Fluorine accumulation and loss from a pasture soil

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Contents

1. Executive Summary

Fluorine (F) is an impurity in phosphorus (P) fertilisers and significant amounts of F can be added to agricultural soils as a result of long-term application of P fertiliser. There is a risk that F accumulation in soil may increase to levels that present a threat to New Zealand's pastoral industries through damage to livestock, the environment, and our international brand reputation. However, we currently have only limited information about the rate of F accumulation and loss from soil in New Zealand. The aims of this study were to i) measure F accumulation rates in a stony soil that has received regular addition of single superphosphate fertiliser (SSP) and ii) assess the effect of SSP inputs and irrigation on the vertical movement of F in soil.

Soils were analysed for total F from plots from the Winchmore long-term fertiliser trial which had three rates of SSP applied annually i.e. Nil, 188 kg SSP ha^{-1} (188PA) or 376 kg SSP ha^{-1} (376PA) between 1952 to 2015. In addition, soils were also analysed for total F from samples collected down the soil profile at intervals to 100 cm from both the long-term fertiliser trial and also the dryland and 20% moisture treatments from the long-term irrigation trial at Winchmore.

Results from the long-term SSP trial showed total soil F concentrations in the Nil treatment decreased slightly during the period of the trial, while F concentrations in the 188PA and 376PA treatments both significantly increased from 251 to 349 mg kg^{-1} and 430 mg kg^{-1}, respectively. Because there are currently no accepted risk based guidelines for soil F available in New Zealand, it is currently not clear if these concentrations are high enough to have a negative effect on soil, plant and animal health.

The rate of F accumulation in the topsoil (0 – 7.5 cm) for the 188PA and 376PA treatments were estimated at 1.1 and 2.1 kg ha^{-1} yr^{-1} respectively. These rates are lower than previous estimates for different soil types and landuse in New Zealand that have received similar rates (34 kg P ha^{-1} yr^{-1}) of SSP fertiliser.

Soil F concentrations in the 376PA treatment decreased with depth and were significantly higher than the Nil treatment to 50 cm, suggesting movement of F down the soil profile. There was also a decrease in soil F concentrations with depth in the dryland and 20% irrigated treatments, although no significant difference in the amount of F between irrigation treatments. We postulate the F was moving predominately in drainage water in this soil in the period after P fertiliser application in mid-winter rather than enhanced by irrigation.

This study has demonstrated that regular P fertiliser inputs (63 years) have significantly increased the amount of F in the topsoil. In addition there is evidence that F could move and accumulate down the soil profile to at least 50 cm, although mobility was not enhanced by the application of irrigation water.

2. Background

Fluorine (F) is a naturally occurring trace element that is also an incidental impurity (1 – 3%) in many phosphorus (P) fertilisers (Loganathan et al. 2003; McLaughlin et al. 1996). As a result of P fertiliser application, F has accumulated in some agricultural soils over time (Loganathan et al. 2001; McLaughlin et al. 2001). The accumulation of F in soils is potentially a problem because at elevated concentrations F may be phytotoxic (Mishra et al. 2014; Arnesen 1997), have adverse effects on soil organisms (Pascoe et al. 2014; Tscherko and Kandeler 1997) and could result in the development of chronic fluorosis in grazing ruminants through the inadvertent ingestion of F-enriched soil (Loganathan et al. 2008).

The historic and ongoing accumulation of F in soil from the use of P fertiliser represents a potential threat to New Zealand's pastoral industries through damage to livestock, the environment, and our international brand reputation. However, we currently have only limited information in New Zealand about the rate of F accumulation and loss from soil, and the impact of F accumulation in soils on plants and soil organisms. As a consequence, New Zealand's Regional Councils' Science Strategy 2015 identified soil F as a priority soil contaminant for investigation, and in 2016 the Fertiliser Association of New Zealand (FANZ) released a list of research priorities outlining information that needs to be collected to enable better management of F accumulation in New Zealand agricultural systems. Two areas identified as important were (i) getting more robust data on F accumulation rates in soil, particular those with low F sorption capacity and (ii) to assess the potential for subsurface movement and losses of F from soil.

The aim of this study was to assess F accumulation and subsurface movement from soil from the long-term fertiliser and irrigation trials at the Winchmore Irrigation Research Station. In particular, we wanted to:

i) measure F accumulation rates in a stony soil with a low F sorption capacity that has received regular addition of single superphosphate fertiliser (SSP) (*viz* F) over a period of 63 years.

ii) assess the effect of SSP application and irrigation on the vertical movement of F from topsoil to the subsoil.

