The environmental fate of fluoride in coal seam water irrigation systems

Final Report

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Executive summary

- The movement of F in the plant-soil environment was investigated by studying:
  a) factors controlling adsorption of F by soils,
  b) factors controlling desorption of F from soil,
  c) movement of F in repacked soil columns irrigated with coal seam (CS) water,
  d) uptake of F from soils by Rhodes grass, lucerne and leucaena, and
  e) uptake of F from overhead irrigation water by the foliage of Rhodes grass, lucerne and leucaena.
- Altogether 95 soil samples were studied for their adsorption and desorption characteristics. Adsorption of F from soil was rapid (94-95% complete in 2 hours). Adsorption isotherms were best described by the Langmuir model which yielded numerical values for binding strength K_L and the maximum sorption capacity Qmax.
- Soils differed in sorption characteristics, with Ferrosols having the strongest adsorption capacity and binding strength. By contrast, sandy soils (Kurosols, Podosols) have low sorption capacity and low binding strength.
- The soils with the greatest affinity for F were the Brown Chromosol from IR8, Black Vertosol from Summerhills site 5, Dermosols from Reuben Downs sites 3 and 8, and the Chromosol from Springwater IR4-256. These soils could be irrigated with more than 400 ML CS water with 3 mg/L F concentration before the concentration of F in soil solution would exceed 2 mg/L.
- The soils with the least F binding capacity were the Dermosol from Mayfield South, the Tenosol from The Bend site 41 and the Brown Vertosol from IR6. These soils could only be irrigated with 23 ML, 31 ML and 42 ML of CS water containing 3 mg/L F respectively before drainage water F concentration would exceed 2 mg/L. The Brown Vertosol from IR6 had a high native F concentration and thus little capacity to adsorb more F from CS water.
- Adsorption of F was affected by pH. Maximum F adsorption in a range of soils occurred around pH 5.5. Higher or lower soil pH resulted in decreased adsorption and increased desorption. At low pH, protonation of F to form HF decreased F adsorption, whereas at high pH, competition with OH decreased F adsorption.
- Adsorption of F resulted in desorption of some OH from the soil minerals (and consequent pH increase), but the ratio of OH to F was below 1. Therefore, binding of F is due to ligand exchange and desorption resulting in a change in the charge of the solid phase.
- Adsorption of F was not diminished by competition from sulfate or chloride ions, therefore, land amendment irrigation (LAI) with saline CS water or pH adjustment of irrigation water with sulfate (under LAI or chemical amendment) will not affect F adsorption.
- Increasing the time of adsorption beyond 2 days resulted in stronger binding of F in all soils examined (Brown Chromosol, Red and Yellow Kandosol, and Ferrosol), but to a

lesser extent the Brown Vertosol. Thus, availability of F in these soils will decrease slightly over time.

- Application of high rates of F to soil resulted in higher relative availability of adsorbed F in soil since most high affinity binding sites in the soil are occupied by F, with the remainder of adsorbed F more weakly bound and therefore more readily desorbed. Thus soils incubated with high F solutions subsequently desorbed a greater proportion of adsorbed F.
- If comprehensive chemical properties were available for the soils, such as mineralogy and content of Fe and Al hydrous oxides, the amount of F adsorbed could be predicted from soil properties (R^2 = 0.855). Without these comprehensive data, F sorption could not be predicted well from soil properties described by routine laboratory analysis (R^2 = 0.459).
- Likewise, the phosphate buffer index did not predict the adsorption of F by soil (R^2 = 0.248). Therefore, it will be more useful to determine F adsorption isotherms directly, rather than relying on soil properties to estimate F binding.
- Adsorbed F was best desorbed with deionised water, whereas buffers or salt solutions were less effective. Desorption with deionised water mimics the effect of rainfall on soils in the field. Therefore, the laboratory desorption data obtained with deionised water are directly relevant to field conditions.
- Desorption of F was greatest from Brown Vertosol (IR6), and more F could be desorbed than was added due to the soil being naturally high in F.
- The least F desorption occurred from the Ferrosol (15% over 10 desorption steps) since this soil bound F strongest.
- Desorption isotherms indicated that there was an initial more rapid desorption of weakly held F, and desorption then decreased to low levels due to dissolution of F minerals in the soil or diffusion-controlled processes.
- Desorption of F did not increase or decrease at higher temperature in Yellow Kandosol IR8, Red Kandosol IR5 and Ferrosol. Desorption increased slightly at 65°C for Brown Chromosol IR8, Red Vertosol IR6 and Brown Vertosol IR6. Therefore, increasing the temperature does not facilitate the determination of desorption isotherms. By implication, mean maximum surface soil temperatures in the field which may range from 15°C to 65°C will have very little effect on mobility of F.
- The pH sensitivity of the desorption process mirrored the earlier observed effect of pH on adsorption. Minimum desorption (and thus maximum adsorption) occurred at the native pH of the soil and desorption increased both at lower and higher pH. Thus, pH can influence mobility of F in soil. Yet, changes in soil pH are likely to be minor in a well-managed CS water irrigation system, which minimises the risk of pH changes and, thus, limit mobility of F in the soil.
- Fluoride desorption increased when the soil:water ratio was increased in line with the prediction of the ‘ratio law’ of Schofield. While this will not affect F dynamics in field

soils where the soil:water ratio is greater than 1, the results predict greater desorption of F from eroded soil particles suspended in a large volume of water. Therefore, soil erosion control in CS water irrigated systems is important to minimise the risk of F movement into the broader ecosystem.

- After eleven desorption steps with deionised water (equivalent to rainfall of 6050 mm, assuming a soil bulk density of 1.1 g/cm^3), between 20-25% of the added F was desorbed from the Ferrosol, Brown Chromosol, and Yellow and Red Kandosol and 60-80% of added F was desorbed from the Black Vertosol. Over 100% of added F was desorbed from the Brown Vertosol indicating native F was desorbed from this soil. Thus, mobility of F in deep drainage or lateral soil water movement would be of concern with Vertosols, but not in soils rich in Fe and Al oxides.
- Drying of soil post F adsorption had no notable effect on F desorption from the Brown Chromosol, Ferrosol, Red and Yellow Kandosol, but increased F desorption from the Brown Vertosol.
- Movement of F in repacked columns containing Red Kandosol IR5 and Yellow Kandosol IR8 was low. Application of an equivalent 23.4 ML/ha CS water (containing 2.8 mg/L F) to the Red Kandosol increased the soil solution F concentration in the top 10 cm, but F did not move to 20 cm depth.
- Batch adsorption isotherms were used to estimate the volume of CS water containing 5 mg/L F that could be applied to the IR5 Red Kandosol (with and without lime-amendment) and the lime-amended IR8 Yellow Kandosol before the F concentration of the deep drainage water would exceed 1 mg/L. This modelling predicted that the IR 5 Red Kandosol (modelled soil depth 0.7 m) can receive 13,000 L CS water per square metre (i.e. 130 ML/ha), and the lime amended IR 5 Red Kandosol (modelled soil depth 0.7 m) can receive 105 ML/ha. The IR8 Yellow Kandosol (modelled depth 90 cm) can receive 139 ML/ha, and lime-amended IR8 Yellow Kandosol (modelled soil depth 90 cm) can receive 146 ML/ha. Under the same conditions, a diverse range of Queensland soils could receive from 18-30 ML/ha (Kurosols and Black Vertosols) to 144-264 ML/ha (Red Ferrosols).
- Foliar F concentrations in lucerne, leucaena and Rhodes grass did not increase significantly when adding up to 500 mg F/kg to the Red Vertosol. The foliar F concentrations remained around 10-20 mg/kg dry matter (DM), which is the detection limit of the method and below the maximum tolerable level of 30-100 mg/kg DM for dietary intake of F by beef cattle.
- In Red Kandosol and Yellow Kandosol, some differences were observed between the three plant species regarding the accumulation of F within the plant tissues, with lucerne potentially accumulating more F than the other two species. Adding up to 500 mg F/kg to the Red Kandosol and Yellow Kandosol did not increase the foliar F concentration in Rhodes grass and leucaena, with concentrations remaining around 10-20 mg/kg plant DM. However, the uptake of F by lucerne from the Red Kandosol and Yellow Kandosol was in a concentration-dependent manner. Specifically, foliar F was below 10 mg/kg DM when up to 50 mg F/kg was added to the soil, increasing to ca. 25

mg/kg DM when 150 mg F was added per kg soil, and up to 80 mg/kg DM when 500 mg F was added per kg soil.

- The soil type influenced the accumulation of F by the plant shoots. The largest accumulation of F within plant tissues was observed in the control (sand) which also corresponded to the treatment with the highest soluble F (1800 mg soluble F/L soil solution). In contrast, soluble F concentrations were moderate in the Red Kandosol (90 mg soluble F/L soil solution) and low in Yellow Kandosol and Red Vertosol (less than 20 mg soluble F/L soil solution).
- Overhead irrigation increased foliar F with both the number of irrigations and the concentration of F in the synthetic CS water. Foliage F levels were between 5-10 mg/kg DM (the detection limit of the method) in the control and 1 mg/kg CS water, and increased to 15 mg/kg DM in Rhodes grass, 22 mg/kg DM in leucaena and 45 mg/kg DM in lucerne with 5 mg F/L CS water after 8 irrigations.
- Following eight irrigations with the F-containing synthetic CS-water, a single fresh water irrigation (to simulate rainfall) decreased foliar F levels from 45 to 30 mg/kg DM for lucerne, from 22 to 18 mg/kg DM for leucaena and from 15 to 13 mg/kg DM for Rhodes grass. The decrease in foliar F levels was only significant for lucerne but not the other species.

Summary and implications of the research

Fluoride (F) may result in health problems for animals when present in their diets (food and water) at elevated levels. Plants are relatively insensitive to F, so interest in plant F concentrations is in the context of their use as animal feed. Fortunately, F is strongly held by soil mineral surfaces, rendering it biologically unavailable (non-toxic).

The research reported here investigated the potential for F from coal seam (CS) water to enter grazing animal food chain by two pathways:

1. Movement through the soil to groundwater or surface water which could be used as animal drinking water; and
2. Movement from the soil into plants, and accumulation in plant tissues that could be consumed by grazing animals.

Measurements were made of the capacity of soils to detoxify F by retaining it on the solid phase. For the soils tested, up to 60 ML/ha of CS water containing 6 mg F/L could be applied before drainage from the surface 1 m of soil would exceed the critical threshold value of 2 mg F/L. Indeed, for the majority of soils tested, the F from this amount of irrigation would be retained in the top 20 cm of soil. Only a soil with a high native F concentration required a greater depth (80 cm) to retain the added F. Soils with low sorption capacity (sands) are not suitable for irrigation with F containing water. It is important to note that most of the CS water currently being considered for land application has F concentration of around 3 mg/L, and in a typical land application scheme a total water application of less than 60 ML/ha would be expected over the life of the scheme.

Accumulation of F in plant tissue was evaluated for three pasture species (Rhodes grass, leucaena, and lucerne). Three soils and sand (a representation of the worst possible scenario) were deliberately contaminated with up to 500 mg F/kg. Rhodes grass and leucaena F levels were consistently lower than the maximum tolerable levels in beef cattle diets (30 to 100 mg F/kg plant dry matter (DM)); indeed they were typically below the detection limit of the analytical method used (20 mg F/kg DM). Lucerne accumulated up to 80 mg F/kg DM in the more acidic soils, though even elevation of F to this extent would not present an animal health problem as lucerne is typically a modest component of short-term animal diets in local beef production systems. It should be noted that to add 500 mg F/kg to the top 20 cm of soil would require the application of 200 ML/ha of 6 mg F/L water. Where CS water irrigation is restricted to meet the drainage threshold limit of 2 mg F/L (as discussed above), plant tissue F accumulation will not present an animal welfare problem.

