investigated F adsorption and desorption rates in an acid soil and two calcareous soils with solutions over the range of 0–5000  $\text{mg F l}^{-1}$ . Adsorption isotherms in these soils were not linear over the range of solution concentrations and the Langmuir equation provided the best fit, especially at the low end of the concentration range. Adsorption and desorption in the calcareous soils are considerably slower than in the acid soil, appearing to be limited by the rate of formation and dissolution of  $\text{CaF}_2$ . In calcareous soils F retention is mostly in the form of  $\text{CaF}_2$  and  $\text{Ca}_5\text{F}(\text{PO}_4)_3$  (Brewer 1966; Eysinga 1972). The percolation experiments of Flühler et al. (1982) showed that although adsorption was effectively instantaneous in acid soils, in the calcareous soils (particularly under high flow rates) slow rates of F adsorption led to its rapid leaching.

The ability of non-calcareous soils (even those that are highly disturbed and strongly leached) to strongly retain F has been demonstrated by MacIntire et al. (1948, 1955) and Murray (1983, 1984). MacIntire et al. (1948) reported that even with application of 5529  $\text{kg ha}^{-1}$  of  $\text{CaF}_2$ , 98% of the F added was retained over 10 years. Murray (1984) added up to 10  $\text{kg F m}^{-2}$  soil surface in the form of NaF and  $\text{Na}_3\text{AlF}_6$  to a highly leached and disturbed soil and found that only 2.6–4.6% of it

leached after a year. In addition, Murray (1984) demonstrated that the link between soil components and F strengthened over time, resulting in lowering of water-soluble F concentrations.

From the observations of Bower & Hatcher (1967), Barrow (1986), Murray (1984), and Barrow & Ellis (1986), it appears that F is adsorbed specifically by displacing  $\text{OH}^-$  from soil surfaces and that the initial adsorption is followed by diffusive penetration of F into the soil particles.

Histeretic desorption in calcareous soils was attributed to the rate-limiting effect of  $\text{CaF}_2$  dissolution (Flühler et al. 1982). However, similar irreversible adsorption was exhibited in soils containing amorphous Al hydroxides as the dominant sorption sites (Peek & Volk 1985). This behaviour and that reported by Murray (1984) indicate that F sorption is more complex than a simple ligand exchange reaction.

More recent work has examined the presence and role of fluoro-aluminium complexes as exchange-phase components in natural acid soils and F-contaminated soils (Anderson et al. 1991; Wenzel & Blum 1992; Manoharan et al. 1996). The cationic  $\text{AlF}^{2+}$  and  $\text{AlF}_2^+$  species exist at  $\text{pH} < 6$  and play an important role in adsorption/desorption of F, increasing the apparent solubility of F under acidic conditions.

### Accumulation of F in soils from industrial sources

The F pollution sources of greatest magnitude are those associated with industrial sites, including manufacturers of bricks, iron, fertilisers, and glass, coal-fired power stations, and, particularly, aluminium smelters (Israel 1974; Polomski et al. 1982a; Pickering 1985; Haidouti 1991; Gritsan et al. 1995). These pollution sources release gaseous (e.g., HF,  $\text{SiF}_4$ ) and particulate fluorides (e.g.,  $\text{AlF}_3$ ,  $\text{Na}_3\text{AlF}_6$ ,  $\text{CaF}_2$ ), and can raise soil F concentrations by between 2 and 20 times (e.g., Polomski et al. 1982a; Gritsan et al. 1995). However, the effect of these F pollution sources is generally restricted to within 10–20 km downwind (e.g., Haidouti 1991) and becomes most serious where the density of F-emitters is high (e.g., Gritsan et al. 1995).

Soils highly polluted by industrial F emissions tend to have their highest total F concentrations at the surface of the profile (opposite to the “natural” situation, e.g., Robinson & Edgington 1946), whereas water-extractable F tends to increase with depth (Polomski et al. 1982a; Haidouti 1991).

### Accumulation of F in soils from long-term fertilisation

A more widespread source of F pollution in agricultural soils is the long-term application of phosphatic fertilisers (McLaughlin et al. 1996). Most phosphate rocks contain around 3–4% F (Table 2), which is reduced by the acidulation process during manufacture of phosphate fertilisers. With the addition of other nutrients such as S in superphosphate (SSP), and  $\text{NH}_4$  in ammoniated phosphates, the F content is typically diluted to between 1 and 3% (Table 2) depending on the type of phosphate rock used. Environmental concern has forced HF, released during acidulation, to be removed from stack gases by lime scrubbers. The scrubber effluent is often used in the granulation process. In this case all phosphate rock F ends up in the SSP fertiliser, and F/P ratios of SSP will be similar to those of the parent phosphate rock. In the years prior to 1980 the scrubber effluent was mostly discharged elsewhere and, therefore, SSP made during that period would have had a lower F content.

Single superphosphate applications of 10–30 kg  $\text{P ha}^{-1} \text{ yr}^{-1}$  are likely to add at least 2–5 kg  $\text{F ha}^{-1} \text{ yr}^{-1}$  to pastoral soils. Where phosphate fertilisers containing higher F-contents are used (e.g., ammoniated phosphates and phosphate rock), the

same application rates of P could add as much as 12 kg  $\text{F ha}^{-1} \text{ yr}^{-1}$ . Given the strong retention of F demonstrated in all but calcareous soils, F is likely to accumulate over years of application. There have been few detailed studies of such F accumulation.

Robinson & Edgington (1946) examined the effects of fertiliser F accumulation in five different soil types in New Jersey by analysing soils from adjacent areas with or without past fertiliser applications. Total soil F concentrations in cultivated soils that had been fertilised for 23–40 years were 36–96% higher in the top c. 150 mm compared with their unfertilised equivalents. The largest increases occurred in the finer-textured soils (loams). In the depth range of c. 150–350 mm, total F concentrations were elevated by 13–39% compared with their unfertilised equivalents. The largest increases at this depth were in the coarser-textured soils (sandy loams), indicating greater F movement to depth in soils with lower particulate specific surface areas. Robinson & Edgington (1946) calculated that the finest textured soils (loams) retained as much as 60% of the fertiliser-applied F in the top 400 mm, whilst the coarser-textured soils (sandy loams and gravelly sandy loams) retained only between 7 and 20% of applied F in the top 350 mm. In a later study, Kudzin &

**Table 2** Fluoride concentration of a range of phosphate rocks and fertilisers that have been used in New Zealand.

Material	F concentration (%)	Reference
<b>Phosphate rocks</b>		
Arad (Israel)	4.0	Syers et al. (1986)
Christmas Island –A	2.2	Evans et al. (1971)
Chatham Rise phosphorite	3.0	Syers et al. (1986)
Gafsa (Tunisia)	4.1	Syers et al. (1986)
Jordan	3.8	Syers et al. (1986)
Makatea Island	3.2	Syers et al. (1986)
Mexican	4.1	Syers et al. (1986)
Khouribga (Morocco)	4.0	Anon. (1990)
Nauru Island	3.0	Syers et al. (1986)
North Carolina	3.5	Syers et al. (1986)
North Florida	4.0	Syers et al. (1986)
Sechura (Peru)	3.4	Syers et al. (1986)
<b>Fertilisers</b>		
Single superphosphate	1.08–1.84	Evans et al. (1971); P. Loganathan et al. unpubl. data; McLaughlin et al. (1997)
Triple superphosphate	1.3–2.4	Mordvedt & Sikora (1992); Evans et al. (1971)
Monoammonium phosphate	1.6–2.2	Mordvedt & Sikora (1992); Evans et al. (1971)
Diammonium phosphate	1.2–3.0	Mordvedt & Sikora (1992); Manoharan et al. (1996)

Pashova (1970) reported a 22–25% increase in total soil F after single superphosphate (SSP) was applied at the rate of c. 26 kg P ha<sup>-1</sup> yr<sup>-1</sup> to Chernozem soils for 35 years.

Larsen & Widdowson (1971) reported a measurable increase in water-soluble soil F in field trials where 38 kg P ha<sup>-1</sup> yr<sup>-1</sup> was applied for seven years as SSP. Control plots had water-soluble F concentrations of 0.22–0.40 µg g<sup>-1</sup>, while treated plots contained 0.31–0.60 µg g<sup>-1</sup>; increases between 40 and 70% of initial values.

#### **Fertiliser effects on soluble F concentration in New Zealand pastoral soils**

Significant changes have been recorded in soil solution F concentration after eight years of varying rates and types of phosphatic fertiliser application on a silt loam pastoral soil (Manoharan et al. 1996). SSP was applied at rates of 15–60 kg P ha<sup>-1</sup> yr<sup>-1</sup> (supplying 2.4–9.0 kg F ha<sup>-1</sup> yr<sup>-1</sup>), North Carolina and Jordan phosphate rocks at a rate of 30 kg P ha<sup>-1</sup> yr<sup>-1</sup> (7 kg F ha<sup>-1</sup> yr<sup>-1</sup>), and diammonium phosphate at a rate of 30 kg P ha<sup>-1</sup> yr<sup>-1</sup> (1.8 kg F ha<sup>-1</sup> yr<sup>-1</sup>). Increasing rates of SSP application resulted in a linear increase in the soil solution F concentration from the control plot (0 kg P ha<sup>-1</sup> yr<sup>-1</sup>) value of 0.05 µg ml<sup>-1</sup> to 0.49 µg ml<sup>-1</sup> for the 60 kg P ha<sup>-1</sup> yr<sup>-1</sup> SSP application rate. However, although more F was added in the phosphate rock applications, soil solution F concentrations rose only to 0.10–0.32 µg ml<sup>-1</sup> due to incomplete dissolution (48–68% dissolution) of the phosphate rocks over the eight-year trial (Manoharan et al. 1995). The diammonium phosphate treatment resulted in an increase to 0.21 µg ml<sup>-1</sup>. Manoharan et al. (1995) also noted that total soil solution F concentrations were not significantly higher in the upper 30 mm of soil compared with samples from the 30–75-mm depth. The free F concentration, however, was higher and Al-F complex concentration lower in the upper depth, due to a higher surface soil pH.