3. Materials and methods

Soil samples were obtained from two long-term field trials at the Winchmore Irrigation Research Station, New Zealand. The soil at Winchmore is a shallow free-draining Lismore stony silt loam (Orthic Brown soil in the New Zealand Soil Classification; Hewitt 2010), formed from moderately weathered greywacke loess over gravels.

3.1 Fertiliser trial

Twelve plots comprising four replicates of three fertiliser treatments arranged in a randomised block design were selected for this study. Fertiliser has been applied annually as SSP in late winter to each plot since 1952. The treatments included a control (Nil P), 188 kg SSP ha^{-1} yr^{-1} (188PA) and 376 kg SSP ha^{-1} yr^{-1} (376PA). Lime was applied in 1947 (5 t ha^{-1}) and again in 1972 (4.4 t ha^{-1}), to maintain pH above 6. The trial received rainfall (740 mm) plus an average of 4.3 irrigation events (100 mm per event) per annum (total c. 1170 mm yr^{-1}). Each plot of each treatment was grazed rotationally by separate flocks of sheep to avoid nutrient transfer between treatments, with the stocking rates designed and adjusted to optimise pasture utilisation. No grazing occurred in winter.

3.2 Irrigation trial

Eight plots comprising four replicates of two irrigation treatments arranged in a randomised block design were selected for this study. The two treatments were a dryland treatment that only received rainfall and a treatment that received irrigation when the topsoil (0 – 100 mm) moisture reached 20% (50% available soil moisture (asm) with 0% asm being wilting point). On average, this resulted in 7.7 irrigations events (100 mm per event) per annum (total C. 1510 mm yr^{-1}). Both treatments received 250 kg ha^{-1} of SSP annually since 1949. Lime was applied to the whole trial in 1948 (5 t ha^{-1}) and 1965 (1.9 t ha^{-1}) to maintain soil pH at 5.5 to 6.0. Each treatment was rotationally grazed by a separate flock of sheep, like the fertiliser trial.

3.3 Soil samples

3.3.1 Temporal samples

Soil samples (0 – 7.5 cm depth) were retrieved from the soil archive for each treatment from the fertiliser trial i.e. Nil, 188PA and 376PA sampled in the spring each year from the years 1952, 1958, 1962, 1967, 1973, 1979, 1986, 1990, 1996, 2003, 2011 and 2015.

3.3.2 Depth samples

Soil sampling was carried out in 2009, from each replicate of the Nil and 376PA treatment from the fertiliser trial and also from the dryland and 20% moisture treatments from the irrigation trial. Conventional soil sampling with a corer was not practicable because of the high soil stone content with depth. Instead bulk soil samples were taken as previously outlined (Condron et al. 2014). Briefly, pits for each treatment were excavated with a mechanical backhoe, and soil and stones were collected from six depths (0–7.5, 7.5–15, 15–25, 25–50, 50–75 and 75–100 cm) using a 40 × 40 × 25 cm^3 steel frame. Each sample was weighed and separated into soil and stones (the roots having been removed) using sieves and weighed again. From each sample, approximately 3 kg of fresh soil subsample was set aside for analysis. From each subsample, a portion was weighed, dried at 105°C for 24 hours and weighed again. The sample's stone content and bulk density were determined by applying the subsample's water content to the sample's fresh soil and stone weights and accounting for the sample's volume.

3.4 Analysis

Soil was air-dried and ground (< 2 mm) prior to analysis. Soil pH was measured in a deionised water suspension with a soil:solution ratio 1:2.5 (Blakemore et al. 1987). Total organic carbon (C) concentration in the soil samples was measured by a combustion method (Kelliher et al. 2012). Amorphous iron (Fe) and aluminium (Al) oxides were determined by oxalate-extraction (McKeague and Day 1966). Determination of total F in soil samples was by the alkaline fusion/ion-selective electrode method of McQuaker and Gurney (1977). In this method, 0.5 g of dried and sieved (180 µm) soil sample is fused with 17 M sodium hydroxide in a nickel crucible at 600°C at 45 min in a muffle furnace, and the resulting fusion mass is dissolved in hot deionised water. The solution is adjusted to pH 8–9 (to precipitate iron and aluminium), filtered, and buffered (TISAB) to constant ionic strength. Fluoride was determined in the aqueous extracts using an ion-selective electrode (Frankenberger et al. 1996). Quality control measures for F analysis included use of blanks, analysis of duplicate samples and a reference quality control sample (CRM BCR-461; 568 ± 60 mg F kg^{-1}). Concentrations of F in procedural blanks were less than the detection limit of 20 mg L^{-1}. Results of duplicate analysis of samples were within 10% of each other. The recovery of F from reference material were within the limits of the certified value.