These studies demonstrate that F containing CS water can be used for irrigation without environmental harm, or adverse health outcomes in grazing animals, provided the irrigated soil has reasonable F adsorption capacity (i.e. it is not sandy, or it does not have inherently high F status), and provided that the F loading is kept within appropriate bounds (concentration not exceeding 6 mg/L, and total irrigation volume not exceeding 60 ML/ha, or determined considering the soils capacity to adsorb F).

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Introduction

Fluoride (F) is of environmental interest because at elevated levels it may result in health problems for animals when present in their diets (food and water). Plants are relatively insensitive to F, so interest in plant F concentrations is in the context of their use as animal feed. Acute F toxicity only occurs when animals are exposed to very high dietary concentrations, and hence is of no relevance in the beneficial use of CS water. In contrast, chronic toxicosis can result from long term intake of relatively low levels (Table 1). Fortunately, F is strongly held by soil mineral surfaces, reducing its biological availability, and reducing its movement in soil solution. The soil effectively acts as a filter for F. The research reported here investigated the potential for F from CS water to enter the grazing animal food chain by two pathways:

- Movement through the soil to groundwater or surface water which could be used as animal drinking water; and
- Movement from the soil into plants, and accumulation in plant tissues that could be consumed by grazing animals.

Table 1. Maximum tolerable levels (MTL) of fluoride (F) in the diet for several animal species (mg/kg dry matter (DM)) (from National Research Council USA 2005)

Animal	MTL (mg F/kg DM)
Young beef calves and heifers	35
Young dairy calves and heifers	40
Heifers for breeding	30-40
Mature animals for breeding	40-50
Mature dairy cattle	40
Mature beef cattle	50
Mature beef cattle (finishing)	100 (reduced overall lifetime exposure)
Horses	40
Sheep (lamb or wool)	60
Lamb (finishing)	150

The key to understanding both of these pathways is the process of retention (and release) of F by the soil. Since CS water in the Fairview and Roma Project Areas typically contains 0.16-0.32 mM F (3-6 mg/L), the ability of soil to bind the added F is important for the sustainable beneficial use of CS water as irrigation water. The aim is to conservatively maintain forage F concentrations below 35 mg/kg dry matter (DM) to avoid fluorosis in young cattle (Table 1).

This Final Report summarises results obtained during Part I and Part II of the Santos-funded research conducted by the School of Agriculture and Food Sciences, The University of Queensland.

Materials and methods

The F concentration was determined with an ion-selective electrode (ISE) (Orion or TPS), stirring for 2-3 min or until the electrode reading stabilised at 25°C. All solutions to be measured were mixed with an equal volume of total ion strength adjusting buffer (TISAB II) containing 57 mL glacial acetic acid, 58 g NaCl and 4 g CDTA per litre adjusted to pH 5.4 (Buck and Cosofret, 1993). Fluoride standards were prepared by dissolving requisite weights of NaF in deionised water and diluting the standards with an equal volume of TISAB II prior to measurement. The pH of soil slurries (1:5 in deionised water) was determined with a combination pH electrode. Mostly, experiments were repeated three times unless otherwise stated.

Soil samples (2.0 g) were weighed into 15 mL conical centrifuge tubes. If not stated otherwise, 8 mL deionised water and 2 mL of NaF solution containing 50 mg/L F were added to the soil, giving a final concentration of 50 mg F/kg soil. Slurries were mixed overnight (14-19 h) on an end-over-end shaker at room temperature unless investigating the effect of temperature on F sorption. Earlier studies showed that incubation for 1 h is sufficient to adsorb over 90% of added F, but for convenience an overnight incubation period was used.

Soil samples

Santos supplied a number of soils comprising examples of soils likely to be irrigated with CS water and these soils were samples at several depths. Furthermore, a suite of soils was collected by UQ from throughout Queensland to increase the variety of soil types under investigation. During Part I of the study, 32 soils were used (Table 2), and during Part II, another 63 soils were investigated (Table 3). Altogether 95 soil samples were used in this study, but experiments often investigated only a limited subset of soil samples due to logistical constraints. If required, soils were crushed to 2 mm with a hammer mill, otherwise soils were only screened to 2 mm.

Table 2. Soils used in Part I of the study.

Soil type	Site name	Depth (cm)	Location
Grey Kurosol	Mt Cotton	5-15	153.2434E, 27.6091S
Podosol	Beerburrum	5-20	153.0545E, 26.9114S
Sand	Stradbroke Island	n/a	Stradbroke Island
Red Ferrosol	Lakelands	0-10	144.8309E, 15.8345S
		50-60	144.8309E, 15.8345S
Red Ferrosol	Toowoomba	50-100	Toowoomba
Brown Ferrosol	Lakelands	0-10	144.8507E, 15.8119S
		50-60	144.8507E, 15.8119S
Red Vertosol	Lakelands	0-10	144.8338E, 15.9141S
		50-60	144.8338E, 15.9141S
Red Vertosol	IR6	0-15	148.9384E, 25.7412S
	IR6	15-35	148.9384E, 25.7412S
	IR6	35-75	148.9384E, 25.7412S
Black Vertosol	Lakelands	0-10	144.4912E, 15.5008S
		50-60	144.4912E, 15.5008S
Black Vertosol	Gatton	0-5	152.3351E, 27.5465S
Brown Vertosol	IR6	0-15	148.9386E, 25.7404S
	IR6	15-35	148.9386E, 25.7404S
	IR6	35-75	148.9386E, 25.7404S
Brown Chromosol	IR8	0-15	148.9107E, 25.6369S
	IR8	15-35	148.9107E, 25.6369S
	IR8	35-75	148.9107E, 25.6369S
Yellow Kandosol (IR8 old)	IR8 old	Intact core	148.8994E, 25.6416S
Yellow Kandosol	Beerburrum	30-50	153.0153E, 26.8652S
Yellow Kandosol	IR8	0-15	148.8994E, 25.6416S
	IR8	15-35	148.8994E, 25.6416S
	IR8	35-75	148.8994E, 25.6416S
Red Kandosol (IR5 old)	IR5 old	Intact core	148.9942E, 25.7104S
Red Kandosol (IR8)	Waddy Brae	5-20	148.9136E, 25.6218S
Red Kandosol	IR5	0-15	148.9942E, 25.7104S
	IR5	15-35	148.9942E, 25.7104S
	IR5	35-75	148.9942E, 25.7104S

Table 3. Soils used in Part II of the study.

Soil type	Site name	Depth (cm)	Location
Brown Dermosol	Mayfield South	0-20	148.8599E, 26.4060S
		20-50	148.8599E, 26.4060S
Brown Dermosol	Broandah site 1	0-10	149.2623E, 26.4832S
		10-60	149.2623E, 26.4832S
		60-110	149.2623E, 26.4832S
		110-150	149.2623E, 26.4832S
Black Vertosol	Summerhills site 3	0-12	149.2778E, 26.4530S
		12-40	149.2778E, 26.4530S
		40-120	149.2778E, 26.4530S
		120-150	149.2778E, 26.4530S
Black Vertosol	Summerhills site 5	0-10	149.2720E, 26.4548S
		10-45	149.2720E, 26.4548S
		45-80	149.2720E, 26.4548S
		80-140	149.2720E, 26.4548S
Brown Dermosol	Summerhills site 10	0-7	149.2894E, 26.4427S
		7-50	149.2894E, 26.4427S
		50-100	149.2894E, 26.4427S
		100-150	149.2894E, 26.4427S
Brown Dermosol	Reuben Downs site 3	0-25	149.2952E, 26.5836S
		25-50	149.2952E, 26.5836S
		50-100	149.2952E, 26.5836S
		100-150	149.2952E, 26.5836S
Black Vertosol/Dermosol	Reuben Downs site 6	0-5	149.2841E, 26.5699S
		5-50	149.2841E, 26.5699S
		50-90	149.2841E, 26.5699S
		90-130	149.2841E, 26.5699S
Red Dermosol	Reuben Downs site 8	0-5	149.2764E, 26.5790S
		5-50	149.2764E, 26.5790S
		50-100	149.2764E, 26.5790S
		100-150	149.2764E, 26.5790S
Brown Dermosol	Reuben Downs site 17	0-30	149.3246E, 26.5882S
		30-70	149.3246E, 26.5882S
		70-100	149.3246E, 26.5882S
		100-140	149.3246E, 26.5882S
Red Chromosol	Springwater IR4-256	0-10	149.0557E, 25.7343S
		10-20	149.0557E, 25.7343S
		20-30	149.0557E, 25.7343S
		50-60	149.0557E, 25.7343S
Brown Chromosol	The Bend site 30	0-10	149.0299E, 26.4703S
		20-30	149.0299E, 26.4703S
		50-60	149.0299E, 26.4703S
		80-90	149.0299E, 26.4703S
Tenosol	The Bend site 41	0-10	149.0204E, 26.4755S
		20-30	149.0204E, 26.4755S
		80-90	149.0204E, 26.4755S
		110-120	149.0204E, 26.4755S

Brown Sodosol	Pleasant Hills site 63	0-10	148.9908E, 26.3986S
		10-20	148.9908E, 26.3986S
		20-30	148.9908E, 26.3986S
		50-60	148.9908E, 26.3986S
Red Chromosol	Pleasant Hills site 88	0-10	148.9920E, 26.4182S
		20-30	148.9920E, 26.4182S
		50-60	148.9920E, 26.4182S
		80-90	148.9920E, 26.4182S
Grey/Brown Vertosol	Weemilah site 1	0-20	148.8745E, 26.5109S
		20-50	148.8745E, 26.5109S
		50-80	148.8745E, 26.5109S
		>80	148.8745E, 26.5109S
Brown Kandosol	Springwater IR5(2)	0-15	148.9926E, 25.7132S
Brown Ferrosol	Kingaroy	0-15	151.8291E, 26.5785S
Grey Vertosol	Moonie	0-15	150.2440E, 27.7742S
Chromosol	Gatton	0-15	152.3389E, 27.5536S
		40-50	152.3389E, 27.5536S

Intact cores of two soil types (Red Kandosol from IR5(2) soil survey site J, GPS coordinates 148.992 E, 25.7104 S) and Yellow Kandosol from IR8 soil survey site FU 1 (GPS coordinates 148.8994 E, 25.6416 S) were obtained from the field trial site near Injune in southern Queensland. Intact 30 cm diameter soil cores were collected to a depth of 0.7 m for the IR5 Red Kandosol and to 0.9 m for the IR8 Yellow Kandosol. The cores were cut into 10 cm thick sections, dried at 105°C for 2 days and the bulk density recorded. These soils were used for the repacked soil columns (see below), and the individual 10 cm soil layers were used for adsorption studies or bulked and used for adsorption studies.

Determination of the physical and chemical properties of the soils

Standard soil chemical analyses (pH, EC, exchangeable cations, DTPA extractable micronutrients, etc.) on the soils were performed by commercial analytical laboratories (Phosyn Analytical, Andrews, QLD; and Pivot Incitec, Werribee, VIC). The surface areas of some of the soils were determined by the University of Adelaide. The mineralogy of some of the soils in Part I of the study was determined by X-ray diffraction (XRD) by CSIRO Land and Water (Urrbrae, SA). The hydrous oxides of Fe and Al in soils for Part I of the study were determined by the citrate dithionite method 13C1 as described by Rayment and Higginson (1992).

Adsorption studies

Adsorption losses of F on laboratory glassware and plastic ware

Laboratory plastic ware used in the studies was tested to determine the extent to which adsorption to sample containers could result in F losses from test solutions. An understanding of potential losses is necessary to obtain reliable results. The materials used in this study are shown in Table 4. The vials were tested by adding 5 mL of NaF solution (0.25 mg/L and 0.025 mg/L F, in TISAB) and incubating with shaking for 15 min or for 7 days. Thereafter, the F concentration remaining was measured with the ISE. Adsorption losses on the polysulfone hollow fibre soil solution samplers (Pall Microza) were determined by placing two solution samplers (5 cm long) in a 10 mL polypropylene vial and adding 5 mL NaF solution. After

incubation, the F remaining in solution was measured. Adsorption losses on white sand were determined by weighing 3.0 g white sand into 10 mL polypropylene vials, adding 5 mL NaF and incubating for 60 min or for 24 hours. The F remaining was measured in the supernatant after settling of the sand.