These few studies demonstrate that the application of phosphate fertilisers, including SSP, over long periods of time increases the concentration of total and soluble F in the soil. The greatest elevation of existing total soil F probably occurs in fine-textured acidic soils, and is highest in the upper 150 mm of soil for all but very coarse-textured soils (e.g., gravelly sandy loams). It also appears that the greater solubility of SSP compared with some phosphate rocks releases more F into the soil solution.

#### **Preliminary assessment of total F accumulation rates in fertilised New Zealand pastoral soils**

Soils from two sets of existing SSP fertiliser trials were used to make a preliminary assessment of the rates of F accumulation. The first is a trial on sheep-grazed farmlets at AgResearch Ballantrae Hill Research Station, and the second a grazing/mowing trial at Massey University. Total soil F was measured by fusing soil with NaOH, followed by dissolution of the fused cake in water, adjusting the pH to 8.5 ± 0.1 with conc. HCl, filtering the solution (Frankenberger et al. 1996), and determining F in the filtrate using an F-ion selective electrode (Larsen & Widdowson 1971; Manoharan et al. 1996).

#### *The AgResearch Ballantrae Hill Research Station*

Soils collected were Brown Soils (New Zealand classification system; Hewitt 1992) or Typic Dystrachrepts (US soil taxonomy) formed from quartzo-feldspathic sandstone and siltstone, under an average annual rainfall of 1200 mm, 20 km north-east of Palmerston North, at an altitude of 250–350 m. The P retention of the soils was <27% (Lambert et al. 1988). Soil pH (H<sub>2</sub>O) was between 5.1 and 5.9 within the top 75 mm. Further soil details are reported by Loganathan et al. (1995). Three sets of fertilised and unfertilised soils were collected from low slope areas (0–12°) facing east, south-west, and north-west. The fertilised soils have received 761 kg P ha<sup>-1</sup> (corrected for slope) over 20 years of SSP application (Loganathan et al. 1995). Using the mean of the F concentration in SSP (1.46% F) reported by Evans et al. (1971) and P. Loganathan et al. (unpubl. data), a total application of 123 kg F ha<sup>-1</sup> is calculated for these soils over 20 years.

The Ballantrae data (Table 3) indicate that 20 years of SSP application has increased topsoil F concentrations by 60–120%. On these soils, between 42 and 54% of F applied in fertiliser is retained in the top 75 mm of soil, depending on the slope and aspect. The same retention patterns for P and S on the three aspects were found in these trial areas and attributed to animal transfer and leaching patterns (Saggar et al. 1990). Sheep grazing these areas spend proportionally more time on the east-facing slopes, sheltering from the prevailing NW wind. Hence, proportionally greater returns of F from urine and dung may occur in these east-facing areas.

*Number 4 Dairy Unit, Massey University*

The soil at this location was a Pallic Soil (New Zealand classification system; Hewitt 1992) or an Aeric Fragiaqualf (US Soil Taxonomy) formed from quartzo-feldspathic loess, located on flat land near Palmerston North, and receiving an average annual rainfall of 1000 mm. The soil pH ( $H_2O$ ) was 5.70 for 0–75 mm depth (Manoharan et al. 1996), and P retention is c. 22% (Saunders 1965). Plots at this site received 0, 30, and 60 kg P ha<sup>-1</sup> yr<sup>-1</sup> for 8 years as SSP, adding a total of 0, 38.9, and 77.9 kg F ha<sup>-1</sup>, respectively (Manoharan et al. 1996). The No. 4 Dairy Unit data (Table 4) indicate that 8 years of SSP application at rates of 30 and 60 kg P ha<sup>-1</sup> yr<sup>-1</sup> have increased total topsoil F concentrations by 37–48%. The proportion of F retained in the top 30 mm of soil is higher than in the Ballantrae soils, which may be in part due to a lack of animal tread-induced mixing of the upper part of the soil on the mowing/grazing No. 4 Dairy Unit trial and lower rainfall. For the rates of SSP application at 30 and 60 kg

P ha<sup>-1</sup> yr<sup>-1</sup> the percentage of applied F retained is similar in the 0–30-mm depth, although at 60 kg P ha<sup>-1</sup> yr<sup>-1</sup> F retention is lower in the 30–75-mm depth increment. This may reflect greater competition of F with P for adsorption sites at 30–75 mm in the SSP(60) treatment.

Both of these data sets indicate that retention of F elevates topsoil F concentrations, even in soils with low P-retention and clay mineral fractions dominated by crystalline layer-lattice clay minerals (New Zealand Soil Bureau 1968; Pollock 1975). Our results obtained for 0–75 mm depth cannot be directly compared with the whole profile values reported by Robinson & Edgington (1946), MacIntire et al. (1948), and Murray (1984). In soils containing appreciable Al- and Fe-hydroxide minerals (e.g., allophanic soils), F retention is likely to be much higher.

In addition to the above data sets, lower retention values were obtained in a 40-year, sheep-grazed pasture irrigation trial at Canterbury, New Zealand

**Table 3** Calculation of the accumulation of soil F from 20 years of SSP application on grazed farmlets at Ballantrae (providing a total of 123 kg F ha<sup>-1</sup>). Values for total soil F concentration are means of two replicate analyses. Bulk density of 900 kg m<sup>-3</sup> is assumed for calculation of increase in soil F storage.

Aspect	Soil depth (mm)	Total soil F concentration (µg g <sup>-1</sup> )		Concentration increase (µg g <sup>-1</sup> )	Increase in soil F storage (kg ha <sup>-1</sup> )	% of applied F retained (%)
		Control	Fertilised			
East	0–30	93.9	203.6	109.7	26.3	21
	30–75	107.6	190.8	83.2	39.7	
	0–75				<b>66</b>	54
South-west	0–30	96.7	186.9	90.2	21.6	18
	30–75	113.9	191.3	77.4	36.9	
	0–75				<b>58.5</b>	48
North-west	0–30	109.7	178.3	68.6	16.5	13
	30–75	120.4	193.0	72.6	34.5	
	0–75				<b>51</b>	42

**Table 4** Calculation of F retention following 8 years of SSP application on a mowing/grazing trial at No. 4 Dairy Unit, Massey University. SSP(30) and SSP(60) represent fertiliser treatments of 30 and 60 kg P ha<sup>-1</sup> yr<sup>-1</sup> as SSP, respectively. † Means of five replicate samples. ‡ Means of four replicate samples. Bulk density of 900 kg m<sup>-3</sup> is assumed for calculation of increase in soil F storage.

Soil depth (mm)	Total soil F concentration (µg g <sup>-1</sup> )			Concentration increase (µg g <sup>-1</sup> )		Increase in soil F storage (kg ha <sup>-1</sup> )		% of applied F retained (%)	
	Control	SSP(30)	SSP(60)	SSP(30)	SSP(60)	SSP(30)	SSP(60)	SSP(30)	SSP(60)
0–30	90.7†	122.2†	154.1†	31.5	63.4	8.5	17.1	22	22
30–75	90.3‡	113.2‡	116.7‡	22.9	26.4	10.3	11.9		
0–75						18.8	29.0	48	37

(P. Loganathan et al. unpubl. data). In this trial, 32 and 37% of F applied in SSP at rates of 376 and 188 kg SSP ha<sup>-1</sup> yr<sup>-1</sup>, respectively, remained in the 0–75-mm depth. This low recovery may have been due to leaching of F as a result of the irrigation treatment.

### Critical levels of F in soils

Increased F uptake is toxic to plants and animals (see below), thus it is desirable to minimise the rates of F accumulation in soils. Establishing single upper threshold F concentrations is a difficult task. This is because soils differ considerably in their ability to retain F. Hence, high concentrations of F strongly retained in fine-textured, amorphous Al-hydroxide-rich, slightly acidic soils may not cause any problems for F leaching into groundwater or being taken up by plants. However, even much lower concentrations within calcareous or very coarse textured soils, low in amorphous compounds, may prove critical for affecting groundwater or plant life. Further, plants take up F to differing degrees (Brewer 1966), and some may show little effect from very large available-F pools (MacIntire et al. 1942; Braen & Weinstein 1985; Singh 1990). Of greatest importance for plant uptake and groundwater pollution are probably the critical levels of the more available forms of F in soils, particularly that in soil solution or in the water-soluble fraction. In soil solution, F exists in various species. In acid soils a significant fraction of F exists as AlF<sup>2+</sup> and AlF<sub>2</sub><sup>+</sup> (Manoharan et al. 1996). Although recent studies indicated that Al-F species are non-toxic to plants at lower concentrations, they are toxic at higher concentrations and vary between species (Manoharan 1997; McLaughlin et al. 1997). Stevens et al. (1997) showed that Al-F species are less toxic than Al<sup>3+</sup>, Al(OH)<sup>2+</sup>, and Al(OH)<sub>2</sub><sup>+</sup> species to tomato and oats. Presently no standard values for critical concentrations of the various F species in soil solution appear to exist. Further research in this area is warranted, because with increasing acidification of pastoral soils, the concentrations of Al-F species in soil solution increase (Stevens et al. 1998a, 1998b).

However, for grazing animal health, the total F levels of soil may also be critical if soil is ingested at high rates (e.g., in winter in New Zealand, Healy 1968; Lee et al. 1996), and if a significant fraction of soil F can be extracted by digestive fluids (see below).

### Effects on soil organisms

Rao & Pal (1978) reported increasing organic matter contents in a series of surface soils progressively closer to an aluminium factory as the concentrations of F in soil and litter rose (soil total F from 380 to 1803 µg g<sup>-1</sup>). They attributed this to inhibition of growth and activity of soil micro-organisms by the elevated F levels, thus reducing organic matter breakdown. However, an additional and opposing effect of F addition to soils is the increased mobilisation of organic matter by F and its subsequent leaching (Polomski et al. 1982b). Subsequent laboratory studies have shown that soil amendments of <200 µg F g<sup>-1</sup> inhibited soil respiration and dehydrogenase activity, but amendments over this level and up to 2000 µg g<sup>-1</sup> did not affect respiration or redox level but influenced denitrification (Ottow & Kottas 1984; Becker & Ottow 1985). Wilke (1987) recorded increased leaching of organic matter, Fe, Al, and P on application of F to acid soils but not in the case of a calcareous soil. After treatments of up to 3700 µg F g<sup>-1</sup>, soil respiration was not affected, although activities of dehydrogenase and other enzymes, as well as nitrification, were inhibited at much lower F concentrations in the acid soils. The microbiological activity of the calcareous soil was unaffected. Wilke (1987) proposed that the soil respiration was not affected by addition of F because the negative effects of F on micro-organisms were balanced by the F-induced dissolution of organic matter, desorption of P, and increasing soil pH.