Statistical analyses were performed by GENSTAT for Windows v17. All data were checked for normality before being subjected to a two-way Analysis of Variance (ANOVA) to test for the effects of treatment and depth. Effects were considered significant if they differed at the probability level of 5% based on Fisher's unprotected least significant difference (LSD) test.

4. Results and Discussion

4.1 Temporal trends

Total soil F concentrations in the Nil treatment from the long-term SSP trial decreased slightly ($P < 0.011$) from 250 mg kg^{-1} in 1952 to 233 mg kg^{-1} in 2015 (Figure 1). The decrease is possibly a function of F that was present in the SSP applied during the trial establishment in 1947 being lost from the topsoil, either by leaching and/or in animal products. The slight decrease also highlights there was no measurable atmospheric or other inputs of F to the soil, which can be a significant source at some sites due to volcanic activity or industry (Gritsan et al. 1995).

The F concentrations in the Nil treatment are within the range of values previously reported for background sites in New Zealand. Gemmell (1946) reported topsoil concentrations of between 68 – 540 mg kg^{-1} (mean 189 mg kg^{-1}) across 23 different soils. Loganathan et al. (2003) found topsoil (0 – 7.5 cm) F concentrations ranged between 43 – 210 mg kg^{-1} for a range of Pallic, Ultic and Allophanic soils. Kim et al. (2016) estimated a mean total soil F value for Brown soils (0 – 10 cm) of 214 mg kg^{-1}.

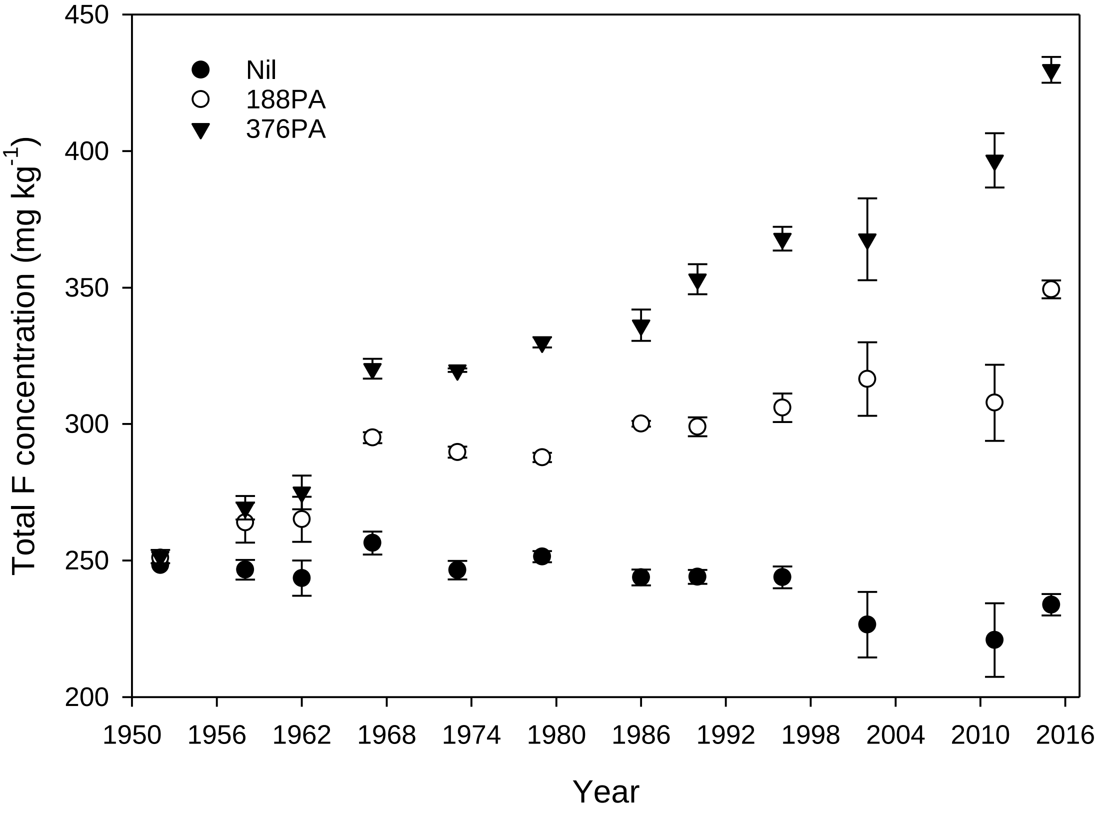

Figure 1. Total soil F concentrations (mg kg^{-1} ± SEM) on different fertiliser treatments in the Winchmore long-term phosphate fertiliser trial between 1952 to 2015.