Kinetics of F adsorption

The kinetics of adsorption onto soil was determined by weighing 2.0 g of bulked soil of IR5 Red and IR8 Yellow Kandosol into 15 mL conical centrifuge tubes. Next, 10 mL solution containing 0.6 mg/L – 5 mg/L F was added and the time recorded. After various time intervals, tubes were randomly selected, centrifuged for 1 min to settle the soil particles, and F determined on the supernatant after mixing with an equal volume of TISABII. The response of the ISE towards F was determined by placing the electrode in NaF/TISABII solutions and measuring the time required for the reading to stabilise.

Determination of adsorption isotherms on soil batches

Into 15 mL centrifuge tubes, 2.0 g of dry soil (sieved to 1 mm to ensure a homogenous sample) was weighed, and resuspended with deionised water containing 0-500 mg/L F as NaF. After mixing the suspensions overnight (14-19 h), samples were centrifuged (10 min, 4000 xg), the supernatant mixed with an equal volume of TISAB, and the F concentration determined with the ISE. The concentration of F bound by the soil was calculated from the concentrations of F added and remaining free after equilibration.

Determination of the buffer capacity of soil

The pH buffer curve of two soils was determined by mixing 10 g of IR5 Red Kandosol and IR8 Yellow Kandosol with 50 mL deionised water and 0 - 5.0 g of $Ca(OH)_2$. Samples were placed on an end-over-end shaker for 2 days before measuring the pH.

Effect of pH on adsorption of F by soil

The topsoil layer of eight soils (Brown Dermosol Reuben Downs 17, IR6 Red Vertosol, Podsol (Beerburrum), Brown Ferrosol (Kingaroy), Red Ferrosol (Lakelands), IR8 Yellow Kandosol, IR5 Red Kandosol and Black Vertosol (Gatton)) was used for this study. Soil (20 g) was weighed into a 70 mL vial, mixed 40 mL of 125 mg/L F solution and placed on a shaker for 24 h. The slurry was then mixed vigorously while withdrawing 4 mL aliquots into 15 mL centrifuge tubes. Between 0.1-1 mL of 0.1 M HCl or NaOH was added to the tubes to achieve a range of pH values. Controls had no HCl or NaOH added. All tubes were made up to a total volume of 7 mL, placed back on an end-over-end shaker for 24 h at room temperature. Slurries were centrifuged at 3000 xg for 10 min and 2 mL of the supernatant mixed with 2 ml TISAB for F determination. The pH was determined on the remaining supernatant.

Comparative adsorption of F onto soil from NaF solution and CSG water

Bulked up soil samples of IR5 Red Kandosol and IR8 Yellow Kandosol were weighed off (2.0 g) and mixed with 8 mL deionised water. Either 2 mL of CS water or NaF solution with three F concentrations (0.2, 0.5 and 5 mg/L) was added to the slurries and the samples placed on an end over end shaker overnight. The composition of the CS water is shown in Appendix 2. Samples were centrifuged (30 min, 4000 xg) and 2 mL supernatant mixed with 2 mL TISAB and the concentration of F determined with the ISE. The concentration of F bound by the soil was calculated from the concentrations of F added and remaining free after equilibration.

Effect of sulfate on F adsorption

Four topsoil layers of Brown Vertosol IR6, Brown Chromosol IR8, Red Vertosol IR6 and Yellow Kandosol IR8 were used to test the effect of sulfate ions on F adsorption. 2.0 g of soil was mixed with 7 mL deionised water and:
1) 0 mL of 0.1 M Na_2SO_4 solution and 1 mL water (control)
2) 0.1 mL of 0.1 M Na_2SO_4 solution and 0.9 mL water (1 mM SO_4 final)
3) 1 mL of 0.1 M Na_2SO_4 solution (10 mM SO_4 final)
After mixing, 2 mL of 50 mg/L F solution was added to each tube and samples placed on a shaker overnight (14-19 h) at room temperature. After centrifugation for 5 min at 800 xg, the F concentration in the supernatant was measured after mixing with equal volume of TISABII. There were four replicates.

Desorption studies

Effect of pH of soil on desorption of F

Eight soils (all topsoil layers) were weighed (20 g) into centrifuge tubes, mixed with 30 mL of 125 mg/L F solution and placed on an end-over-end shaker for 5 days. Slurries were then centrifuged (3000 xg, 10 min). The supernatant was discarded and the pellet made up to 50 mL total volume. After the pellet was resuspended, 4 mL aliquots of the slurry were mixed with 0-1.5 mL of 0.1 M HCl or NaOH and made up to 7 mL total volume with deionised water. After shaking for 24 h, slurries were centrifuged (3000 xg, 10 min) and 2 mL supernatant mixed with 2 mL TISAB and F concentration measured. The pH was determined on the remaining supernatant.

Effect of temperature on desorption

Increased duration of incubation may result in stronger binding of F and decreased desorption. Therefore, desorption isotherms were determined for soil with short-term F adsorption (14-19 h) and long-term adsorption (12 weeks).

<u>Long term adsorption (12 weeks) with 30 min desorption</u>
The effect of long-term (12 weeks) adsorption and short-term desorption (30 min) steps was investigated for Brown Vertosol (IR6), Brown Chromosol (IR8) (15-35 cm depth), Red Kandosol (IR5), Yellow Kandosol (IR8) and Ferrosol (Toowoomba).

Slurries (2.0 g soil plus 10 mL F solution (500 mg F/L)) were incubated for 12 weeks, centrifuged (800 xg, 5 min) and the amount of F in the supernatant measured to calculate the amount of F bound by the soil. The pellet was resuspended in 10 mL deionised water and incubated for 30 min at either 25°C (control) or 65°C with occasional mixing by hand. The slurries were centrifuged and the supernatant collected for F analysis. The pellets were resuspended and incubated at the two temperatures for a total of five times and there were four replicates per soil and temperature.

<u>Short term adsorption (18 h) with 18 h desorption</u>
The effect of short-term adsorption (18 h) and short-term desorption (18 h) steps was investigated for Yellow Kandosol (IR8), Red Kandosol (IR5) and Red Vertosol (IR6) (from the 15-35 cm depth layer).

Slurries (2.0 g soil plus 10 mL F solution (500 mg F/L)) were incubated for 18 h, centrifuged (800 xg, 5 min) and the amount of F in the supernatant measured to calculate the amount of F bound by the soil. The pellet was resuspended in 10 mL deionised water and incubated overnight (14-19 h) at either 25°C (control) or 65°C with occasional mixing by hand.

Auxiliary studies showed that desorption of F from Red or Yellow Kandosol reached equilibrium after 100-120 min, but for convenience, desorption was routinely measured after overnight (14-19 h) equilibration. After incubation, the slurries were centrifuged and the supernatant collected for F analysis. The pellets were resuspended and incubated at the two temperatures for a total of five times and there were four replicates per soil and temperature.

Effect of solution composition on F desorption

The effect of sulfate ions, NH_4Cl and buffer on desorption of F was determined. First, Yellow Kandosol (2.0 g) was mixed with 8 mL deionised water and 2 mL of 50 mg F/L solution to adsorb F. After mixing overnight (14-19 h) at room temperature, the slurries were centrifuged and the pellet resuspended with 8 mL deionised water.

The F in the slurry was then desorbed with either

- 2 mL water (control)
- 0.1 mL 0.1 M Na_2SO_4 solution and 1.9 mL water (1 mM SO_4 final)
- 1 mL of 0.1 M Na_2SO_4 solution and 1 mL water (10 mM SO_4 final)
- 2 mL 1.5 M NaCl
- 0.1 mL 0.1 M Na_2SO_4 solution in 1.5 M NaCl and 1.9 mL of 1.5 M NaCl (1 mM SO_4 final)
- 1 mL of 0.1 M Na_2SO_4 solution in 1.5 M NaCl and 1 mL of 1.5 M NaCl (10 mM SO_4 final)

After mixing overnight (14-19 h) at room temperature, samples were centrifuged (800 xg, 5 min) and F in the supernatant measured. The desorption steps a-c were repeated another four times and there were four replicates.

Three desorbents have been tested for the efficacy in desorbing F from soils. Deionised water was used as control, and compared to 0.2 M NH_4Cl or 0.2 M TISAB3b (300 g Na_3citrate, 4 g CDTA, 60 g NaCl, 17.4 g citric acid, made up to 5 L) (Selig, 1973; Buck and Cosofret, 1993). After adsorption of F onto soils for 8-42 days at 25°C, slurries were centrifuged (800 xg, 5 min) and the pellet resuspended in either 10 mL deionised water, 10 mL of 0.2 M NH_4Cl or 10 mL of 0.2 M TISAB3b. After shaking overnight (14-19 h), the slurries were centrifuged (800 xg, 5 min), 2 mL of the supernatant mixed with 2 mL of TISABII and the concentration of F measured with the ISE. The desorption step was repeated 5-11 times.

Effect of soil:water ratio on desorption

A Brown Vertosol (labelled “Control 35-70 cm”, supplied by Santos in July 2012 for the soil and foliar F determination study), Red Kandosol IR5, Red Vertosol IR6 and Brown Chromosol IR6 was used for this study. No F was added to the soils. Soil (1-5 g) was weighed into 50 mL centrifuge tubes and mixed with deionised water give soil:water ratios (on weight basis) of 1:1, 1:2, 1:5, 1:10 and 1:20. Soil slurries were shaken for at least 1 h, centrifuged (800 xg, 5 min), and the F concentration in the supernatant determined. The experiment was repeated three times.

Effect of ageing on desorption

Five soils (Brown Chromosol IR8, Brown Vertosol IR6, Ferrosol, Yellow Kandosol IR8 and Red Kandosol IR5, topsoil layer) were incubated with 500 mg F/kg soil for 10 min, 2 days, 8 weeks and 12 weeks. Triplicate soil slurries were centrifuged and the pellets resuspended with 10 mL deionised water, shaken overnight, centrifuged (30 min, 4000 g) and 2 mL supernatant

mixed with 2 mL TISABII and the concentration of F determined with the ISE. These steps were repeated five times and the concentration of F desorbed measured each time.

Effect of soil drying on desorption

Triplicate soil slurries (Brown Chromosol IR8, Brown Vertosol IR6, Ferrosol, Yellow Kandosol IR8 and Red Kandosol IR5, topsoil layer) were mixed with F solution (50 mg/L) for 14-19h, and then centrifuged (800 xg, 5 min). The pellets were either stored moist at room temperature or dried at 65°C for 72 h. The pellets were resuspended with 10 mL deionised water, shaken for 7 h at 25°C, centrifuged (800 xg, 5 min) and the concentration of F in the supernatant determined after mixing with an equal volume of TISABII.

Determination of desorption isotherms

For Yellow Kandosol, Red Vertosol, Red Kandosol, Brown Vertosol and Brown Chromosol, 2.0 g samples were mixed with 8 mL CS water (Appendix 2) augmented with F to a final F concentration of either 5 mg/L or 125 mg/L (three replicates each) and allowed to equilibrate in an end-to-end mixer for 7 days. The samples were then centrifuged (800 xg, 5 min) and the supernatant removed and measured for F content to identify how much F had originally adsorbed to the soil. The supernatant was then replaced with water and placed in an end-over-end mixer for at least one hour. The samples were then centrifuged (800 xg, 5 min) and the supernatant removed, mixed with TISABII and F concentration measured with an ISE, indicating how much F^- was desorbed from the soil. This process was repeated seven times and desorption curves produced.

Determination of total F in soils and plants by NaOH fusion

To determine the total concentration of F within the plant tissues or soil samples, samples were prepared for NaOH fusion as outlined in Appendix 3.