A recent study of the effects of airborne F accumulation on grassland (Tscherko & Kandeler 1997) reported more detailed threshold concentrations of water-extractable F that affect microbiological activity. In a series of sites at increasing distances from an Al smelter, water-extractable F concentrations decreased from 189 to 10 µg g<sup>-1</sup>, and microbiological activities showed a strong inverse trend. In the most polluted soils, microbiological activities were only 5–20% of those in the uncontaminated soils and more organic matter had accumulated. When water-extractable F concentration was >100 µg g<sup>-1</sup>, microbial biomass and dehydrogenase activity decreased substantially, while at 20 µg g<sup>-1</sup> the arylsulphatase activity was inhibited.

### Soil quality regulations for agricultural soils

There are currently no global regulations or recommendations that apply to permissible levels

of F in soils. This is probably due in part to the paucity of data on the concentrations of various forms of F in natural soils world-wide, and the huge variation of reported F levels in the limited data set in existence (Table 1). In parts of Europe a maximum permissible level of  $45 \mu\text{g g}^{-1}$  water-extractable F is applied to soils (Fiedler & Rösler 1993), which is considerably higher than most natural soil levels (Table 1).

## EFFECTS OF SOIL F ON PLANTS

Most plant material in the absence of any pollution sources contains between 2 and  $20 \mu\text{g F g}^{-1}$  on a dry weight basis (Robinson & Edgington 1946; Brewer 1966; Weinstein 1977; Robinson 1978). Reported F concentrations in pastures range between 0.7 and  $16 \mu\text{g F g}^{-1}$  (Blakemore et al. 1948; Agate et al. 1949; Compton et al. 1953; Allcroft et al. 1965; Oelschläger et al. 1968; Farrier & Pullen 1973; Manley et al. 1975). McLaughlin et al. (1997) reported that F concentrations in clover collected from a P fertiliser trial were extremely low ( $<10 \mu\text{g g}^{-1}$ ), often near the detection limit for the analysis technique ( $1 \mu\text{g g}^{-1}$ ). F concentrations in mixed herbage from pasture lands in New Zealand were  $<10 \mu\text{g g}^{-1}$ , most samples being  $<2 \mu\text{g F g}^{-1}$ . However, some plants are known accumulators of F, such as tea (*Camellia sinensis*) (Fung et al. 1999) and species of *Camellia*, *Dichapetalum*, *Gastrolobium*, *Oxylobium*, and *Palicourea* (Zimmerman 1952; Brewer 1966; Hall 1972; Vickery & Vickery 1976). Some of these species can accumulate up to  $4000 \mu\text{g F g}^{-1}$  and not show signs of toxicity (Jacobson et al. 1966). Most other plants show signs of toxicity at much lower concentrations (c. 30–300  $\mu\text{g F g}^{-1}$ ; Brewer 1966), while some species are extremely sensitive to concentrations  $<20 \mu\text{g F g}^{-1}$ , e.g., *Gladiolus* and *Freesia* (Jacobson et al. 1966; Istas & Alaerts 1974).

**Table 5** Pasture F concentrations following eight years of SSP application on a mowing/grazing trial at No. 4 Dairy Unit, Massey University. †Mean of three replicate plots; others are means of four replicate plots.

Treatment	Mean F	
	concentration ( $\mu\text{g g}^{-1}$ )	Standard error ( $\mu\text{g g}^{-1}$ )
Control	5.3	0.5
30 kg P ha <sup>-1</sup> yr <sup>-1</sup> as SSP	5.7	1.1
60 kg P ha <sup>-1</sup> yr <sup>-1</sup> as SSP	7.1†	2.1

Fluoride toxicity in plants is normally indicated by marginal necrosis (tip-burn, scorching, or lesions) on foliage, which begins on the margins or tips of the leaves and moves inward (Brewer 1966). Chronic F toxicity may also be indicated by interveinal chlorosis, before marginal necrosis develops (Thomas 1951; Brewer 1966). Both of these conditions lead to decreased photosynthetic efficiency and lower plant yields (Brewer et al. 1967; Robinson 1978). Other effects include reduction in flower production (Koster 1972) and flower quality (Bruyn & Hulsman 1972).

Many studies have revealed that, adjacent to industrial areas and active volcanoes, airborne contaminants are the most important source of excess F in plants (Thomas 1951; Adams 1956; Treshaw 1971; Istas & Alaerts 1974; Gritsan et al. 1995). Atmospheric F is absorbed by the plant leaves and remains within the foliage (Brewer 1966). Irrigation water can also be an important source of F, and Singh et al. (1995) have demonstrated its uptake by plant roots grown in sand, although much of the F remained within the roots.

Some studies have suggested that F complex ions, such as Al-F complexes (Takmaz-Nisancioglu & Davison 1988; MacLean et al. 1992) and Si-B-F complexes (Collet 1969), may be taken up by plants to a greater degree than free F<sup>-</sup>. Davison (1983) suggested that low pH may drive increased F uptake by plants. This is probably due to low pH encouraging formation of Al-F species (Barrow & Ellis 1986) and, at very low pH ( $<4.5$ ), possible formation of the highly permeable HF species (Kronberger 1988). In nutrient solution studies, Stevens et al. (1998a, 1998b) have shown that F as HF is much more readily taken up by oats and tomato than F<sup>-</sup> and Al-F complexes. Takmaz-Nisancioglu & Davison (1988) demonstrated that F given as AlF<sub>3</sub> to plants in solution culture caused root and new shoot F concentrations to be more strongly elevated than when NaF was applied.

## Availability of soil and fertiliser F to crops and pastures

As discussed above, most natural soils have a very high affinity for F and retain it strongly. Hence, plant uptake (like leaching loss) of excess F from soils is generally minimal. The amount of F taken up by plants appears to be unrelated to the total F concentration of the soil, and instead depends on soil type, pH, organic matter, and Ca and P content (MacIntire et al. 1942; Prince et al. 1949; Hurd-Karrer 1950; Treshaw 1971; Hall & Cain 1972;

Cooke et al. 1976; McClenahan 1976). Adding large quantities of soluble F ( $50 \mu\text{g g}^{-1}$  soil, as HF and NaF) to acid soils (pH 5.0) can produce increased uptake of F by plants, but for well-limed soils or the application of less soluble compounds (e.g., CaF) increase in F uptake was minimal (Prince et al. 1949; Hurd-Karrer 1950; MacIntire et al. 1951; Singh et al. 1995). However, Keerthisinghe et al. (1991) demonstrated in a pot trial that addition of NaF, at rates of  $25\text{--}100 \mu\text{g F g}^{-1}$  soil, to a soil limed to pH 5.4 increased clover shoot concentrations of F by 50–360%. Formation and uptake of Al-F complexes were thought to be responsible for the increasing plant F concentrations.

On the basis of results in the literature, Brewer (1966) suggested that water-soluble F levels in soils may be better predictors of plant uptake than total soil F. Eysinga (1974) found a corresponding relationship of increasing F uptake by plants with water-soluble F concentrations in soils, but other studies found no such relationship (Hall & Cain 1972; Cooke et al. 1976). However, such relationships are likely to be complicated by plants that accumulate F in their roots rather than leaves (Cooke et al. 1976; Singh et al. 1995) and plants with mechanisms that can impede F uptake (Koster 1972). Later, Davison (1982) found that water-soluble F concentration was highly correlated with plant F levels in sodic soils, but not in mildly acidic soils.

Hart et al. (1934) observed that F in fertilisers did not significantly increase the F content of plants. Later, MacIntire et al. (1942) reported that the addition of superphosphate and CaF<sub>2</sub>-bearing slag to soils, increasing their F concentration by as much as  $2300 \mu\text{g F g}^{-1}$ , caused only very slight increases to the F content of grass and clover. Kudzin & Pashova (1970) reported increases in the F content of maize of 23% (whole plant), 65% (leaves), 15% (stems), and 11% (grain) after application of superphosphate ( $60 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1} \text{ yr}^{-1}$ ) for 35 years. However, later studies have revealed little change in plant F content due to application of P fertilisers. In a two-year greenhouse experiment Singh (1990) noticed only slight increases in F content of oats and rape caused by P fertiliser application during the first year and no increases in the second year, presumably due to increasing retention of F with time within the soil. However, these levels were well within the normal range of plant F contents ( $2\text{--}20 \mu\text{g g}^{-1}$ ; Brewer 1966). McLaughlin et al. (1992) found that on a pasture soil to which superphosphate had been added at a

rate of  $>4000 \text{ kg of P ha}^{-1}$  over 80 years, pasture herbage F contents were not significantly higher than pasture on adjacent unfertilised soil. Similar results have also been found for F in herbage from pasture lands in New Zealand where SSP had been applied for 20–40 years (P. Loganathan et al. unpubl. data).

We measured F concentrations (using the method of Frankenberger et al. 1996) in pasture collected from the previously described No. 4 Dairy Unit mowing/grazing fertiliser trial. Eight years of SSP application in the No. 4 Dairy Unit trial caused substantial increases in total soil F concentrations (Table 4). However, the same total application of  $38.9$  or  $77.9 \text{ kg F ha}^{-1}$  over 8 years did not cause significant ( $P = 0.05$ ) increases in pasture F concentrations (Table 5). The plots with fertiliser applied showed a greater variability between replicates.