A linear regression indicated a significant ($P < 0.001$) increase in mean concentration per year of 1.156 ± 0.159 mg kg F kg^{-1} in the 188PA treatment and 2.470 ± 0.171 mg kg F kg^{-1} in the 376PA treatment. Total soil F concentrations on the 188PA treatment increased from 251 to 349 mg kg^{-1}, and on the 376PA treatment from 251 to 430 mg kg^{-1}. These F concentrations are within the range of values previously reported for agricultural soils that have received P fertiliser in New Zealand. Loganathan et al. (2001; 2006) found topsoil (0 – 7.5cm) F concentrations from grazed pasture sites across predominantly North Island New Zealand ranged from 212 to 617 mg kg^{-1}. Jeyakumar and Anderson (2016) reported a range of 197 to 683 mg kg^{-1} (n = 10; 0 – 10 cm) in a number of soil orders under different land uses. Gray (2013) reported F concentrations between 168 – 580 mg kg^{-1}; mean 316 mg kg^{-1} from 14 dairy pasture soils in Marlborough, New Zealand. More recently, Kim et al. (2016) reported a mean F concentration for soil under sheep/beef of 389 mg kg^{-1} (n = 90; 0 – 10 cm) and 481 mg kg^{-1} (n = 120; 0 – 10 cm) under dairy, respectively. In an overseas study, Robinson & Edgington (1946) investigated the effect of SSP application on F concentrations in five different soil types in New Jersey. Total soil F concentrations in cultivated soils that had received SSP for between 23 to 40 years were on average 36 to 96% higher in surface soils (c. 15 cm) compared with soils that didn't receive SSP, with soil F concentrations ranging between 70 – 405 mg kg^{-1}.

Unfortunately no archival samples of SSP fertiliser were available for F analysis from this trial. Further, there is only data on F concentrations in two SSP fertiliser samples previously analysed in New Zealand 0.98% (Evans et al. 1971) and 1.84 % (Loganathan et al. unpublished). Also, given the variation in the source of P rock used to manufacture SSP fertiliser in New Zealand over the last 60 years (Anonymous 2008), and therefore likely variability of F content of the final fertiliser, an estimation of the percentage recovery of F in soil with any accuracy was not possible. Therefore, only the relative accumulation of F over time determined between treatments. Fluorine accumulation rates in the topsoil (0 – 7.5 cm) calculated for the 188PA and 376PA treatments, using a bulk density of 1.0 g cm^{-3} measured for this soil, were 1.1 and 2.1 kg ha^{-1} yr^{-1}, respectively. These rates are lower than those previously reported for pasture soils that have received F via P fertiliser. Loganathan et al. (2001) found F accumulation rates (0 – 7.5 cm) for two different New Zealand hill pastures grazed by sheep that had received 50 and 38 kg P ha^{-1} yr^{-1} had accumulated rates of 3.7 and 5.4 kg ha^{-1} yr^{-1}, respectively. On a soil under intensive dairy that received 60 kg P ha^{-1} yr^{-1}, an F accumulation rate of 7 kg ha^{-1} yr^{-1} was reported (Loganathan et al. 2001). More recently, using the topsoil (0 – 10 cm) F concentrations reported by Kim et al. (2016) for Brown soils under sheep and beef farming in New Zealand, adjusting soil depth to 0 – 7.5 cm, and assuming a bulk density of 1.0 g cm^{-3}, estimated accumulation rates were 3.8 kg ha^{-1} yr^{-1}. In soil from a long-term grazed pasture trial in Ireland that received 30 kg P ha^{-1} yr^{-1} for 30 years, McGrath and Tunney (2010) calculated a F accumulation rate of 1.9 kg ha^{-1} yr^{-1} (0 – 20 cm), which when adjusted to a depth of 0 – 7.5 cm was 5.1 kg ha^{-1} yr^{-1}. In contrast, using the soil F data from another long-term (59 years) grazed pasture site in Australia (McLaughlin et al. 2001), an accumulation rate of 1.3 kg ha^{-1} yr^{-1} adjusted to a depth of 0 – 7.5 cm was calculated, although this trial only received the equivalent of 8.5 kg P ha^{-1} yr^{-1}.