Plant uptake of F

Leucaena (*Leucaena leucocephala* cv. Tarramba), lucerne (*Medicago sativa* L. cv. L91) and Rhodes grass (*Chloris gayana* cv. Top Cut) were selected for investigation in the glasshouse experiments due to differences in leaf morphology and their importance to irrigated pasture systems. Lucerne is a perennial legume grown extensively throughout Australia, Rhodes grass is a leafy tufted grass, and leucaena is a leguminous shrub or tree (if unpruned) which is often grown in rows with accompanying grass species. Rhodes grass-leucaena pasture systems are extensively used in Queensland and have been proposed for CS water irrigation systems. Leucaena seeds were germinated on germination trays in the laboratory for 6 d prior to planting while lucerne and Rhodes grass seeds were sowed directly into the pot.

Plant uptake of F from soil

The top (0-15 cm) layer of the Red Kandosol (IR5), Yellow Kandosol (IR8) and Red Vertosol (IR6) soils provided by Santos were utilised in the root uptake pot trials. Preliminary experiments found that F binds strongly to most soils and hence most would be retained within 10 cm of the soil surface. Therefore, the surface layer of these soils is of most relevance in a pot trial. The Stradbroke Sand was also included in the pot trial, as the adsorption trials showed negligible F adsorption. The soils were amended with 0, 50, 150 and 500 mg F/kg. The NaF salt was dissolved in 5 L of deionised water and sprayed evenly across the surface of the soil. The soil was then mixed thoroughly. The remaining sample of soil was kept as the control treatment (0 mg F/kg). Due to its low adsorption capacity, F was added to Sand by adding the F to the amount of water required for each pot to reach field capacity (approx. 1 L).

The soil was filled into ANOVA pots (200 mm, Anova Solutions Pty Ltd. (2010)), pots were wrapped in reflective insulation foil (to ensure consistent soil temperature across pots), and positioned on a capillary watering bench with 'Ebb and Flow' matting (Figure 1). This was utilized to reduce leaching through the pot and maintain constant water content within the soil, whilst also preventing plant roots growing through the base of the pot.

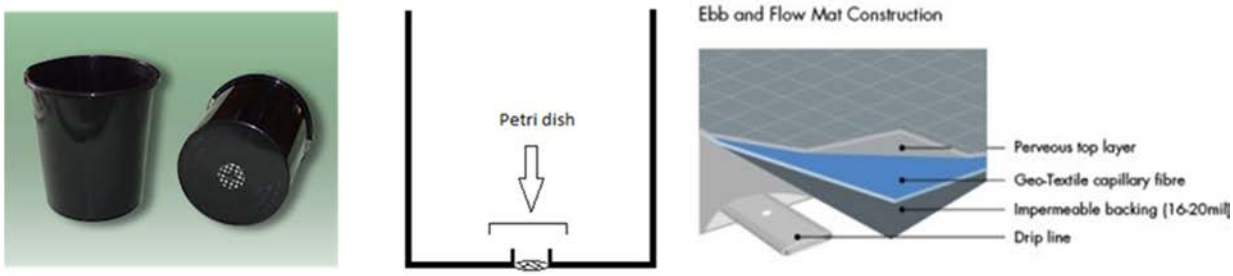


Figure 1. From left to right - Anova pots (200 mm) selected for the glasshouse experiments, petri dish positioned within each Anova pot to prevent root growth through the base of the pot, and general Ebb and Flow matt design, with conductive capillary fibre between a pervious top layer and impermeable backing

The soil surface was covered with white polypropylene beads to reduce water evaporation. A base rate of 'Flowfeed' fertiliser was added at 50 g/660 mL (15 mL per pot), one and three weeks after sowing of seeds. Leucaena, lucerne and Rhodes Grass were grown in the pots and thinned to around 3-5 plants per pot.

Germination was good for all treatments other than the F-containing Sand treatments. No seeds germinated in the 150 and 500 mg F/kg treatments in the Sand. Poor (or no) germination was observed in the 50 mg F/kg Sand treatment. For this reason, seeds of all species were germinated in the laboratory before transplanting in the Sand-F treatments; however, there was again 100% mortality. Finally, transplanting of week old seedlings from Sand control to F-treatment pots was also attempted, although again, most of these more mature seedlings also died after ca. 1 d.

Following their establishment, seedlings were thinned to three plants per pot. The plants were left to grow for a period of ca. eight weeks prior to harvest on 14 January 2013. All plant material from ca. 1-2 cm above the soil was harvested, weighed and dried in an oven at 60°C for 4 d. Once dried, the plant material was reweighed and ground to a powder then placed in labelled plastic bags prior to the fusion process.

Soil solution was extracted from the soil using centrifugation as described by Gillman (1976). Briefly, 300 g of soil at field capacity was centrifuged until >3 mL soil solution had been extracted. Where the extracted soil solution contained particulates, the solution was transferred to 10 mL tubes for further centrifugation (4000 xg, 5 min). The solution was analysed for electrical conductivity (EC), pH, F (1:1 with TISABII) and major cations and anions (ICP-OES).

Plant uptake of F from overhead irrigation

This experiment aimed to investigate foliar retention of F from direct contact between foliar surfaces and CS water containing F. In order to reduce potential F uptake by plant roots, a Red Ferrosol (not previously irrigated with CS water) was used as growing medium. Red Ferrosol was shown to have an extremely high F adsorption capacity, ensuring that little, if any F will

be taken up by the plant roots. To further prevent F reaching the plant roots, plastic covers were placed over the pot to deflect irrigation from the soil.

Leucaena, lucerne and Rhodes grass were grown in the Ferrosol and fertilised with 'Flowfeed' approximately every 2-3 weeks for the duration of the trial. Plants were irrigated twice weekly using irrigation chambers connected to a pump and a 100L containing one of the four F treatments (artificial CS water with either 0, 1, 3 or 6 mg/L F). Since CS water has a background F concentration of 2-3 mg/L, artificial CS water was used to vary the F concentration. The artificial CS water contained 26.6 g $CaCl_2$.$2H_2O$, 0.8 g KCl, 37.9 g NaCl, 18.2 g $NaHCO_3$ and 139 g Na_2SO_4 per 100 L.

Foliar material was randomly harvested from each plant in each pot after 0, 4 and 8 irrigations with F treatments. After the third harvest (following eight F irrigations), the plants were irrigated with deionised water for 10 mins to simulate a rainfall event, allowed to dry overnight and harvested. After 2 weeks samples of the plants were harvested again (to see if any F in the foliar material is removed over time).

Movement of F in repacked soil columns

Acrylic columns (6 cm internal diameter × 120 cm long) were sealed at the bottom with an acrylic plate and a circular piece of capillary matting placed over the bottom plate on the inside. Access holes were drilled into the wall of the column every 10 cm from the bottom. The empty weight of each column was recorded.

Intact PVC soil cores collected from the IR5 (Red Kandosol) and IR8 (Yellow Kandosol) were cut into 10 cm sections, dried, ground and repacked in the correct sequence into the acrylic tubes in 10 cm layers and compacted to the approximate bulk density of the native soil. The final weight of the soil-filled column was determined and the bulk density checked. This process was repeated for the other two replicates and for the other soil type. The columns were gradually wet up with deionised water until drainage started and the volume of water required to start drainage recorded. This provided an estimate of the pore volume. Finally, steel rods were inserted into the sampling ports to create holes and hollow fibre solution samplers were inserted. The columns were tapped on a firm surface to compact the soil to form a seal between soil and the solution sampler. Soil solution was collected by applying vacuum with a syringe to the hollow fibre sampler. An outflow tube was attached to the base of each column for collection of eluate.

To test the influence of pH on F sorption, the soils were mixed with lime ($CaCO_3$) at a ratio of 10 g $CaCO_3$ per kg soil (equivalent to 15 t/ha) and packed into soil columns as outlined above. Columns were irrigated with CS water (for composition see Appendix 2) with volumes corresponding to 1/3 of the column pore volume and the eluate and soil solution was sampled after one pore volume was applied to the columns (i.e. after every third application). Soil solution and eluate was collected and analysed for F and pH.

Data analysis

Two-way ANOVAs were used to investigate the relationships between F-additions to soils, soil types, and plant species. The F concentration of soil solutions of the four soils was also investigated by conducting a two-way ANOVA, although Sand treatments were removed for the soil F concentrations as the variance did not conform to the normal distribution. Statistical analysis was conducted using Genstat and Minitab 16. Thermodynamic speciation of F within soil solution was estimated using PhreeqcI (Parkhurst and Appelo, 1999). Total F in the soil solution and speciation of F in the soil solution was correlated to F in plant material using

Pearson's correlation coefficient. All other statistical analyses utilised one-way ANOVA using Proc GLM in SAS and treatment difference were tested for significance at the 5% level using Tukey's t-test.

Results and discussion

Adsorption studies

Adsorption losses of fluoride

Contact of solutions containing low F concentrations (0.25 and 0.025 mg/L F) with plastic ware, glassware and other materials to be used in trials, showed that adsorption losses of F were low. Losses ranged from 3 to 5%, and -4 to 1%, using 0.25 mg/L F and 0.025 mg/L F, respectively (Table 4). This indicates that adsorption losses are negligible, but borosilicate glass appears to release F from the glass into the solution, leading to a slight increase in F concentration over 45 min. Likewise, white sand appeared to release some F. Therefore, the use of glassware should be avoided, but polypropylene labware can be used to accurately determine F adsorption in soil matrices. Consequently, all experimentation reported in this study was undertaken in polypropylene labware.

Table 4. Adsorption loss/gain of F on labware from various manufacturers.

Item	Manufacturer	Material	F loss (%) from 0.25 mg/L F	F loss (%) from 0.025 mg/L F
30 mL vial, yellow cap	TechnoPlas	polypropylene	4	1
15 mL conical centrifuge tube	Neptune	polypropylene	3	0
50 mL conical centrifuge tube	BD	polypropylene	3	0
15 mL conical centrifuge tube	BD	polypropylene	3	0
70 mL specimen jar	TechnoPlas	polypropylene	3	0
10 mL flat bottom tube	TechnoPlas	polypropylene	3	0
Soil solution samplers	Pall Microza	polysulfone	5	1
Borosilicate beaker	Schott	Pyrex glass	n.d *	-4
White sand			n.d	-0.3

*) not determined

Kinetics of F adsorption

Adsorption of F from dilute solutions (0.6 mg F/L) onto IR5 Red Kandosol and IR8 Yellow Kandosol was rapid (94-97% adsorbed within 2 min) and reached a maximum (98% adsorbed) within 26 hours and decreased slightly after 888 hours (Figure 2). The slight decrease in adsorption after 26 hours may be an artefact of the chemical composition of the F-containing solution. This synthetic solution contained a low concentration of TISABII, which may have reacted with soil constituents such as Al and Fe oxides, thereby decreasing available binding sites for F and complexing Al and Fe from Al-F and Fe-F complexes, and increasing the measured F concentration.

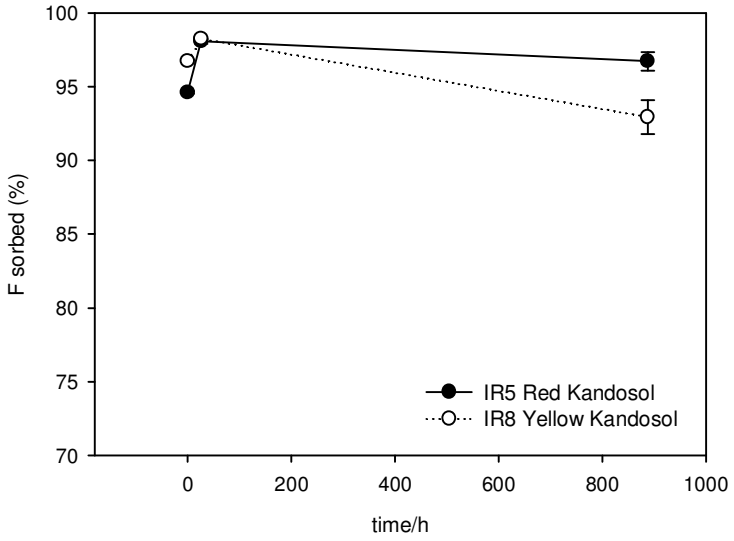


Figure 2. Time course of F adsorption from a solution containing 0.6 mg/L F in TISABII (1:20 diluted). Values are the mean of triplicate samples with the standard deviation shown for the IR5 Red Kandosol and IR8 Yellow Kandosol.