Our results and those of previous plant studies, together with results from soil F mobility studies, indicate that, within the pH range of 5.5–6.5, increasing soil F levels are not likely to cause substantial increases in pasture or crop F concentrations. Increases to levels causing plant toxicity or toxicity to animals fed with the plants are unlikely, providing soil ingestion is excluded (see below). However, at lower soil pH some studies indicate that more F may be available for plant uptake as Al-F complexes. Factors controlling F uptake in acidic soils require further clarification, particularly in areas subject to soil acidification.

## EFFECTS OF SOIL F ON WATER QUALITY

In most instances, water with high F concentrations ( $5\text{--}45 \mu\text{g g}^{-1}$ ) is sourced from deep aquifers in areas of phosphatic or recent volcanic geology (Walker & Milne 1955; Bower & Hatcher 1967; Paliwal et al. 1969; Somani 1974). Other shallower aquifers with varying geology as well as land surface drainage waters are generally much lower in F ( $0.08\text{--}0.22 \mu\text{g g}^{-1}$ ; Köpf et al. 1968; Eysinga 1972; Manley et al. 1975). The F leaching and adsorption studies described above indicate that in most instances soil F is not likely to degrade the quality of ground water. This is borne out by soil solution F concentrations, which are generally  $<1 \mu\text{g g}^{-1}$  (Pickering 1985). Conversely, the opposite may be true, and many types of soils may be useful filters to purify groundwater containing high F concentrations (Bower & Hatcher 1967; Gilpin & Johnson 1980).

## EFFECTS OF SOIL F ON GRAZING ANIMALS

### Accumulation and effects of dietary F on grazing animals

Fluorine occurs throughout bones, teeth, soft tissue, and fluids of animals but, despite its ubiquitous presence, its function is unknown and its necessity not unequivocally proven (Underwood 1981). Some studies have demonstrated various symptoms that were attributed to F deficiency in laboratory animals in artificially F-depleted environments (Schwarz & Milne 1972; Milne & Schwarz 1974; Messer et al. 1974), while others could find no such effects (Maurer & Day 1957; Doberenz et al. 1964; Weber & Reid 1974; Tao & Suttie 1976). However, the toxic effects of F in animals are well proven. The earliest records of acute and chronic fluorosis in farm animals are in Iceland, during and after volcanic eruptions (Roholm 1937). In many other areas of the world, chronic fluorosis in grazing farm animals has been identified from 1931 onward (Underwood 1981).

In humans and in rats, F is absorbed in both the stomach and small intestine (Cerklewski 1997). At the low pH within the stomach, formation of highly permeable HF is encouraged and absorption is rapid (Whitford & Pashley 1984). Studies of rats indicate that most F is absorbed in the small intestine, where F is absorbed by non-pH-dependent diffusion (Nopakun et al. 1989; Nopakun & Messer 1990). If the animal is in a fasted state, greater F absorption occurs rapidly in the stomach (up to 100% absorption), whereas in the presence of food, absorption is 50–80% efficient (Cerklewski 1997). Passive absorption of F occurs predominantly in the rumen of ruminants (National Research Council 1980).

Absorption of F by ruminants is affected by other dietary factors; Al salts protect against high F intakes by reducing its absorption in the intestinal tract (Becker et al. 1950; Hobbs & Merriman 1959; Krishnamachari 1987), as do Ca salts in rats (Weddel & Muhler 1954). Increasing levels of dietary fat seem to exacerbate toxicity of F (McGown & Suttie 1974) by increasing F absorption.

Chronic fluorosis has been reported in grazing animals due to volcanic gas and ash (Roholm 1937; Araya et al. 1990, 1993; Shanks 1997), ingestion of commercial phosphorus licks and supplements (Shupe et al. 1992; Jubb et al. 1993; Schultheiss & Van Niekerk 1994; Schultheiss & Godley 1995;

Singh & Swarup 1995), ingestion of phosphate fertiliser residues (O'Hara & Cordes 1982; Clark & Stewart 1983), ingestion of forage or waters polluted by industrial emissions (e.g., Karstard 1967; Kay et al. 1975; Singh & Swarup 1995; Kierdorf et al. 1996), and intake of F-rich groundwater or geothermal waters (Harvey 1952; Shupe et al. 1984; Botha et al. 1993).

The effects of chronic F toxicity usually take weeks or months to manifest themselves while excess F is excreted in urine and deposited within bones (Underwood 1981). The skeleton of animals normally contains the greatest proportion of F within the animal and normal whole bone F concentrations range between 300 and 600  $\mu\text{g g}^{-1}$  (fat-free, dry basis), the highest concentrations being within cancellous bones such as ribs and vertebrae (Underwood 1981). Teeth contain around half the F concentration of bone, and soft tissue around 204  $\mu\text{g g}^{-1}$  on a dry basis in ruminants (Underwood 1981). The kidney has the highest F concentration of soft tissue because F is lost mainly in urine (National Research Council 1974). Plasma F concentrations reflect short-term changes in F uptake with levels of  $<0.1 \mu\text{g g}^{-1}$  in normal animals and 1  $\mu\text{g g}^{-1}$  indicating a high F uptake (Suttie et al. 1972). Fluoride does not readily pass the mammary barrier, and milk and milk products contain less F than soft tissue (Underwood 1981; Miller et al. 1991). Milk from cows fed with 10, 19, 55, and 109  $\mu\text{g F g}^{-1}$  from the age of 3 months to 7.5 years, contained 0.06, 0.10, 0.14, and 0.20  $\mu\text{g F g}^{-1}$  on a fresh weight basis, respectively (Greenwood et al. 1964). Suttie et al. (1957) reported fresh milk F concentrations of 0.1–0.4  $\mu\text{g g}^{-1}$  in fluorotic cattle, and values up to 0.64  $\mu\text{g g}^{-1}$  have also been reported by others (Krishnamachari 1987).

When animals are continually exposed to large amounts of F, build-up in bones occurs up to a saturation point of 15 000–20 000  $\mu\text{g F g}^{-1}$  (30–40 $\times$  normal levels), at which point soft tissues are flooded with F, resulting in metabolic breakdown and death (Underwood 1981).

In chronic fluorosis under lesser doses of F, rises in skeletal F concentrations are accompanied by small rises in tissue and blood F levels (Suttie et al. 1972; Underwood 1981) and the activities of various enzymes are affected (Sievert & Phillips 1959; Shupe et al. 1962; Zebrowski et al. 1964). In young animals, tooth development is hindered by uptake of F, resulting in mottling and erosion of enamel and excessive tooth wear (National

Research Council 1974; Shupe 1980; Milhaud et al. 1987). Other symptomatic effects include lameness, skeletal deformity, reduced feed and water intake, and lower weight gain and milk production (National Research Council 1980; Shupe 1980; Singh & Swarup 1995).

In dairy cattle, fluorosis is associated with F concentrations of  $>5500 \mu\text{g g}^{-1}$  and  $>7000 \mu\text{g g}^{-1}$  in compact and cancellous bone, respectively (Suttie et al. 1958). In sheep, F concentrations of  $2000\text{--}3000 \mu\text{g g}^{-1}$  (compact bone) and  $4000\text{--}6000 \mu\text{g g}^{-1}$  (cancellous bone) are consistent with fluorosis (Jackson & Weidmann 1958). Sheep and cattle urine normally contains  $<10 \mu\text{g F g}^{-1}$ . In long-term experiments with dairy cows, urine F concentrations were  $<5 \mu\text{g g}^{-1}$  for normal animals,  $20\text{--}30 \mu\text{g g}^{-1}$  in animals on the borderline of fluorosis, and  $>35 \mu\text{g g}^{-1}$  in animals with signs of fluorosis (Suttie et al. 1961; Shupe et al. 1963a). Plasma F concentrations  $>0.2 \mu\text{g g}^{-1}$  are normally associated with dental lesions in young cattle; below this concentration, few adverse effects are evident (Suttie et al. 1972).

#### Critical levels of F intake for grazing animals

Doses of  $>100 \mu\text{g F g}^{-1}$  of body weight are acutely lethal in most mammals (National Research Council 1974). Doses of  $\geq 100 \mu\text{g g}^{-1}$  of dietary F normally induce immediate systematic toxic effects in grazing animals (Underwood 1981). Tolerance to lower doses of F depends on the animal species (Table 6), animal condition, age at exposure, form of F uptake, duration and continuity of uptake, and the amount of F being consumed (Underwood 1981; National Research Council 1988).

Cattle are less tolerant of F toxicity than other livestock (Phillips & Suttie 1960). In long-term experiments with beef cattle,  $30 \mu\text{g g}^{-1}$  of dietary F caused excessive wear and staining of teeth (Hobbs & Merriman 1959). In another study, beginning with young calves and lasting 7 years, the tolerance for soluble F was also  $30 \mu\text{g g}^{-1}$  of the dry diet (Shupe et al. 1963b). Lactating cows, however, could tolerate  $30 \mu\text{g g}^{-1}$  dietary F, with  $40 \mu\text{g g}^{-1}$  being marginal and a rate of  $50 \mu\text{g g}^{-1}$  causing fluorosis within 3–5 years (Suttie et al. 1957). Finishing cattle can tolerate up to  $100 \mu\text{g g}^{-1}$ , due to a short feeding period (National Research Council 1988).

For New Zealand standards, forage must not exceed  $40 \mu\text{g F g}^{-1}$  of dry matter (DM) for more than one year,  $60 \mu\text{g F g}^{-1}$  DM for more than two consecutive months, or  $80 \mu\text{g F g}^{-1}$  DM for more than a month (Farrier & Pullen 1973).

The chemical form of dietary F is important. The availability of F in the form of  $\text{CaF}_2$  and raw phosphate rock has been estimated to be 50% of that in NaF, which was 75% available (Clay & Suttie 1985). In a study of dairy cattle, animals were fed a diet containing  $65 \mu\text{g F g}^{-1}$ , in the form of NaF,  $\text{CaF}_2$ , and atmospherically contaminated hay. Examination of F retention in bones and urinary F indicated that F as  $\text{CaF}_2$  was only around half as available as the other two sources, which were 75% bioavailable (Shupe et al. 1962). Harkins et al. (1963) estimated that NaF administered in solution to rats was rapidly absorbed to a level of 79%; from solid form  $\text{CaF}_2$ , 60–70% of F was absorbed.