The lower rates of F accumulation found in this study are in part likely related to the generally lower rates of P fertiliser (*viz* F) applied to soil (i.e. 17 and 34 kg P ha^{-1} yr^{-1}) compared to other studies. However, even at sites where similar rates of P fertiliser were applied, there were still significant differences in F accumulation rates. Another factor may be the loss of topsoil F in outwash water from the application of border dyke irrigation at the Winchmore site. Although not measured, an earlier study at the same site estimated cadmium loss in outwash was a small but important loss pathway, at least as great as losses measured via leaching (McDowell 2010). However, a more likely factor is the differences in soil properties between studies that affect the ability of the topsoil to retain F. The acidic (pH 5.4) nature of the Lismore topsoil, along with the small amounts of oxalate extractable Al (2000 mg kg^{-1}) and organic matter (36 g C kg^{-1}), limits the F sorption capacity of this soil (Loganathan et al. 2006; Harrington et al. 2003; Omueti and Jones 1977). Furthermore, the soil in the fertiliser trial received on average 400 mm yr^{-1} of irrigation from four 100 mm irrigation events. This is on top of an annual rainfall of 740 mm. It is possible the combination of irrigation and low F sorption capacity has enhanced the movement of F out of the topsoil. This is something which has been assessed and is discussed in section 4.3.

4.2 Guidelines

At present, no nationally accepted risk-based guidelines protective of plants, animals or soil organisms have been developed for F in soil. There are however some ‘indicative’ soil F thresholds values that have been proposed for chronic fluorosis in grazing animals (Cronin et al. 2000). Cronin et al. (2000) estimated soil F threshold values for potential chronic fluorosis ranging from 326 to 1085 mg kg^{-1} for cattle and 372 to 1460 mg kg^{-1} for sheep, respectively, based on different soil ingestion rates and soil F bioavailability. Using these indicative thresholds, soil F concentrations found for the 188PA and 376PA treatments exceeded the lowest of these respective thresholds for cattle, and were exceeded for sheep in the 376PA treatment. However, importantly these thresholds are based on continuous absorption of F from soil ingestion. Subsequent studies by Grace et al. (2007) showed that during extended periods of lower ingestion of F, for example during summer months when soil ingestion is lower, up to 30 – 40% of the absorbed F in bones was remobilised. This may indicate that the indicative soil F thresholds causing fluorosis reported by Cronin et al. (2000) may need to be refined upwards, if ingestion rates vary with season.

Elevated soil F concentrations have been reported to adversely affect a wide range of plant functions including germination, photosynthesis, respiration, enzyme activity and biomass yield (Panda 2015; Mishra et al. 2014). Singh et al. (2013) reported that compared to a control, increasing soil F concentrations up to 200 mg kg^{-1} inhibited radish seedling germination percentage, length of root and shoot, plant height, and the number and size of leaves. Arnesen (1997) investigated the effect of increasing F concentrations on clover and ryegrass growth in a sand and a sandy loam soil. At 400 mg kg^{-1} there were visible signs of toxicity in both plants and soils, with negligible growth of clover in the sand. At 800 mg kg^{-1} there was plant growth in the sandy loam soil, although plants very stunted, and no growth in the sand soil. Telesinski et al. (2012) reported soil F EC_{50} values for root growth of 441 mg kg^{-1} and 203 mg kg^{-1} for white mustard and spring wheat, respectively. Jha et al. (2008; 2009) investigated the effect of increasing soil F concentrations on biomass yield in both onion and spinach. In onion there was a 70% decrease in bulb biomass at the equivalent of 362 mg kg^{-1} of added F. In comparison, the shoot yield of spinach only deceased by c. 25% at the same concentration. Based on these data, soil F concentrations in this study have increased by a magnitude that could potentially affect several plant functions including pasture production, although this is something that hasn't been yet determined experimentally for New Zealand soils and conditions. Furthermore, these studies applied F salts (often NaF) to soils. It is currently not clear how F added to soils from a P fertiliser source relates to a F salt with respect availability and toxicity.