The experiment was repeated using 0.6 mg/L F (NaF) solutions without TISABII and focussing on short-term adsorption. In this case, adsorption was observed to happen quickly (87-88% after 3 min) and increased (88% adsorption) with time up to 2 hours (the duration of the experiment) (Figure 3).

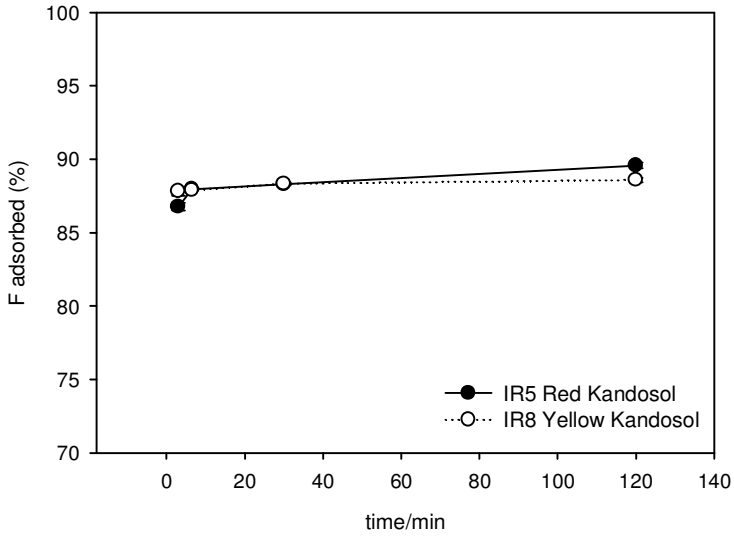


Figure 3. Time course of F adsorption from a solution containing 0.6 mg/L F in water. Values are the mean of triplicate samples with the standard deviation shown for the IR5 Red Kandosol and IR8 Yellow Kandosol.

Repeating the experiment using higher F concentrations (5 mg/L F) and a longer time scale, showed again that F adsorption occurred quickly (92-94% in 2 min) and reached a plateau (94-95% F adsorption) after 2 hours and adsorption increased slightly over 312 hours (Figure 4).

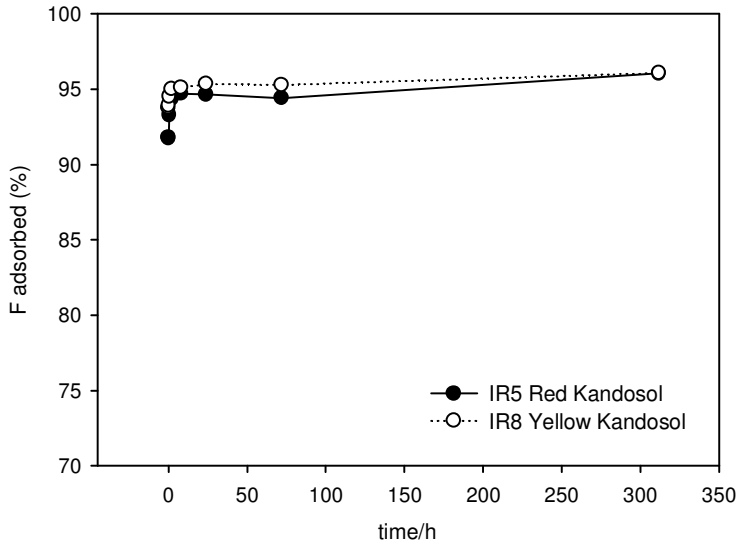


Figure 4. Time course of F adsorption from a solution containing 5 mg/L F in water. Values shown are the mean of duplicate samples for the IR5 Red Kandosol and IR8 Yellow Kandosol.

In summary, the adsorption of F onto these two soils at their natural pH values (pH 4.45 for IR5 Red Kandosol; pH 4.85 for IR8 Yellow Kandosol) was rapid (87-94% in 2 min) and nearly complete (88-95% F adsorbed) within 2 hours. The rapid adsorption of F is in agreement with numerous studies (Bia et al., 2012; Sujana et al., 2009). Adsorption of F may slightly increase over time. Thus, binding of F is caused by rapid adsorption of F to binding sites, but there appears to be minimal conversion of adsorbed F to precipitated or occluded forms as is known for phosphate. The implication of these results is that application of CS water to soil results in rapid immobilisation of F, with very little risk of F moving from the site of application by percolation through the soil profile. Therefore, water application rates (as mm/hour) are likely to be unimportant as long as application rates do not result in runoff, which would not be the case in a well-managed irrigation system.

Adsorption isotherms

Four adsorption isotherms (Langmuir, Freundlich, Generalised Freundlich and Langmuir-Freundlich) were fitted to the experimental data by non-linear regression. Of these models, the Langmuir model gave the best fit for most soils, followed by the Freundlich isotherm. Both models have two adjustable parameters, but the Langmuir model assumes that sorption capacity reaches a maximum and levels off, whereas the Freundlich model has infinite adsorption.

The adsorption isotherms for the 95 soil samples differed. For example, F adsorption onto Red Ferrosol increased linearly with F concentration (Figure 5). This is due to strong binding of F by the soil and a high sorption capacity. F sorption onto IR6 Brown Vertosol was low (Figure 5), and the soil desorbed F in the control (no F added) due to high native F concentration of the soil. Therefore, the soil could not bind much more F and the binding strength of F was low. Sorption of F onto the Stradbroke Island Sand was negligible (Figure 5), since sand has few binding sites for F. Sorption on IR5 Red Kandosol differed between soil layers (Figure 5), with the topsoil having much greater F sorption than the subsoil layers and these differences may be due to mineralogy and/or pH. Although topsoil will have higher organic matter content, than the subsoil, organic matter is considered not to bind much F due to a low number of binding sites. Sandy soils like the Podsol have a smooth isotherm (Figure 5), with sorption gradually increasing due to low binding strength and low number of binding sites. The 30-70 cm and 70-100 cm depth layers of the Brown Dermosol from Reuben Downs 17 had non-

conforming isotherms and this was due to precipitation reactions occurring when higher concentrations of F were added. Soil solution chemistry of the 30-70 cm and 70-100 cm depth layers was used to model the reactions of F in the Dermosol. Modelling was performed with the PhreeqcI software with the MINTEQV4 database and predicted that precipitation of F as fluorite (CaF_2) would occur, with some minor contribution of carbonate-rich fluoroapatite ($Ca_5(PO_4,CO_3)_3(F,O)$). Precipitation of CaF_2 in these layers occurred when then added F concentration exceeded 120 mg F/kg, whereas adsorption occurred at lower F concentrations.

The sorption characteristics determined for the Red and Yellow Kandosol differed for the soil in the intact cores and the three depth layers (Table 5). We consider the differences to be caused by the unrepresentative nature of the soil samples used for the intact core soil (single 30 cm diameter core), compared to the bulked soil collected from a 1 m^2 area used for the three depth layers.

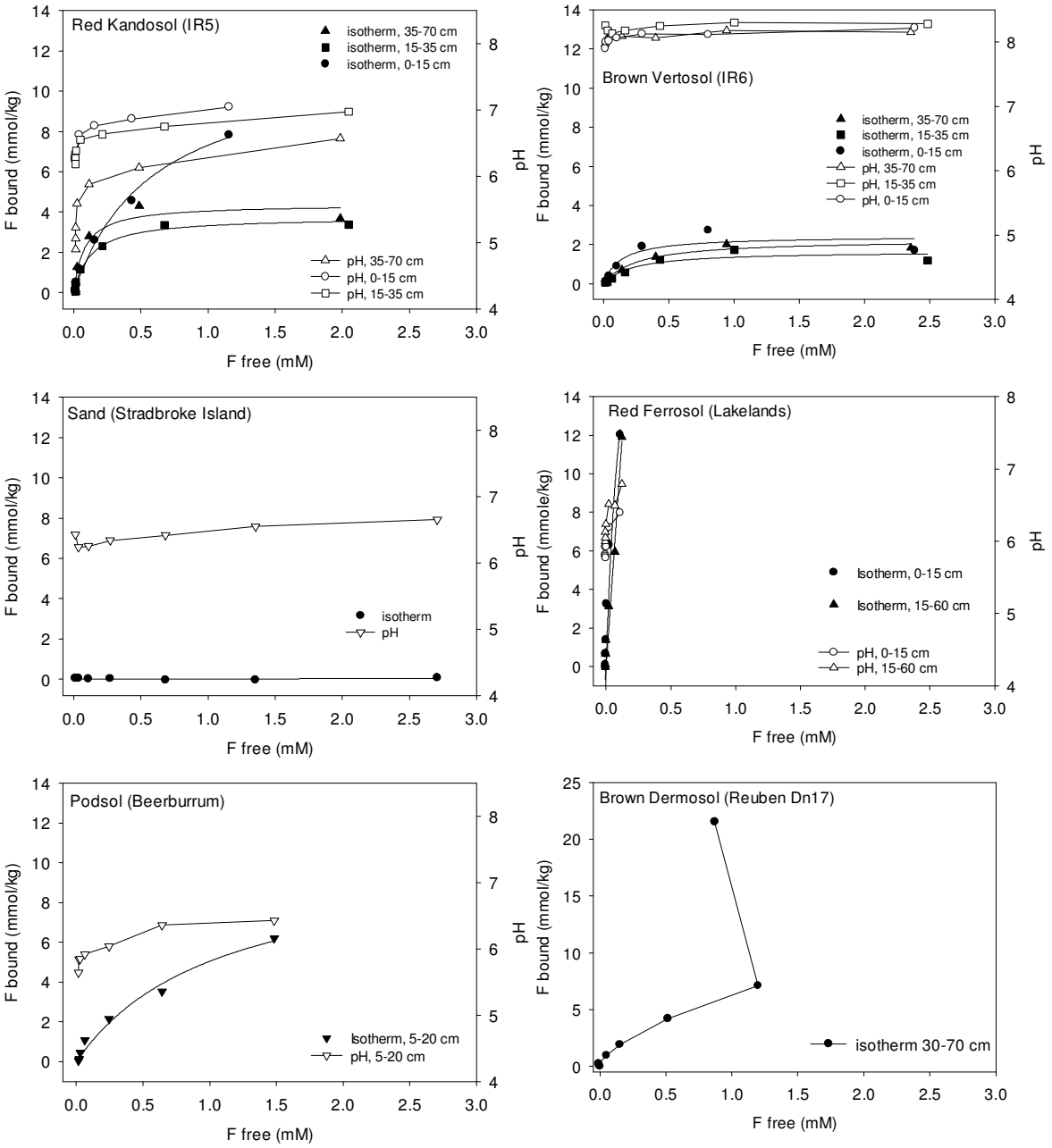


Figure 5. Adsorption isotherms for F on various soils. Filled circles are measured adsorption values, the line represent the fitted Langmuir isotherms. The triangles represent the pH of the soil slurry, with the points connected by straight line segments. Values shown are the mean of triplicate samples.

Table 5. Adsorption parameters for F sorption by various soils in Part I of the study. The Freundlich isotherm was fitted by non-linear regression to obtain values for the Freundlich sorption constant KF and homogeneity factor b and the quality of fit for the isotherm is expressed as correlation coefficient R^2. The Langmuir isotherm was also fitted and parameters for Langmuir binding constant KL and maximum sorption capacity Qmax (mmol/kg) determined.