Sheep have a higher tolerance to dietary F than cattle (Table 6), but its effects are also strongly dependent on the continuity of F uptake. In the hot

**Table 6** Dietary F tolerance for grazing animals, adapted from the data of Suttie (1977), Thompson (1978), and National Research Council (1980). Values assume an otherwise adequate diet and the ingestion of soluble F (e.g., NaF).

Animal	Tolerance ( $\mu\text{g F g}^{-1}$ dry diet)	Definitely unsafe ( $\mu\text{g F g}^{-1}$ dry diet)
Beef or dairy calves ( $<4$ months old)	–	$\geq 40$
Beef or dairy heifers (4 months–2 years old)	30–40	$\geq 50$
Mature beef or dairy cattle ( $>3$ years old)	40–50	$\geq 60$
Finishing cattle	100	$\geq 120$
Breeding ewes	60	$\geq 70$
Feeder lambs	150	$\geq 170$

and dry Queensland climate, bore water containing  $5 \mu\text{g F ml}^{-1}$  has been enough to induce fluorosis symptoms in sheep (Harvey 1952). However, water containing  $20 \mu\text{g F ml}^{-1}$  did not cause ill effects in sheep in cool and moist conditions in South Australia, where water intake was variable and seasonally low (Pierce 1954). Some of the F stored within the skeleton is exchangeable and is excreted in urine during periods of low F uptake, hence, more F can be immobilised during a later period of high uptake (Suttie et al. 1972). Rapidly alternating periods of high and low F uptake can be more damaging to animals than an equivalent continuous intake due to rapid increases and decreases of skeletal F concentrations (Suttie et al. 1972). This is exacerbated with short-term exposures of high intakes, e.g., in dairy cattle with short-term intakes of  $90 \mu\text{g g}^{-1}$ , dietary F induced weight loss and decreased appetite (Suttie et al. 1972). The effects of chronic fluorosis are also exacerbated in animals that are undernourished (Suttie & Faltin 1973).

### Sources of F intake for grazing animals

#### *Pasture and other feeds*

As previously described, most pasture species contain between  $0.7$  and  $16 \mu\text{g F g}^{-1}$ , do not accumulate large amounts of F, and absorb only very limited amounts from the soil. Even where large quantities of F-bearing, phosphatic fertilisers are added to soils, pasture F concentrations are not strongly affected (MacIntire et al. 1942; Singh 1990; McLaughlin et al. 1992). Other feeds such as lucerne hay are also low in F (Suttie 1969); 107 samples of lucerne hay from throughout the USA contained a mean of  $3.6 \mu\text{g F g}^{-1}$  (range  $0.8$ – $36.5 \mu\text{g F g}^{-1}$ ). Cereals and other grains usually contain lesser amounts of F than plant leaves, usually only  $0.5$ – $6 \mu\text{g F g}^{-1}$  (McClure 1949; Ammerman & Henry 1983). From the evidence of Shupe et al. (1962), F within hay appears to be just as available to animals as within the form of NaF.

Due to their low F concentration if uncontaminated, pastures and other common plant feeds are not likely to be a major factor in the incidence of fluorosis. This is supported by the overwhelming number of reports of fluorosis citing F-sources other than pastures. However, numerous cases of fluorosis result from contamination of plant leaves by airborne industrial pollutants (Walton 1988; Singh & Swarup 1995; Vikøren & Stuve 1996), superphosphate residues (O'Hara & Cordes 1982; O'Hara et al. 1982), evaporation of F-rich irrigation

water (Botha et al. 1993), and volcanic gases (Araya et al. 1990).

Other types of feeds and animal supplements, particularly those that contain phosphate or those produced from animal bone, can be high in F and have been incriminated as causes of fluorosis. Ten percent of the dairy feed supplements used in the 1960s in 7 states in the USA exceeded  $30 \mu\text{g F g}^{-1}$  and some have contained over  $200 \mu\text{g F g}^{-1}$  (Suttie 1969), while some meat and bone meals may also contain as much as  $200 \mu\text{g F g}^{-1}$  (Underwood 1981). The F contained within these phosphate additives or bone meal products has been estimated to be only one to two thirds as available as soluble NaF (Underwood 1981). Jubb et al. (1993) described severe chronic fluorosis in a herd of cattle in Northern Australia after they were fed a supplement containing monoammonium phosphate and diammonium phosphate as well as meat meal. Estimated dietary F intake of the cattle was approximately  $100 \mu\text{g F g}^{-1}$ , with the mineral supplement containing  $2000 \mu\text{g F g}^{-1}$  and the meat meal  $130 \mu\text{g F g}^{-1}$ . In South Africa, a phosphate rock-based commercial lick containing  $1400 \mu\text{g F g}^{-1}$  caused seasonal chronic fluorosis symptoms in a herd of adult cattle (Schultheiss & Godley 1995). During winter, stock were ingesting an estimated  $63.5 \mu\text{g g}^{-1}$  of dietary F and showing signs of fluorosis; symptoms went into remission during summer where dietary intake rates of F reduced to  $28 \mu\text{g g}^{-1}$ . Pasture and water F concentrations were  $0.3 \mu\text{g g}^{-1}$  and  $0.03 \mu\text{g g}^{-1}$ , respectively, hence the supplement supplied the bulk of the animals' diet. The level of F intake compared with the tolerance level for adult cattle (Table 6) indicates that, in this case, F within the phosphate rock was as available to animals as that in NaF. Schultheiss & Van Niekerk (1994) described a case of fluorosis in a flock of sheep fed a phosphate rock-bearing lick for 20 months. During this time sheep were ingesting at least  $91 \mu\text{g g}^{-1}$  dietary F from the lick, affecting 17–37% of various groups of animals depending on their age and condition.

#### *Water supplies*

Water supplies enriched in F have often been the cause of fluorosis in grazing animals. As described above, water enriched in F is usually found only in deep bores, particularly in areas with underlying phosphatic geology where F concentrations can reach as high as  $45 \mu\text{g ml}^{-1}$ . The tolerance levels for F in drinking water for cattle are  $4$ – $8 \mu\text{g ml}^{-1}$

(Shupe & Olsen 1987). Botha et al. (1993) reported two outbreaks of fluorosis in cattle and sheep whose main water sources contained 19.8 and 26.6  $\mu\text{g F ml}^{-1}$ . Other cases have occurred in parts of India, Australia, and Africa where bore water concentrations of up to 40  $\mu\text{g F ml}^{-1}$  may occur (e.g., Harvey 1952; Zumpt 1975; Underwood 1981). Water concentrations as low as 5  $\mu\text{g F ml}^{-1}$  have caused fluorosis in sheep in hot and dry climates (Harvey 1952).

However, outside such F-enriched areas, and in surface drainage waters, F concentrations are typically very low ( $<0.22 \mu\text{g ml}^{-1}$ ). Hence, normal water sources are likely to contribute very little to the F intake of grazing animals. In New Zealand, F concentrations in lakes and streams are all  $<0.5 \mu\text{g ml}^{-1}$  (Chamberlain 1944; Denmead 1946; Hewat & Eastcott 1955; Manley et al. 1975), with the exception of mineral springs and thermal pools and lakes which can reach up to 5200  $\mu\text{g F ml}^{-1}$  (Mahon 1964).

#### *Fertiliser residue*

Residues of phosphatic fertilisers or basic slags on pastures have caused numerous cases of poisoning of sheep and cattle (Swan & McIntosh 1952; Crowley & Murphy 1962; Jones & Jones 1962; Rosney 1962; Clark et al. 1976). In New Zealand, O'Hara & Cordes (1982) reported 37 outbreaks of superphosphate poisoning in sheep between 1965 and 1975. They stated that outbreaks typically occurred in late winter and spring, mostly affecting pregnant and lactating ewes which were already under nutritional stress. Most outbreaks occurred during fine weather when sheep grazed short pastures within a week of topdressing with superphosphate.

Clark et al. (1976) considered F to be the toxic component of superphosphate. Stewart et al. (1974) described temporarily elevated urine F concentrations in an experiment with sheep grazing pastures recently dressed with superphosphate. O'Hara et al. (1982) compared experimental poisoning of sheep with NaF and superphosphate and concluded that the course of the poisoning was very similar, although superphosphate poisoning was more protracted. O'Hara et al. (1982) found NaF doses of 45–135  $\mu\text{g F g}^{-1}$  of body weight to be toxic compared with toxic superphosphate doses of 70–90  $\mu\text{g F g}^{-1}$ . The cause of the superphosphate poisoning was probably more protracted than with NaF, due to lower availability of  $\text{CaF}_2$  in super-

phosphate F (Shupe et al. 1962), reducing the effective F dose of superphosphate by up to 50%. O'Hara et al. (1982) considered that phosphate plays a contributing role in superphosphate poisoning, but that the role of F is dominant.

#### *Volcanic ash*

The first recorded cases of acute and chronic animal fluorosis were caused by excessive F concentrations in volcanic ash and gases in Iceland (Roholm 1937). Tens of thousands of sheep, cattle, and horses died, mostly from fluorosis, following the 1783 eruption of Lakagigar in Iceland (Thorarinsson 1979). In another Icelandic eruption, F concentrations of ash-covered pastures exceeded 4000  $\mu\text{g g}^{-1}$  and 7500 deaths ensued. Óskarsson (1980) reported that F was adhering to the outside of volcanic ash grains and was in a highly soluble form as the salts  $\text{CaSiF}_6$ , NaF, and  $\text{AlF}_3$ .

Chronic fluorosis in cattle also occurred during and following the 1988–1989 eruption of Lonquimay in southern Chile (Araya et al. 1990, 1993). Pastures contained 240–315  $\mu\text{g F g}^{-1}$  on a dry weight basis and the affected animals had elevated bone, urine, and blood F levels (means of 10 707, 87, and 1.30  $\mu\text{g F g}^{-1}$ , respectively). The animals began showing signs of fluorosis 10 weeks after the eruption began. In the two years following the eruption, pasture F concentrations ranged between 7 and 34  $\mu\text{g g}^{-1}$ , which was enough to maintain fluorosis symptoms in cattle that lived during the eruption and cause some tooth wear in bulls that were not exposed during the eruption (Araya et al. 1993).