Several studies have also demonstrated that soil microbiological processes can be affected by elevated soil F concentrations. Tscherko and Kandeler (1997) found that the soil microbial biomass (SMB) and dehydrogenase activity decreased when soil F concentrations exceeded 100 mg kg^{-1}. Poulsen (2011) reported phosphatase activity decreased significantly in soil, but at a soil F concentration of 1000 mg kg^{-1}. While Ropewelaska et al. (2016) only found a decrease in SMB at F doses in excess of 5000 mg F kg^{-1}, with a stimulatory effect reported at lower F concentrations. Based on these data, it is again not clear if the soil F concentrations are high enough in this study to negatively affect soil microbiological processes, although research is currently underway to start to collect relevant New Zealand data (Geretharan et al. 2017).

4.3 Depth samples

4.3.1 Fertiliser trial

A feature of the Lismore soil is the very low concentrations of Fe and Al oxides, along with low to very low soil carbon contents to a depth of 50 cm (Table 1).

Table 1. Mean ± 95% confidence interval for pH, soil carbon, oxalate extractable Fe and Al concentrations, bulk density and stone mass in soil taken at depth intervals.

Depth (cm)	pH	C (g kg^{-1})	Fe (mg kg^{-1})	Al (mg kg^{-1})	Bulk density kg m^{-3}	Stone mass kg m^{-2}
7.5	5.4 ± 0.1	35.9 ± 4.1	2175 ± 260	2073 ± 207	905 ± 40	1 ± 3
15	5.4 ± 0.1	29.3 ± 4.1	2334 ± 154	2161 ± 134	909 ± 253	15 ± 9
25	5.6 ± 0.1	19.6 ± 2.8	2319 ± 167	2111 ± 176	1270 ± 257	23 ± 14
50	5.7 ± 0.2	10.5 ± 2.1	2685 ± 144	2625 ± 391	691 ± 186	222 ± 116
75	5.8 ± 0.2	9.5 ± 1.3	2250 ± 171	5222 ± 422	426 ± 165	247 ± 88
100	5.9 ± 0.1	6.1 ± 0.7	1158 ± 225	4411 ± 378	484 ± 183	336 ± 94

These constituents have previously been shown to be important for F sorption in New Zealand soils, with F strongly bound to both Al polymers sorbed to soil organic matter and amorphous Al oxides (Loganathan et al. 2006).

Total soil F concentrations in the Nil treatment were relatively constant down to 50 cm (221 – 236 mg kg^{-1}), but then increased significantly (283 – 312 mg kg^{-1}) to 100 cm (Figure 2). The increase in soil F below 50 cm is likely of native origin and has been noted in other studies (Schuppli 1985; Omueti and Jones 1980; Robinson and Edgington 1946). It is recognised that native soil F is highly dependent on the soil parent material (Kim et al. 2016; Cronin et al. 2000). The Lismore soil is formed from a mantle of greywacke loess overlying older alluvium gravels. It would appear that the older, more weathered gravel material which occurs below 50 cm (Table 1) contains more F than the overlying loess material.

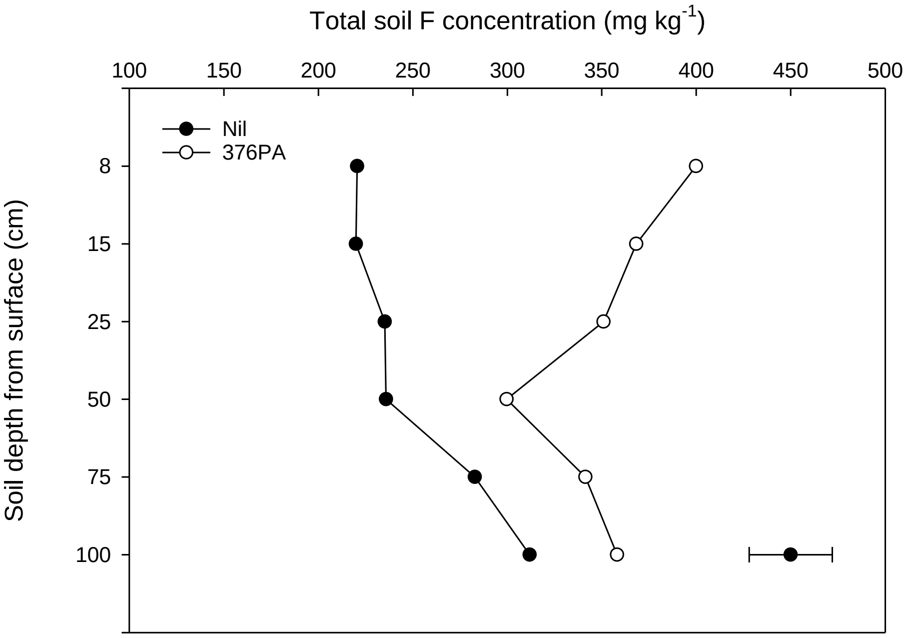

Figure 2. Mean concentration of F (mg kg^{-1}) with depth in the Winchmore long-term fertiliser trial. The LSD at the $P < 0.05$ level of significance is given for the comparison of means for the interaction of fertiliser treatment and depth.