Soil	Origin	Depth	Freundlich			Langmuir		
		(cm)	KF ± s.d.	b ± s.d.	R^2	KL ± s.d.	Qmax ± s.d.	R^2
Brown Ferrosol	Lakelands	0-15	15.3 ± 0.4	1.9 ± 0.1	0.998	5.3 ± 2.8	13.9 ± 3.2	0.945
		15-60	27.3 ± 2.0	1.8 ± 0.1	0.993	6.8 ± 5.4	19.6 ± 8.0	0.886
Red Ferrosol	Lakelands	0-15	42.1 ± 7.3	1.8 ± 0.2	0.973	8.3 ± 11.4	26.0 ± 20.7	0.792
		15-60	78.5 ± 20.6	1.1 ± 0.1	0.983	0.1 ± 3.0	1308 ± 5305	0.945
	Toowoomba	50-100	47.1 ± 8.9	1.3 ± 0.1	0.986	1.5 ± 1.4	59.7 ± 44.3	0.985
Red Vertosol	Lakelands	0-15	17.3 ± 0.7	2.1 ± 0.1	0.997	9.9 ± 3.6	12.9 ± 1.8	0.971
		15-60	21.2 ± 0.7	1.9 ± 0.1	0.998	8.9 ± 3.9	15.0 ± 2.8	0.960
	IR6	0-15	15.9 ± 1.2	1.4 ± 0.1	0.981	2.2 ± 0.5	18.9 ± 2.3	0.992
		15-35	13.2 ± 0.9	1.5 ± 0.1	0.978	2.5 ± 0.5	16.0 ± 1.5	0.993
		35-70	13.0 ± 0.9	1.3 ± 0.1	0.980	1.2 ± 0.3	21.5 ± 3.8	0.991
Black Vertosol	Gatton	0-5	7.0 ± 0.6	1.5 ± 0.2	0.954	0.9 ± 0.2	13.3 ± 1.5	0.995
	Lakelands	0-15	21.3 ± 1.2	1.7 ± 0.1	0.995	7.2 ± 2.3	15.0 ± 2.1	0.980
		15-60	12.1 ± 0.3	1.9 ± 0.1	0.998	4.7 ± 1.2	11.8 ± 1.3	0.986
Brown Vertosol	IR6	0-15	1.5 ± 0.4	2.5 ± 1.4	0.512	9.1 ± 5.8	2.4 ± 0.4	0.867
		15-35	0.5 ± 2.7	2.5 ± 3.6	0.283	4.7 ± 2.7	1.6 ± 0.2	0.890
		35-70	0.8 ± 0.3	2.5 ± 2.4	0.414	4.0 ± 1.2	2.2 ± 0.2	0.972
Grey Kurosol	Mt Cotton	5-15	8.5 ± 0.5	1.6 ± 0.2	0.976	2.2 ± 0.4	11.9 ± 0.9	0.993
Red Kandosol	IR8 Waddy Brae	5-20	5.6 ± 0.2	2.0 ± 0.2	0.987	2.5 ± 1.0	8.0 ± 1.2	0.963
	IR5 old	Intact core	12.7 ± 0.8	2.1 ± 0.2	0.976	8.6 ± 2.1	11.5 ± 0.9	0.983
	IR5 new	0-15	7.3 ± 0.2	1.7 ± 0.1	0.992	1.7 ± 0.3	11.7 ± 1.1	0.991
		15-35	3.0 ± 0.3	2.9 ± 0.7	0.868	7.7 ± 1.6	3.8 ± 0.2	0.985
		35-70	3.7 ± 0.6	3.4 ± 1.1	0.740	12.3 ± 4.9	4.4 ± 0.5	0.929

Table 5 continued

Soil	Origin	Depth	Freundlich			Langmuir		
		(cm)	KF ± s.d.	b ± s.d.	R^2	KL ± s.d.	Qmax ± s.d.	R^2
Yellow Kandosol	Beerburrum	30-50	25.0 ± 4.3	1.0 ± 0.1	0.966	2.9 ± 0.8	11.8 ± 1.3	0.985
	IR8 old	Intact core	15.1 ± 1.1	2.0 ± 0.2	0.972	9.4 ± 1.6	12.6 ± 0.7	0.990
	IR8 new	0-15	13.3 ± 1.1	1.7 ± 0.2	0.967	3.7 ± 0.9	14.2 ± 1.4	0.986
		15-35	13.1 ± 1.2	1.7 ± 0.2	0.961	4.3 ± 1.1	13.6 ± 1.3	0.984
		35-70	16.6 ± 1.9	1.6 ± 0.2	0.955	3.7 ± 1.3	16.3 ± 2.6	0.973
Brown Chromosol	IR8	0-15	23.3 ± 3.8	1.5 ± 0.2	0.940	5.0 ± 1.7	18.1 ± 3.0	0.970
		15-35	14.6 ± 2.2	1.8 ± 0.3	0.905	6.7 ± 2.1	13.4 ± 1.6	0.962
		35-70	37.4 ± 9.6	1.4 ± 0.2	0.915	5.6 ± 3.0	22.3 ± 6.3	0.941
Podosol	Beerburrum	5-20	4.8 ± 0.2	1.6 ± 0.1	0.991	0.9 ± 0.3	10.5 ± 1.8	0.984
Sand	Stradbroke					5E23 ± 1E36	0 ± 0	0.897

Table 6. Adsorption parameters for F sorption by various soils in Part II of the study. The Freundlich isotherm was fitted by non-linear regression to obtain values for the Freundlich sorption constant KF and homogeneity factor b and the quality of fit for the isotherm is expressed as correlation coefficient R^2. The Langmuir isotherm was also fitted and parameters for Langmuir binding constant KL and maximum sorption capacity Qmax (mmol/kg) determined.

Soil	Origin	Depth	Freundlich			Langmuir		
		(cm)	KF ± s.d.	b ± s.d.	R^2	KL ± s.d.	Qmax ± s.d.	R^2
Brown Dermosol	Mayfield South	0-20	3.0 ± 0.1	2.0 ± 0.1	0.991	0.7 ± 0.1	7.9 ± 0.4	0.990
		20-50	3.6 ± 0.1	1.7 ± 0.1	0.986	0.5 ± 0.0	12.5 ± 0.6	0.996
	Broandah 1	0-10	8.8 ± 0.1	2.4 ± 0.1	0.994	1.6 ± 0.3	15.9 ± 1.1	0.976
		10-60	3.1 ± 0.1	1.8 ± 0.1	0.717	0.6 ± 0.1	9.2 ± 0.5	0.993
		60-110	8.0 ± 0.2	1.7 ± 0.1	0.988	0.6 ± 0.1	23.2 ± 2.7	0.978
		110-150	11.1 ± 0.2	2.8 ± 0.1	0.987	3.5 ± 1.0	15.9 ± 1.3	0.950
	Summerhills 10	0-7	4.9 ± 0.1	2.2 ± 0.1	0.995	1.0 ± 0.2	10.9 ± 0.7	0.981
		7-50	6.2 ± 0.3	2.5 ± 0.2	0.950	2.1 ± 0.3	10.8 ± 0.4	0.989
		50-100	1.5 ± 0.1	1.9 ± 0.2	0.950	0.6 ± 0.1	4.3 ± 0.3	0.986
		100-150	0.6 ± 0.0	1.2 ± 0.0	0.993	0.1 ± 0.0	9.5 ± 1.9	0.995
	Reuben Downs 3	0-5	6.8 ± 0.1	2.2 ± 0.1	0.998	1.1 ± 0.2	14.5 ± 1.2	0.974
		5-50	7.3 ± 0.1	2.3 ± 0.1	0.966	1.3 ± 0.3	14.2 ± 1.1	0.974
		50-90	12.9 ± 0.2	3.0 ± 0.1	0.992	4.4 ± 1.2	17.1 ± 1.2	0.958
		90-130	14.5 ± 0.5	2.8 ± 2.1	0.972	6.2 ± 1.4	18.3 ± 1.1	0.968
	Reuben Downs 17	0-30	2.5 ± 0.1	1.7 ± 0.1	0.992	0.4 ± 0.1	8.9 ± 0.5	0.993
		30-70	6.4 ± 0.1	1.6 ± 0.0	0.997	2.2 ± 0.7	7.9 ± 1.4	0.978
		70-100	6.4 ± 0.3	1.8 ± 0.1	0.989	3.9 ± 0.6	6.5 ± 0.4	0.993
		100-140	5.1 ± 0.1	2.4 ± 0.1	0.993	1.4 ± 0.2	9.9 ± 0.6	0.980
Red Dermosol	Reuben Downs 8	0-5	9.9 ± 0.0	3.0 ± 0.0	0.999	2.6 ± 0.8	15.0 ± 1.2	0.952
		5-50	23.7 ± 0.5	2.5 ± 0.1	0.993	5.3 ± 1.3	27.0 ± 2.1	0.966
		50-100	15.4 ± 0.3	2.3 ± 0.1	0.993	2.5 ± 0.6	22.8 ± 1.9	0.969
		100-150	13.8 ± 0.2	2.9 ± 0.1	0.996	3.6 ± 0.8	19.1 ± 1.3	0.969

Table 6 continued

Soil	Origin	Depth	Freundlich			Langmuir		
		(cm)	KF ± s.d.	b ± s.d.	R^2	KL ± s.d.	Qmax ± s.d.	R^2
Black Vertosol	Summerhills 3	0-12	4.7 ± 0.1	2.0 ± 0.1	0.996	0.8 ± 0.1	11.6 ± 0.7	0.986
		12-40	3.8 ± 0.2	1.7 ± 0.1	0.978	0.4 ± 0.1	13.3 ± 1.7	0.973
		40-120	6.8 ± 0.4	1.7 ± 0.2	0.947	0.7 ± 0.2	18.0 ± 2.1	0.967
		120-150	9.6 ± 0.3	3.3 ± 0.2	0.975	4.3 ± 1.5	13.3 ± 1.1	0.936
	Summerhills 5	0-10	11.0 ± 0.1	2.2 ± 0.0	0.999	1.6 ± 0.3	19.4 ± 1.4	0.978
		10-45	15.5 ± 0.3	2.2 ± 0.1	0.994	2.0 ± 0.4	24.6 ± 1.9	0.980
		45-80	19.1 ± 0.4	2.8 ± 0.1	0.992	6.3 ± 1.4	22.5 ± 1.4	0.971
		80-140	16.9 ± 0.4	2.4 ± 0.1	0.986	3.2 ± 0.9	23.2 ± 2.0	0.960
	Reuben Downs 6	0-5	10.0 ± 0.2	2.2 ± 0.1	0.994	1.5 ± 0.3	18.6 ± 1.3	0.979
		5-50	2.4 ± 0.2	2.0 ± 0.3	0.909	0.9 ± 0.2	5.8 ± 0.4	0.975
		50-90	13.5 ± 0.2	2.1 ± 0.1	0.995	1.8 ± 0.3	22.8 ± 1.4	0.986
		90-130	17.8 ± 0.3	2.5 ± 0.1	0.991	3.1 ± 1.1	24.3 ± 2.8	0.933
Grey Vertosol	Weemilah 1	0-10	12.5 ± 0.2	2.3 ± 0.1	0.994	2.2 ± 0.4	20.2 ± 1.2	0.981
		20-30	8.8 ± 0.3	1.8 ± 0.1	0.982	0.8 ± 0.2	21.3 ± 2.5	0.968
		50-60	4.7 ± 0.2	2.0 ± 0.1	0.981	0.9 ± 0.1	10.8 ± 0.4	0.968
		80-90	24.4 ± 0.8	2.0 ± 0.1	0.984	2.9 ± 0.7	31.5 ± 3.0	0.973
	Moonie	0-15	0.6 ± 0.1	1.0 ± 0.1	0.964	0.0 ± 0.0	161 ± 1405	0.964
Red Chromosol	Springwater	0-15	19.7 ± 0.4	2.9 ± 0.1	0.993	8.2 ± 1.9	21.5 ± 1.4	0.966
	IR4-256	15-30	20.7 ± 0.5	2.6 ± 0.1	0.987	5.3 ± 1.1	24.4 ± 1.6	0.971
		30-55	18.6 ± 0.5	2.4 ± 0.1	0.985	3.3 ± 0.9	25.0 ± 2.2	0.960
		55-70	15.7 ± 0.7	2.9 ± 0.3	0.949	6.4 ± 2.0	19.0 ± 1.5	0.944
	Pleasant Hills 88	0-10	3.6 ± 0.1	1.8 ± 0.1	0.995	0.4 ± 0.1	12.8 ± 1.6	0.974
		20-30	5.0 ± 0.1	2.8 ± 0.2	0.984	1.8 ± 0.5	8.6 ± 0.6	0.961
		50-60	4.6 ± 0.1	2.6 ± 0.1	0.986	1.9 ± 0.4	8.0 ± 0.5	0.969
		80-90	1.9 ± 0.1	3.1 ± 0.2	0.980	2.6 ± 0.5	3.1 ± 0.1	0.973