Following the October 1995 eruption and ash fall of Ruapehu volcano in New Zealand, sheep deaths in the Rangitaiki plains area were attributed to ingestion of ash and resultant fluorosis (Shanks 1997; Cronin et al. 1998). Approximately 2.5% of pregnant or lactating ewes died in the area; the only other stock that suffered comparable effects were a flock of 1–2-year-old sheep that had been kept in yards for some time before the ash fall. Hence, in all cases the animals most affected were those having the greatest energy demands, grazing on short pastures covered by 2–3 mm of ash. Pasture samples collected 10 days after ash fall (after heavy rain) contained 20–90  $\mu\text{g F g}^{-1}$ , but the F concentration was probably much higher in the first few days after ash fall considering the fact that the ash had total F concentration ranging from 350–850  $\mu\text{g g}^{-1}$  (S. J. Cronin et al. unpubl. data). Elevated rumen

F concentrations of 360–520  $\mu\text{g g}^{-1}$  were found (normally 5–40  $\mu\text{g g}^{-1}$ ; Shanks 1997), and, as well as classic symptoms of fluorosis, proton microprobe analysis of teeth indicated a zone of pitting of the enamel indicative of high F intake.

### Soil ingestion

Ingestion of soil has not yet been implicated as a cause of chronic fluorosis but, given the accumulation of F in most soils from various pollution sources (including phosphatic fertilisers), soil must be considered as an additional source of dietary F at present and future levels.

Under normal conditions, pastoral grazing animals, including sheep and cattle, can ingest large amounts of soil along with pasture (Field & Purves 1964; Healy & Ludwig 1965; Arnold et al. 1966; Healy 1967, 1968). Soil splash adheres to leaves of pasture, particularly during wet periods, and soil is also ingested via worm casts and when root crops are grazed to ground level (Healy & Drew 1970; Healy 1973). Healy (1968) reported that dairy cattle in various areas of New Zealand ingested between 100 and 450 kg of soil per year (rates were mostly >180  $\text{kg yr}^{-1}$ ). Dewes (1996) reported that a typical soil ingestion rate may be as much as 670  $\text{kg yr}^{-1}$  in some areas. Factors such as grazing root crops, over-grazing, break-feeding, feeding on sacrifice areas, and abundant worm casts may substantially increase soil ingestion rates. Healy (1968) found that ingestion rates were highest in winter and autumn, and when stocking rates were higher. Annual soil ingestion rates for stocking rates of 3.7 cattle  $\text{ha}^{-1}$  were 200–300% of those for stocking rates of 2–2.5 cattle  $\text{ha}^{-1}$ . For stocking rates of 2–2.5 cattle  $\text{ha}^{-1}$ , winter soil ingestion rates ranged between 900 and 1600  $\text{g d}^{-1}$ , and summer rates between 220 and 470  $\text{g d}^{-1}$ . Variations in these rates reflect the different parts of the southern North Island of New Zealand where measurements were made. From Healy's (1968) results, an overall average soil ingestion rate for cattle is c. 700  $\text{g d}^{-1}$ , with c. 350  $\text{g d}^{-1}$  in summer and c. 1200  $\text{g d}^{-1}$  in winter.

Sheep in New Zealand are reported to ingest soils at rates of up to 75  $\text{kg yr}^{-1}$  (Healy & Drew 1970), with similar seasonal and stocking rate effects as cattle leading to a maximum intake of >300  $\text{g d}^{-1}$ . A later study by Lee et al. (1996) found soil ingestion rates for New Zealand sheep of 11–30  $\text{g d}^{-1}$  in summer, 92–102  $\text{g d}^{-1}$  in autumn, and 264–275  $\text{g d}^{-1}$  in winter. For sheep in Scotland, Field & Purves (1964) found a maximum uptake

of 200  $\text{g}$  of soil  $\text{d}^{-1}$  in winter. In Ireland, McGrath et al. (1982) reported that sheep ingested up to 400  $\text{g}$  of soil  $\text{kg}^{-1}$  of body weight during a grazing season of May to November. During this period, higher rainfall and stocking rates increased amounts of soil uptake. McGrath et al. (1982) also found that silt and clay was preferentially ingested from the soil. Vaithiyathan & Singh (1994) found total soil ingestion by sheep in India to be 39  $\text{kg yr}^{-1}$ , ranging between 71 and 163  $\text{g d}^{-1}$ , the highest rates being in winter. In climates such as in Ireland, Scotland, and New Zealand, the average rate of soil ingestion by sheep is probably around 100  $\text{g d}^{-1}$  or 10% of total dry matter intake (Field & Purves 1964; McGrath et al. 1982; Lee et al. 1996).

It has been recognised for some time that ingested soil may be an important source of micronutrients in animals. Rigg & Askew (1934) prevented Co-deficiency symptoms in sheep by drenching them with 20  $\text{g}$  of soil per week for 6 months. Later, Andrews et al. (1958) attributed increased liver Co concentrations in sheep grazing short pastures to soil ingestion. Healy et al. (1970) dosed soil with radioisotopes of micronutrients to determine the proportions of these absorbed by sheep ingesting the soil. They found minimum animal absorption rates of 34% for  $^{75}\text{Se}$ , 14% for  $^{65}\text{Zn}$ , 1% for  $^{60}\text{Co}$ , and 0.4% for  $^{54}\text{Mn}$ . In another study, Healy (1972) used ruminal duodenal/abomasal and ileal liquors collected from sheep to extract each of 17 different soils. Soil addition increased the ruminal liquor concentrations of Mg, Al, Fe, Mn, Se, and Zn. Duodenal/abomasal liquors were elevated in Ca, Mg, Al, Mn, and Se, and ileal liquor concentrations of Al, Cu, Fe, Mn, and Se increased upon addition of soil. The amount of elemental absorption from the soils by the liquors varied considerably between soils, mostly depending on the available amounts present within the soil. Hence, the composition or type of soil ingested as well as the quantity has an effect on elements absorbed. Using an average soil ingestion rate of 100  $\text{g d}^{-1}$  (of Brown Soil) Grace et al. (1996) demonstrated changes in the storage of various micronutrients in the liver, blood plasma, and digestive fluids of sheep. Soil ingestion increased plasma and liver Se and vitamin B<sub>12</sub> (related to Co intake) concentrations, but not those of Cu, Mn, Fe, Zn, and Cd.

The above studies have demonstrated that soil ingestion contributes significantly to animal uptake of various micronutrients, particularly Se, Co, and possibly Zn. These elements are apparently

available to the animal in proportions of 1 to 34% of their total content in the soil.

#### *Bioavailability of soil F in grazing animals*

There have been very few studies on the bioavailability of soil F in grazing animals. Milhaud et al. (1989) conducted a balanced feeding trial in which sheep were given a concentrated feed mixture containing 30% soil by weight. Seven soils were used covering a range of types (including those derived from schist and limestone), from sites polluted by Al smelter emissions and also from unpolluted sites. Total F concentrations in the soils ranged from 235 to 1030  $\mu\text{g g}^{-1}$ , and water-extractable F concentrations from 0.4 to 15.9  $\mu\text{g g}^{-1}$ . They found from 28 animals (4 for each soil type) that apparent digestive absorption of F ranged between 5 and 23% (averaged for the four animals in each treatment), and four of the groups had F absorption in the range 18–23%. Fluoride absorption was positively correlated with total soil F, but not correlated to extractable F. Water-extractable F was significantly higher in the smelter-polluted soils but F absorption by sheep from these soils was not significantly higher than uncontaminated soils with similar total F levels. In lambs, Clay & Suttie (1985) found that in comparison to NaF, F added as phosphate rock was absorbed by a proportion of 65%, defluorinated phosphate by 20%, and  $\text{CaHPO}_4$  by 50%. Also in lambs, Chaso et al. (1991) estimated that the bioavailability of F within sepiolite (a clay mineral in the palygorskite group) was 3% of that as NaF, based on monitored blood plasma concentrations.

In a study of cattle, Wöhlbier et al. (1968) dosed animal feed for almost a year with a soil containing 718  $\mu\text{g g}^{-1}$  total F and 16.5  $\mu\text{g g}^{-1}$  water-extractable F. Absorbed F ranged between 30 and 41% (38% average). Shupe et al. (1962) found that with dairy heifers, F within hay and as NaF was 75% absorbed,

but in the form of  $\text{CaF}_2$  only around half as much was absorbed (i.e., c. 38%). The National Research Council (1980) reported that in ruminants, F absorption from dietary bone meal ranges from 37 to 54% and in phosphate rock 50% of the F is absorbed.

From the study of Wöhlbier et al. (1968) it appears that the bioavailability of F in natural and polluted soils is similar or slightly lower than that of rock phosphate, dietary bone meal, and  $\text{CaF}_2$ . However, the results of Milhaud et al. (1989) indicate soil F absorption of half or less than the other sources, and that F absorption is positively correlated to total soil F concentrations. Hence, it appears that soil F bioavailability is extremely variable between different soil types, and probably depends on the species of F that occurs within different soils (e.g.,  $\text{CaF}_2$  in calcareous soils,  $\text{AlF}_x$  complexes in acidic soils).

#### **A PRELIMINARY MODEL OF SHEEP AND CATTLE F INTAKE**

The following calculations are made to determine potential effects of accumulation of soil F on grazing ruminants in New Zealand. The cases of both cattle and sheep are considered, initially under "normal" conditions. An average total F soil concentration of 200  $\mu\text{g F g}^{-1}$  is considered for New Zealand soils (Gemmel 1946), and an average pasture concentration of 5  $\mu\text{g F g}^{-1}$  (Table 5). Soil and dry matter ingestion rates of sheep (Table 7) are based on the data of Lee et al. (1996), and dry matter intake of cattle on the data of Coop (1965) (Table 8). Cattle soil ingestion rates (Table 8) are based on the data of Healy (1968) under the lower stocking rates reported (2–2.5 cattle  $\text{ha}^{-1}$ ). The absorption of pasture F is assumed to be 75%, based on the data of Shupe et al. (1962) and Clay & Suttie (1985). Absorption of soil F is more difficult to

**Table 7** Calculation of the daily available dietary F intake of sheep under an average New Zealand pastoral system; source of input parameters is described in the text. Low soil bioavailable soil F assumes 20% of soil F is absorbed. High soil bioavailability assumes 38% of soil F is absorbed.