Fluorine concentrations in the 376PA treatment decreased from 400 mg kg^{-1} in the 0 – 7.5 cm depth to 300 mg kg^{-1} at 50 cm, and like the Nil treatment increased below 50 cm due to a change in parent material (Figure 2). Fluorine in the applied P fertiliser has moved down the profile and accumulated to at least 50 cm (Figure 2 and Table 2). This is deeper than has been typically reported for the limited number of previous studies that have investigated the downward movement of F in soil (Loganathan et al. 2001). For example, Loganathan et al. (2007) compared the downward movement of F derived from 21 years of SSP application (27 kg P ha yr^{-1}) to a Pallic soil under pasture. There was only significant movement of F down the soil to 15 cm. Kim et al. (2016) measured the surface enrichment ratio of F for 95 pastoral farms (57 dairy and 38 sheep/beef) sampled at two depths (0 – 10 and 10 – 20 cm). Topsoil samples (0 – 10 cm) were enriched in total F by a mean factor of 1.24, corresponding to a decrease of 19.6 % moving to 10 – 20 cm. In several Australian soils that received P fertiliser under permanent pasture, McLaughlin et al. (2001) reported that the majority of F added to the soil remained in the top 10 cm of the soil profile. In contrast, Robinson & Edgington (1946) investigating the effect of SSP application on F concentrations in different soil types reported that at a depth of c. 15 – 35 cm, total F concentrations were elevated by 13 to 39% compared to control soils that had received no F. Interestingly, the largest increases in F at this depth were found in the sandy loam and gravelly sandy loam, a texture similar to Lismore soil.

The reason for the difference between studies include differences in the F sorption capacity of soils (Lismore soil is low), amount of drainage water (Winchmore rainfall plus irrigation) and differences in the F content of P fertilisers. Another feature of the irrigated plots of the Winchmore study is the high earthworm activity in the topsoil throughout the year. It has previously been shown that the numbers and biomass of earthworms in the Lismore soil is higher in the fertiliser treatments compared to the Nil P treatment (Fraser et al. 1994). The dominant earthworm species identified at the site is *Aporrectodea caliginosa*, which is very active in the top 120 cm of soils. This might well contribute to the vertical distribution of F in the soils sampled for our study.

Table 2. Mean quantity ± SEM (kg ha^{-1}) of F (corrected for stones) for soils taken at depths to 100 cm from the Nil and 376PA treatments from the long-term fertiliser trial. Means followed by the same letter are not significantly different ($P < 0.05$).

Depth	Treatment	
(cm)	Nil	376PA
0 – 15	299 ± 40a	500 ± 20b
15 – 50	590 ± 138b	921 ± 84c
50 – 100	541 ± 14ab	731 ± 145bc

4.3.2 Irrigation trial

In the irrigation trial, F concentrations were significantly higher in the dryland treatment than the 20% irrigation treatment in the 7.5 – 15 cm depth, but there were no other significant differences between treatments with depth (Figure 3). As was found in soils from the fertiliser trial, F concentrations in both irrigation treatments decreased to 50 cm and then increased below this depth.