Table 6 continued

Soil	Origin	Depth	Freundlich			Langmuir		
		(cm)	KF ± s.d.	b ± s.d.	R2	KL ± s.d.	Qmax ± s.d.	R2
Brown Chromosol	The Bend 30	0-10	4.6 ± 0.1	2.0 ± 0.1	0.997	0.6 ± 0.1	12.3 ± 1.2	0.974
		20-30	14.0 ± 0.2	2.5 ± 0.1	0.996	2.6 ± 0.5	21.0 ± 1.4	0.975
		50-60	8.8 ± 0.3	1.8 ± 0.1	0.982	0.1 ± 0.0	22.2 ± 4.2	0.988
		80-90	1.3 ± 0.1	1.2 ± 0.1	0.992	0.1 ± 0.0	12.9 ± 1.8	0.995
Yellow Chromosol	Gatton	0-15	4.0 ± 0.3	2.3 ± 0.3	0.939	0.8 ± 0.4	9.2 ± 1.5	0.907
		35-50	7.5 ± 0.4	1.5 ± 0.1	0.971	0.5 ± 0.1	24.0 ± 1.8	0.992
Bleached Tenosol	The Bend 41	0-10	3.4 ± 0.2	1.8 ± 0.2	0.957	0.4 ± 0.2	12.0 ± 2.7	0.923
		20-30	3.1 ± 0.1	1.8 ± 0.1	0.983	0.3 ± 0.1	12.1 ± 2.1	0.957
		80-90	1.1 ± 0.1	1.2 ± 0.1	0.967	0.1 ± 0.0	15.3 ± 8.0	0.964
		110-120	0.2 ± 0.0	0.6 ± 0.0	0.993	0.0 ± 0.1	9167 ± 7.2E6	0.925
Brown Sodosol	Pleasant Hills 63	0-10	7.7 ± 0.1	2.5 ± 0.1	0.995	1.6 ± 0.4	14.2 ± 1.1	0.968
		10-20	4.6 ± 0.1	2.0 ± 0.1	0.995	0.6 ± 0.1	12.3 ± 1.2	0.974
		20-30	12.6 ± 0.2	2.4 ± 0.1	0.991	2.1 ± 0.4	20.6 ± 1.5	0.974
		50-60	5.2 ± 0.1	3.1 ± 0.2	0.977	3.3 ± 0.9	7.8 ± 0.5	0.960
Brown Kandosol	IR5	0-15	18.4 ± 0.1	3.0 ± 0.1	0.974	4.5 ± 0.5	22.6 ± 0.8	0.996
Brown Ferrosol	Kingaroy	0-15	24.0 ± 0.2	3.2 ± 0.1	0.996	5.3 ± 2.1	28.2 ± 3.7	0.948

Effect of pH on F adsorption on soils

Optimum pH for F sorption was between pH 5 and 6, irrespective of soil type (Figure 6). Generally more than 80% of added F was adsorbed within 24 h, only Podsol (which is a sandy soil) had only 55% F sorption. When the soil was below pH 5, sorption decreased gradually in IR5 Red Kandosol, IR6 Red Vertosol, IR8 Yellow Kandosol and Brown Ferrosol (Kingaroy) (Figure 6). Sorption of F by Red Ferrosol (Lakelands), and to a lesser extent by Brown Ferrosol was not very sensitive to pH in the range pH 4- pH 7 (Figure 6). Sorption of F drastically decreased in Brown Dermosol, Red Kandosol and Black Vertosol when the soil was increased to >pH 6 (Figure 6). Since fluoride is a weak conjugated base (pKa 3.2) (Bia et al., 2012; Harrington et al., 2003; Prkic et al., 2012), protonation of fluoride ions (forming HF) results in decreased binding at low pH (Barrow and Ellis, 1986). It has also been suggested that formation of soluble AlF complexes at low pH may lower F sorption (Adriano, 2001b). It was claimed that maximum sorption of F would occur at pH 3.2 (i.e. the pKa of F^-) (Hingston et al., 1972) but their statement was only supported for F sorption onto goethite, and not gibbsite (where maximum sorption took place at pH 5.0). While there appears to be a slight increase in F sorption at pH 3.2 (e.g. in the Podsol), maximum sorption occurs at pH 5.5, in agreement with work by Barrow and Ellis (1986). It has been suggested that at pH >5.3, fluoride adsorbs to uncharged and negatively charged surface hydroxide groups bound to Al and Fe (Du et al., 2011; Harrington et al., 2003; Sujana et al., 2009) and the binding of F may take place via inner-sphere complexes (Bia et al., 2012). A similar pH response was observed for F sorption onto montmorillonite (Bia et al., 2012) and F-contaminated soils (Adriano, 2001a). It was claimed that acid soils bind more F than alkaline soils (Pickering, 1985), but this depends on the pH as can be seen from Figure 6. The decreased sorption at pH >6 can be attributed to the deprotonation of metal-OH groups on the edge of clay minerals and development of negative charges that repel the negatively charged F- anion.

Interestingly, the native pH of 1:5 soil water slurries of the Brown Dermosol, Red Vertosol and Black Vertosol ranged between pH 7 and 8 (arrows next to pH axis in Figure 6). Therefore, F sorption on these soils could be increased by acidifying the soil to pH 5-6. For the other soils, the native pH ranged between pH 5 and 6, corresponding to the pH of optimum F sorption. The results suggest that a soil pH needs to be maintained between pH 5 and 6 in CS water irrigation systems to maintain optimum F adsorption. Acidification of the soil (e.g. through extensive use of nitrogen fertilisers) or alkalinisation (due to insufficient sulfur application) will decrease the adsorption of F. Yet, within anticipated fluctuation on soil pH during land application of CS water, very little effect of pH on F adsorption could be expected.

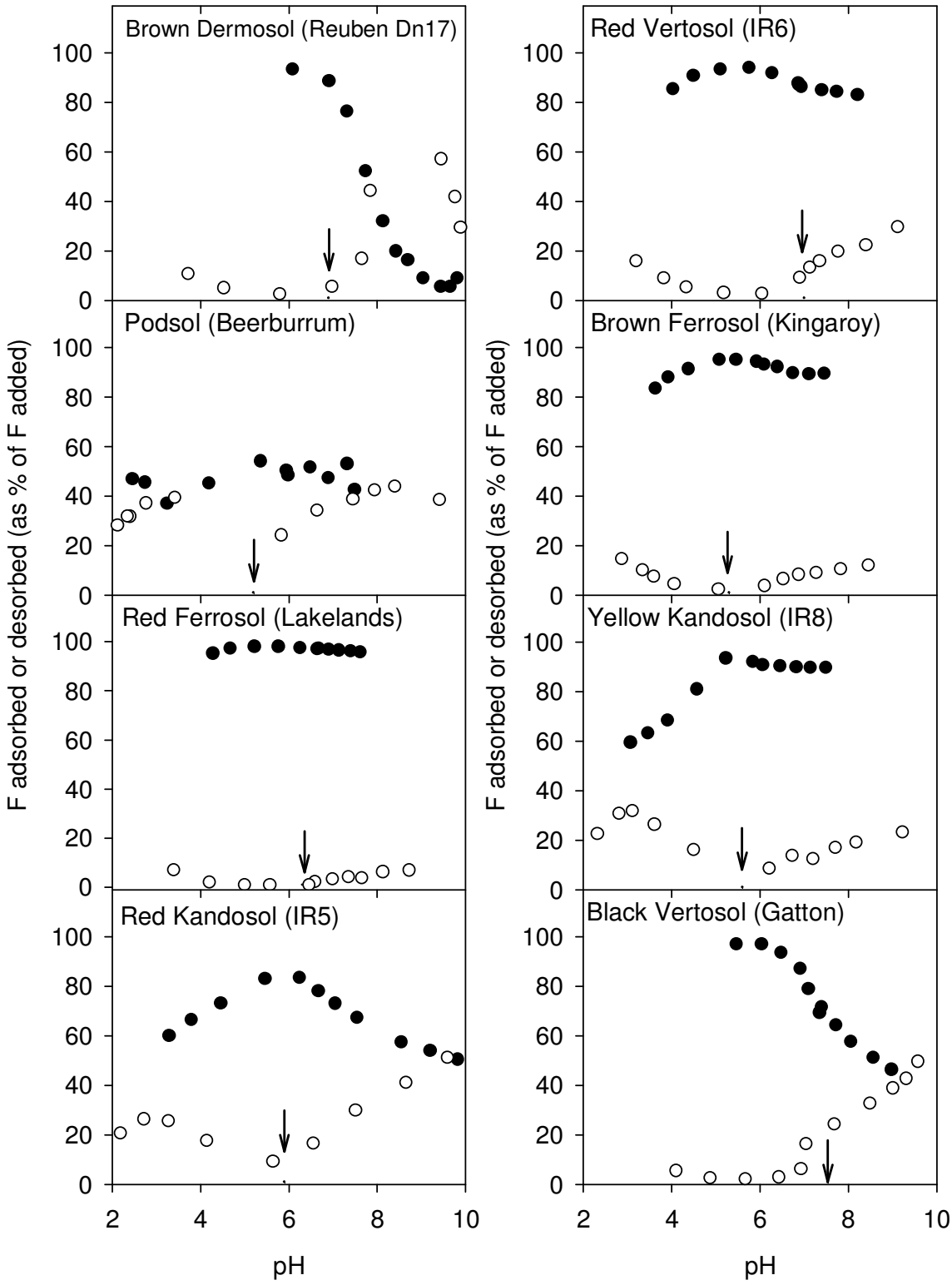


Figure 6. Effect of pH on the adsorption (filled circles) and desorption (open circles) of F from eight soils. The pH of the 1:5 soil water slurry is shown by the vertical arrow.

Effect of pH on buffering capacity of the IR 5 Red Kandosol and IR8 Yellow Kandosol

The soil pH buffer capacity was only determined for the IR5 Red Kandosol and IR8 Yellow Kandosol. Both soils were strongly buffered at alkaline pH, which prevented the pH increasing above 7.2 when applying realistic quantities of limestone (Figure 7). Thus, application of alkaline CS water to these two soils types will quickly increase the pH to 7.2-7.5, at which 85-90% of applied F will be adsorbed to these soils (Figure 7). However, pH increasing to above 7.5 is unlikely in these two soils due to strong buffering.

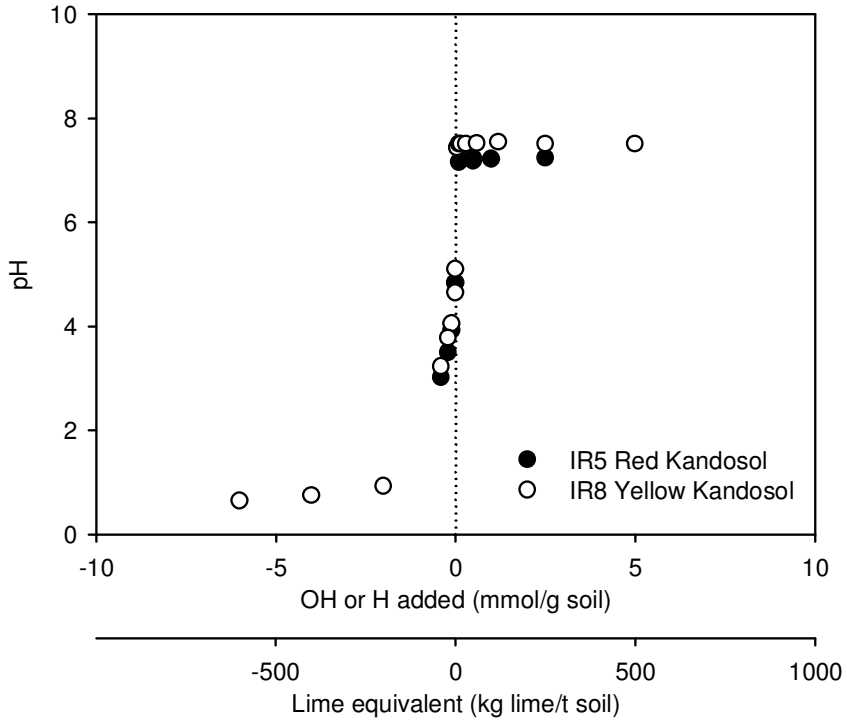


Figure 7. The pH buffer curves for the IR5 Red Kandosol and IR8 Yellow Kandosol.