Season	Total dry matter intake ( $\text{g d}^{-1}$ )	Soil intake ( $\text{g d}^{-1}$ )	Soil F concentration ( $\mu\text{g g}^{-1}$ )	Pasture F concentration ( $\mu\text{g g}^{-1}$ )	Bioavailable pasture F ( $\mu\text{g d}^{-1}$ )	Bioavailable soil F (low) ( $\mu\text{g d}^{-1}$ )	Bioavailable soil F (high) ( $\mu\text{g d}^{-1}$ )	Absorbed dietary F (low) ( $\mu\text{g g}^{-1} \text{d}^{-1}$ )	Absorbed dietary F (high) ( $\mu\text{g g}^{-1} \text{d}^{-1}$ )
Summer	1800	30	200	5	6638	1200	2280	4.4	5.0
Winter	1000	250	200	5	2813	10000	19000	12.8	21.8
Average	1400	100	200	5	4875	4000	7600	6.3	8.9

quantify, but based on the studies previously described, 20% was chosen as a low value and 38% as a high value (based on the data of Wöhlbier et al. 1968). The other assumption made in these calculations is that intake of F in drinking water is negligible. Since most natural waters contain  $<0.22 \mu\text{g F ml}^{-1}$ , drinking water is expected to make no difference to the calculations for New Zealand sheep and only small differences for cattle. Using these input variables, calculations of the available F dietary intake for sheep and cattle under normal conditions are presented in Tables 7 and 8.

From these calculations it appears that under normal conditions (i.e., without any human addition of F to the soils) during winter months sheep can ingest a NaF-equivalent dose (i.e., accounting for only 75% absorption of NaF) of up to  $17 \mu\text{g F g}^{-1} \text{ d}^{-1}$  ( $12.8/0.75$ ; using the low soil F bioavailability), or  $29 \mu\text{g F g}^{-1} \text{ dry matter d}^{-1}$  ( $21.8/0.75$ ; using the high soil F bioavailability). These doses are 28 and 48% of the daily dietary NaF tolerance ( $60 \mu\text{g F g}^{-1} \text{ dry diet}$ ), respectively (Table 6). The other feature shown by these calculations is that 45–61% of average daily dietary F is derived from soil ingestion, and that this may reach levels of 78–87% in winter.

Cattle during winter months can ingest NaF-equivalent doses of up to  $14 \mu\text{g F g}^{-1} \text{ d}^{-1}$  ( $10.6/0.75$ ; low soil F bioavailability), or  $23 \mu\text{g F g}^{-1} \text{ d}^{-1}$  ( $17.3/0.75$ ; high soil F bioavailability). These doses are 31 and 51% of the daily dietary NaF tolerance ( $45 \mu\text{g F g}^{-1} \text{ dry diet}$ ), respectively. Of the average daily dietary F of dairy cattle, soil ingestion appears to supply 47–63%, which may increase up to 71–82% in winter.

Using the same model parameters, we can calculate the threshold soil F concentration at which the daily dietary F tolerances of sheep and cattle are reached with the relationship:

$$\text{Tolerance}[\mu\text{gFg}^{-1}] = \frac{\text{pastureF}[\mu\text{gFd}^{-1}] + \left( \frac{\text{Soilintake}[\text{gd}^{-1}] \times \text{bioavailability}[\% / 100]}{\times \text{thresholdsoilF}[\mu\text{gFg}^{-1}]} \right)}{\text{DMintake}[\text{gd}^{-1}]}$$

Where:

$$\begin{aligned} \text{PastureF}[\mu\text{gFd}^{-1}] &= \text{pastureintake}[\text{gd}^{-1}] \\ &\quad \times \text{pastureFconcentration}[\mu\text{gFg}^{-1}] \\ &\quad \times 0.75 \end{aligned}$$

Tolerance = the tolerance limit of absorbed dietary F  
 pastureF = daily bioavailable pasture F intake  
 bioavailability = soil F bioavailability  
 thresholdsoilF = threshold soil F concentration  
 DMintake = daily dry matter intake.

This equation rearranges to:

$$\text{ThresholdsoilF} = \frac{\{(\text{Tolerance} \times \text{DMintake}) - \text{pastureF}\}}{\text{soilintake} \times \text{bioavailability}}$$

In Table 9, threshold soil F concentrations required to reach a NaF tolerance level of  $60 \mu\text{g F g}^{-1}$  for sheep (tolerance limit of absorbed dietary F of  $60 \times 0.75 = 45 \mu\text{g F g}^{-1}$ ) and  $45 \mu\text{g F g}^{-1}$  (tolerance limit of absorbed dietary F of  $45 \times 0.75 = 33.75 \mu\text{g F g}^{-1}$ ) for cattle during the winter months are calculated for low (20%) and high (38%) soil F bioavailabilities (Wöhlbier et al. 1968) and low ( $143 \text{ g d}^{-1}$  for sheep, Healy & Drew 1970;  $900 \text{ g d}^{-1}$  for cattle, Healy 1968) and high ( $300 \text{ g d}^{-1}$  for sheep, Healy 1967;  $1600 \text{ g d}^{-1}$  for cattle, Healy 1968) soil ingestion rates. The soil F concentrations ranged from 372 to  $1461 \mu\text{g F g}^{-1}$  for sheep and 326 to  $1085 \mu\text{g F g}^{-1}$  for cattle.

**Table 8** Calculation of the daily available dietary F intake of dairy cattle under an average New Zealand pastoral system; sources of input parameters are described in the text. Low bioavailable soil F assumes 20% of soil F is absorbed. High soil bioavailability assumes 38% of soil F is absorbed.

Season	Total dry matter intake ( $\text{g d}^{-1}$ )	Soil intake ( $\text{g d}^{-1}$ )	Soil F concentration ( $\mu\text{g g}^{-1}$ )	Pasture F concentration ( $\mu\text{g g}^{-1}$ )	Bioavailable pasture F ( $\mu\text{g d}^{-1}$ )	Bioavailable soil F (low) ( $\mu\text{g d}^{-1}$ )	Bioavailable soil F (high) ( $\mu\text{g d}^{-1}$ )	Absorbed dietary F (low) ( $\mu\text{g g}^{-1} \text{ d}^{-1}$ )	Absorbed dietary F (high) ( $\mu\text{g g}^{-1} \text{ d}^{-1}$ )
Summer	11600	350	200	5	42188	14000	26600	4.8	5.9
Winter	6400	1200	200	5	19500	48000	91200	10.6	17.3
Average	9000	700	200	5	31125	28000	53200	6.6	9.4

Regular application of phosphatic fertilisers is likely to increase the total F concentrations of soils as described above. Our results indicate that New Zealand Brown and Pallic Soils can retain between 40 and 60% of applied F in the top 75 mm of soil (Tables 3 and 4). The corresponding retention in Allophanic soils is expected to be much higher (70–90%). The following calculations are made to determine the effects of a regular maintenance application of 20 or 40 kg P ha<sup>-1</sup> yr<sup>-1</sup> to pastoral soils, on cattle and sheep dietary F intake. Given the parameters of a SSP fertiliser containing c. 9% P, and 1.46% F (Evans et al. 1971; P. Loganathan et al. unpubl. data), maintenance application rates are likely to add 3 or 6 kg F ha<sup>-1</sup> yr<sup>-1</sup>. For a phosphate rock fertiliser containing c. 13–14% P, and 3.2–3.4% F (e.g., Jordan or North Carolina phosphate rock, Manoharan et al. 1996), maintenance application is likely to add 4.9 kg F ha<sup>-1</sup> yr<sup>-1</sup>. If we assume that 80% of applied F is retained within the top 75 mm of an Allophanic Soil, and an average dry bulk density of the soil of 0.9 Mg m<sup>-3</sup>, then maintenance applications of SSP and phosphate rock fertilisers at 40 kg P ha<sup>-1</sup> yr<sup>-1</sup> will increase total soil F concentrations by 7.6 µg g<sup>-1</sup> yr<sup>-1</sup> and 11.6 µg g<sup>-1</sup> yr<sup>-1</sup>, respectively. In Pallic and Brown Soils (20 kg P ha<sup>-1</sup> yr<sup>-1</sup>) with an average F-retention of 50%, soil F concentrations will probably rise by 2.4 µg g<sup>-1</sup> yr<sup>-1</sup> and 4.1 µg g<sup>-1</sup> yr<sup>-1</sup>, respectively.

Given these F accumulation rates from phosphatic fertiliser application, the time taken for total soil F concentrations in an average pastoral soil to reach the thresholds for F intake of sheep and cattle

during winter can be calculated. For the case of Allophanic Soils with present soil F concentration of 200 µg g<sup>-1</sup> and a low soil F bioavailability, depending on the soil ingestion rate 55–166 years of superphosphate fertilisation is required, or 36–109 years of phosphate rock application. However, if the high rate of soil F bioavailability applies, only 17–75 years of superphosphate, or 11–49 years of phosphate rock fertilisation are required. Many of the higher P-fixing volcanic ash pastoral soils of New Zealand may have already received this amount of fertilisation.

A whole series of factors may influence these calculated predictions. The F content of SSP, and site-specific factors including soil type, soil pH, pasture management (and renewal), grazing management, and drainage, can markedly change local rates of soil F accumulation and rates of soil ingestion. In many Allophanic Soils (e.g., in Taranaki), high P-fixation occurs, and phosphate fertiliser application rates can be 45–60 kg P ha<sup>-1</sup> yr<sup>-1</sup> on dairy farms (Cornforth & Sinclair 1984). With an application rate of 60 kg P ha<sup>-1</sup> yr<sup>-1</sup> as SSP, F deposition rates could be as high as 10 kg F ha<sup>-1</sup> yr<sup>-1</sup> and the tolerance soil F levels would be reached in 36–76 years (low soil F bioavailability) or 11–32 years (high soil F bioavailability).