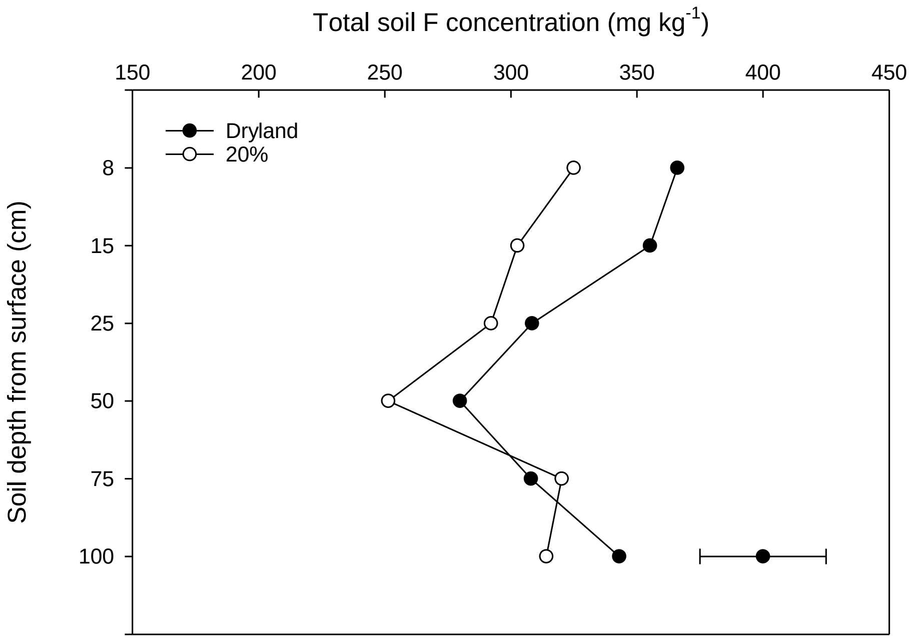

Figure 3. Mean concentration of F (mg kg^{-1}) for the dryland and 20% irrigated plots receiving 250 kg SSP ha^{-1} with depth in the Winchmore long-term irrigation trial. The LSD at the *P* < 0.05 level of significance is given for the comparison of means between the interaction of irrigation treatment and depth.

It was hypothesised that the addition of irrigation (approximately 770 mm yr^{-1}) compared to the dryland treatment would enhance the downward movement of F in this soil. However, there were no significant measurable differences in the quantity of F measured between the dryland and 20% irrigation treatment at any depth (Table 3).

Table 3. Mean quantity ± SEM (kg ha^{-1}) of F (corrected for stones) for soils taken at depths to 100 cm from the dryland and 20% treatments from the long-term irrigation trial. Means followed by the same letter are not significantly different (*P* < 0.05).

Depth	Treatment	
(cm)	Dryland	20%
0 – 15	551 ± 34a	376 ± 26a
15 – 50	872 ± 64b	811 ± 111b
50 – 100	845 ± 141b	616 ± 86ab

We postulate that the absence of a pronounced irrigation effect on F movement is due to the timing of SSP fertiliser application to the soil relative to the start of irrigation scheduling. Fertiliser is applied to all plots each year between mid-July and mid-August (Ray Moss, personal communication). We suggest that the small but significant amount of F that has moved to at least 50 cm in this soil is soluble F from SSP fertiliser that has moved downward in drainage during July and August before being sorbed by soil constituents i.e. Al oxides and Al associated with carbon. It is known that rainfall exceeds evaporation for these two months with a water surplus i.e. drainage of 46.8 ± 5.2 mm and 35.8 ± 4.2mm in July and August respectively (Kelliher et al. 2012). The irrigation season doesn't commence until on average mid-September each year (Srinivasan and McDowell 2009), by which time the concentration of F in solution is small and therefore leaching losses in drainage due to irrigation are comparatively low.

5. Conclusions

An understanding of the relationship between the inputs and outputs (i.e. losses) of F from pasture soils is important because of the potential threat F poses to New Zealand's pastoral industries through impacts on livestock, pastures and the environment, and the spill over to our international brand reputation. This study has demonstrated that regular P fertiliser inputs (63 years) have significantly increased the amount of F in the topsoil. The lower F accumulation rates found in the present study on the Lismore soil compared to previous studies is likely a result of the low soil F sorption capacity, in particular the very low amounts of Al oxides and organic matter down the soil profile to at least 50 cm depth. The absence of a pronounced irrigation effect might reflect the timing of P fertiliser inputs.

6. Recommendations

- At present there are only 'provisional' soil ecological guideline values available for F in New Zealand because of the dearth in availability of relevant data. It is therefore recommended that work is undertaken to collect data on the effects of soil F concentrations on pasture and forage crop production for the main soil types in New Zealand.

- It is recommended that data is also obtained on soil F concentrations which could affect soil microbiological processes.

- While this study showed that F could move downwards in a soil with a low F sorption capacity, what is unclear is how much F can be lost from soil via surface runoff. It is recommended work is undertaken to determine F loss via this pathway, perhaps 'piggy-backing' on existing trials that are investigating nutrient loss from soil.

7. Acknowledgements

We thank Professor Leo Condron for sharing archived soil samples which had been collected in the Winchmore plots in 2009. Chikako van Koten provided statistical advice and some analysis. Funding for this work was provided by the Fertiliser Association of New Zealand (FANZ) and Ministry of Business Innovation and Employment AgResearch Core funding contract number A20560.

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