The use of phosphate rock fertilisers may lead to greater dietary F uptakes than those predicted so far. The low solubility of these fertilisers may lead to substantial amounts of undissolved phosphate rock incorporated in the surface soil. Manoharan et al. (1995) demonstrated that only 48% of Jordan phosphate rock, and 68% of North Carolina

**Table 9** Calculation of soil F concentration required to reach daily dietary intake tolerances for sheep and cattle in winter. Assuming 75% of F is absorbed from NaF doses of 60 µg F g<sup>-1</sup> d<sup>-1</sup> (sheep) and 45 µg F g<sup>-1</sup> d<sup>-1</sup> (cattle), from Shupe et al. (1962). Low soil bioavailability assumes 20 % of soil F is absorbed. High soil bioavailability assumes 38 % of soil F is absorbed.

Animal	Tolerance limit of absorbed dietary F (µg g <sup>-1</sup> )	Total dry matter intake (g d <sup>-1</sup> )	Soil intake (g d <sup>-1</sup> )	Pasture F concentration (µg g <sup>-1</sup> )	Bioavailable pasture F (µg g <sup>-1</sup> )	Required bioavailable soil F (µg d <sup>-1</sup> )	Threshold soil F concentration (low) (µg g <sup>-1</sup> )	Threshold soil F concentration (high) (µg g <sup>-1</sup> )
Sheep	45	1000	143	5	3214	41786	1461	
Sheep	45	1000	300	5	2625	42375	706	
Sheep	45	1000	143	5	3214	41786		769
Sheep	45	1000	300	5	2625	42375		372
Cattle	33.75	6400	900	5	20625	195375	1085	
Cattle	33.75	6400	1600	5	18000	198000	619	
Cattle	33.75	6400	900	5	20625	195375		571
Cattle	33.75	6400	1600	5	18000	198000		326

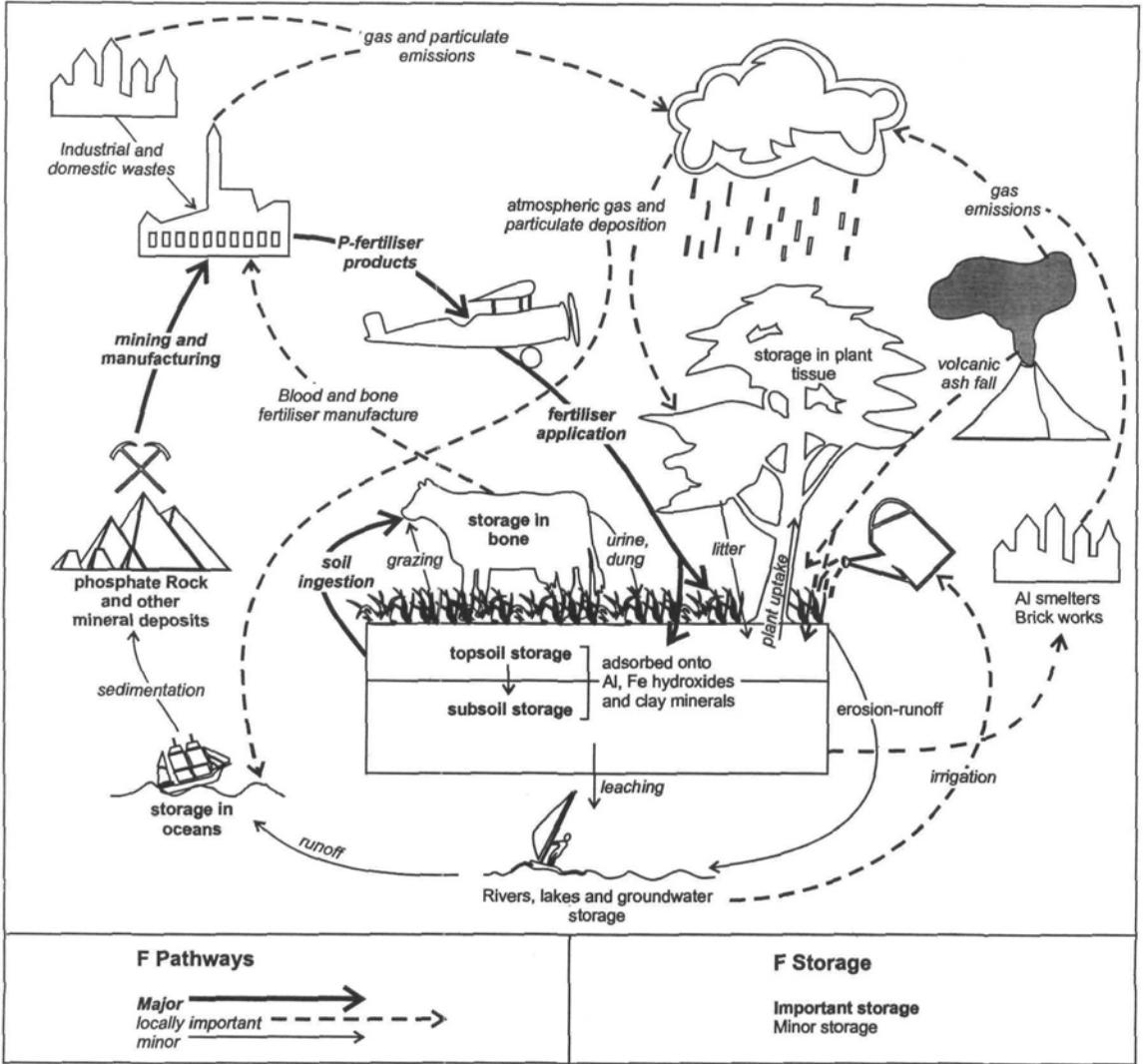


Fig. 1 Cycling of fluoride in grazed pasture systems.

phosphate rock dissolved during an 8-year trial. Fluoride within phosphate rock is around 38% bioavailable in grazing ruminants (Clay & Suttie 1985). Hence, on the basis of an average daily dry matter intake (Tables 7 and 8), sheep could obtain their daily tolerance level of bioavailable dietary F by ingesting just 5.1 g of phosphate rock residue with soil, and cattle by ingesting 24 g.

Accumulation of F in soil within the pH range 5.5–6.5 (general pH range of New Zealand pastoral soils) may lead to slightly elevated pastoral F contents over long periods, but, as discussed above, these increases are likely to be minor and should not provide much additional dietary F. However, at

lower or higher pH, greater uptake of F may occur, enriching pasture in F and leading to substantially higher dietary F intakes.

### CONCLUSIONS AND FUTURE DIRECTIONS

This review allows the preparation of an F cycle (Fig. 1), identifying important F-transfer pathways and F-storage locations. Fluoride is accumulating in most topsoils through atmospheric pollution and fertiliser addition. Rates of F input exceed losses because F is strongly held by many specific and non-specific adsorption sites in soils. Soils rich in

amorphous Al and Fe hydroxides and other clay minerals can retain up to 80% of applied F within the top 75 mm. Although F accumulation increases the soil solution and soluble and labile pools of F in soils, due to its strong adsorption, these comprise only a minor fraction of total soil F. Hence, the effect of F accumulation in soils does not appear to pose a threat to groundwater supplies. A combination of the strong adsorption of F in soils and its low rate of uptake by most plants means that normal pastoral plants are not likely to be greatly affected by increasing soil F concentrations. However, at low soil pH (<5), greater plant uptake of F may occur due to a possible preference for  $AlF_x$ , Si-FB, and HF species. At high pH (>6.5), desorption of non-specifically adsorbed F may also result in higher plant F uptake. The activity of soil micro-organisms is likely to be negatively affected as soil F concentrations rise. Data on the critical soil F concentration affecting soil microbial activity is scarce and inconclusive. In one study the activity of some microbial enzymes has been reported to have been inhibited at water-extractable soil F concentrations of  $\geq 20 \mu\text{g F g}^{-1}$ .

Although soil F is not likely to be passed on to grazing animals via pasture, it can be directly taken up by soil ingestion during grazing. Our model indicates that under normal conditions, soil ingestion probably provides more than 50% of the average dietary F of grazing sheep and cattle, and this may rise to >80% during the winter months. Ingestion of soil containing  $326\text{--}1461 \mu\text{g F g}^{-1}$  is likely to lead to chronic fluorosis in sheep and cattle, depending on the soil ingestion rate and bio-availability of F within the soil. Some New Zealand topsoils (0–75 mm) may already be within this F concentration range (Gemmel 1946) or close to this range (P. Loganathan unpubl. data), and certainly many agricultural soils around the world contain even higher concentrations of F. In another 17–166 years of SSP fertilisation and 11–109 years of phosphate rock fertilisation (depending on the application rate and F content of fertilisers, soil ingestion rate, and bioavailability of soil F), most New Zealand dairy and sheep farm soil F levels could rise into this potentially toxic concentration range. Currently, no alternative source of P fertilisers with low F content is available for use in our pastoral lands to reduce this rate of F accumulation.

Research is required to establish present F concentrations in New Zealand pastoral soils and accurately quantify the rate of F accumulation. From

this work, areas of greatest risk from chronic fluorosis problems can be identified, based on their soil, fertiliser, and pasture management characteristics. In addition, research is needed to determine the rates of dietary absorption of soil F within grazing ruminants. Particular attention must be paid to dietary F absorption from different soil types, e.g., those containing high allophane contents (which require high doses of P fertiliser), and those containing layer-lattice clay mineral assemblages (e.g., Pallic Soils). Further research also needs to ascertain rates of plant uptake of F under differing pH and consequent F speciation conditions, and potential impacts of elevated F levels on microbiological processes such as nitrogen fixation and nitrification.

Only once this additional information is obtained can adequate recommendations be made for mitigating the risks of increasing F levels in our pastoral systems, and developing practices that are sustainable in the future.

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