Comparative adsorption of F onto soil from NaF solution and CS water

Adsorption of F from NaF solution was slightly higher than from CS water for both the IR5 Red Kandosol and IR8 Yellow Kandosol, although the magnitude of this difference was not great (average adsorption across both soils was 100 ± 0.7% for NaF/water and 94 ± 0.4% for NaF/CS water) (Figure 8). Sorption of F from NaF solution was higher because the pH of the soil slurry is lower (pH 5-pH 5.5), whereas CS water increased the pH of the soil slurry to pH 7.2-7.5 and it has been shown in Figure 6 that pH has an effect on sorption of F. The sorption of F in excess of 100% in IR5 Red Kandosol was due to the fact that the control also contained F as a contaminant which was subsequently adsorbed by the soil, lowering the F concentration in the slurry to below the value in the control.

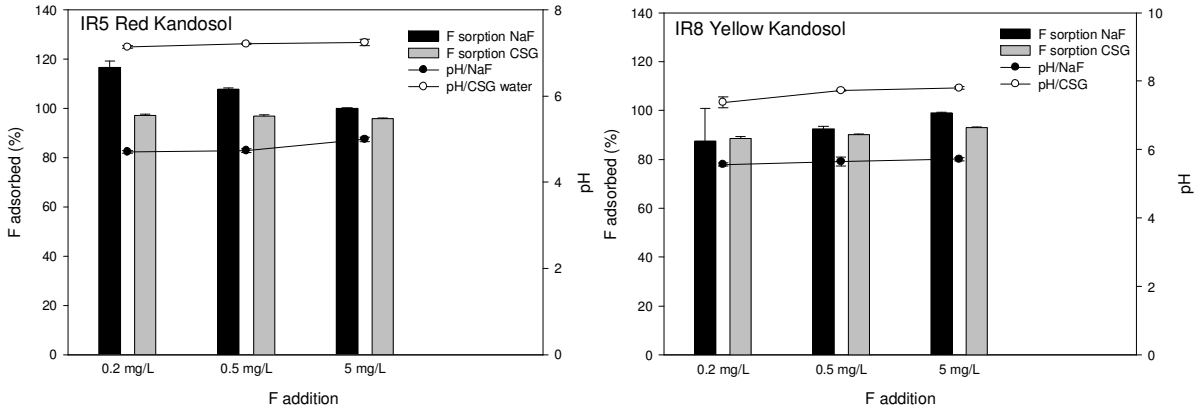


Figure 8. Percentage adsorption of F on IR5 Red Kandosol and IR8 Yellow Kandosol from deionised water or CS water, with three different additions of NaF (bars). The effect of deionised water and CS water containing F on the pH of the soil slurries is shown by the circles connected by straight lines. Error bars, if not obscured by the symbols, represent the standard deviation of triplicate samples.

Effect of sulfate on F adsorption

Despite both sulfate (SO_4^{2-}) and fluoride (F^-) being anions, there was no indication that sulfate competes with F for binding sites on Brown Vertosol and Brown Chromosol since there was no significant difference is sorption when sulfate was added (Table 7). Remarkably, sorption of F on Red Vertosol and Yellow Kandosol increased with sulfate concentration (Table 7), from 81.4% to 86% in the Red Vertosol and from 93.3% to 95.3% in the Yellow Kandosol. This sulfate-enhanced sorption F is most likely due to an electrostatic effect on clay mineral surfaces (Barrow and Shaw, 1977). Thus, application of sulfur or gypsum ($CaSO_4$) to soils in the field is unlikely to have detrimental effects on sorption of F.

Table 7. Percentage of F bound by Brown Vertosol IR6, Brown Chromosol IR8, Red Vertosol IR6, and Yellow Kandosol IR8 (all 0-15 cm depth layer). The F was made up in water (control), 1 mM Na_2SO_4 and 10 mM Na_2SO_4. The mean values ± standard deviations refer to four replicates.

	Brown Vertosol	Brown Chromosol	Red Vertosol	Yellow Kandosol IR8
water	98.5 ± 0.0	90.0 ± 0.4	81.4 ± 1.3	93.3 ± 0.6
1 mM SO_4^{2-}	98.9 ± 0.5	90.3 ± 0.3	83.1 ± 2.2	94.8 ± 0.3
10 mM SO_4^{2-}	98.8 ± 0.1	89.9 ± 1.3	86.0 ± 1.1	95.3 ± 0.1

Mechanisms of F sorption

Adsorption of F by the soils resulted in a slight increase in pH due to displacement of OH groups from the soil colloids (Figure 9).

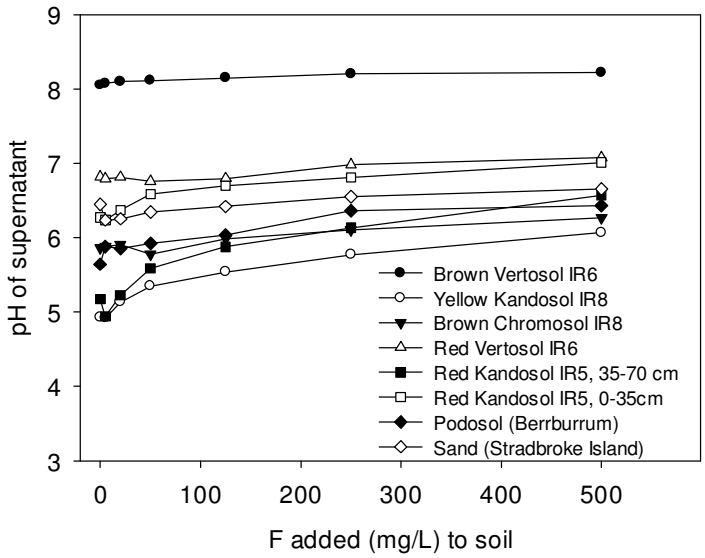


Figure 9. The pH of the supernatant extracted from all seven soils (layers averaged) in the adsorption experiment. The Red Kandosol 35-70 cm layer has been separated from the 0-35 cm layers due to a notable difference in pH.

However, the exchange ratio of OH for F was neither constant nor near unity. Therefore, adsorption of F does not follow a single mechanism and adsorption may follow different mechanisms in different soils. In Yellow Kandosol, Red Kandosol and Red Vertosol, the average OH/F ratio was 0.63, 0.66 and 0.67, respectively. In the Brown Chromosol and Ferrosol, the OH/F ratios were higher with 0.76 and 0.74, respectively (Table 8). This implies that for every four F ions bound to Ferrosol or Brown Chromosol, three OH ions are released. For Yellow Kandosol, Red Kandosol and Red Vertosol, for three F ions bound, two hydroxyl ions are released. These ratios are similar to those determined on Ferrosols in China, with ratios ranging from 0.42-1.04 (Zhang et al., 1987a).

The results suggest that adsorption of F can follow two processes: firstly, via ligand exchange on an uncharged site at neutral pH, resulting in an increase in pH (Figure 10). Secondly, F can bind to protonated sites at low pH, with release of water molecules and a change in charge of the solid phase (Figure 10). At alkaline pH, deprotonation of hydroxyl groups and development of negative charges will repel negatively charged F ions and result in low F binding at alkaline pH.

Table 8. Effect of increasing F addition on the calculated OH/F ratio of several soil suspensions. The OH released was determined by back titration with 0.1 M HCl. Values are means of three replicates and their standard deviation.

F added (mmole/kg)	Yellow Kandosol	Brown Chromosol	Ferrosol	Red Vertosol	Red Kandosol
12.5	0.52	0.69	0.64	0.65	0.65
25	0.66	0.72	0.76	0.65	0.68
50	0.68	0.72	0.70	0.75	0.74
75	0.76	0.83	0.79	0.69	0.70
100	0.49	0.82	0.80	0.67	0.62
125	0.69	0.77	0.76	0.62	0.61
Avg ± s.d.	0.63 ± 0.10	0.76 ± 0.06	0.74 ± 0.06	0.67 ± 0.05	0.66 ± 0.05

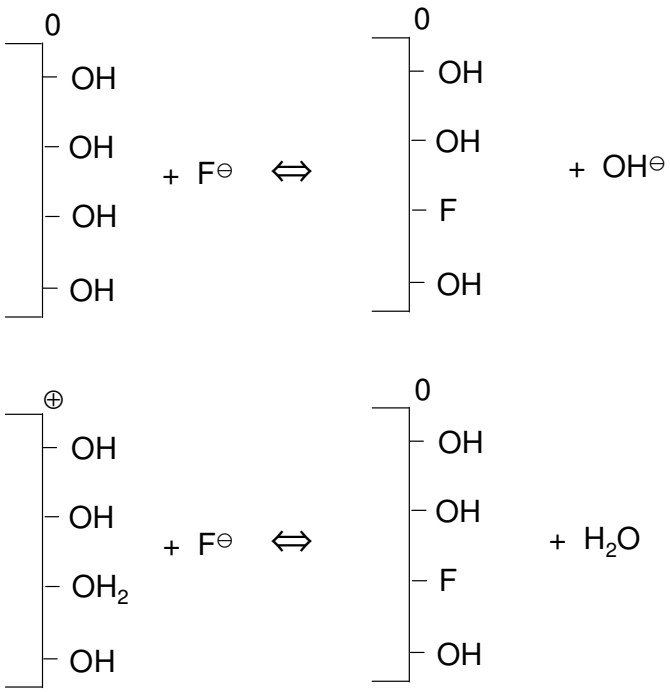


Figure 10. Proposed mechanisms of F binding to soil minerals. F ions can bind to uncharged soil minerals, displacing OH- groups, or bind to protonated minerals and releases water. The latter process will change the charge of the soil mineral.

Effect of soil characteristics on F sorption

The amount of F bound onto the soils at an equilibrium solution concentration of 1 mg/L was calculated from the Langmuir binding constant K_L and the maximum sorption capacity Qmax. The calculated amount of F bound is considered to be more reliable since it is calculated from the two sorption parameters (K_L and Qmax) and is an interpolated value. In contrast, the Qmax is an extrapolated value at infinitely high F equilibrium concentration. If the isotherm does not reach a plateau, the estimate of Qmax can be unreliable with a high standard error (Tables 5 and 6). Since both the Langmuir and Freundlich isotherms gave a good fit at low F equilibrium concentrations, either model could be used to calculate the amount of F adsorbed. However, it should be kept in mind that a good fit does not necessarily validate the underlying model.

The calculated amount of F bound was correlated to the soil physical and chemical parameters. The amount of F bound was negatively correlated (r = -0.519) with the contents of quartz and the primary mineral albite (r = -0.283) (Table 9). This could be expected since these minerals have no binding sites for F (Pickering, 1985). Sorption was positively correlated with content of the iron sesquioxide hematite (r = 0.630), goethite (r = 0.558) and maghemite (r = 0.603) and the 1:1 aluminosilicate clay kaolinite (r = 0.703), but not correlated with the content of the 2:1 clays illite (r = -0.532) and smectite (r = -0.111) (Table 9). Since F can bind to sesquioxides and the edge aluminium-oxide groups found on 1:1 clay minerals, it could be expected that F sorption increases with sesquioxide and 1:1 clay content (Harrington et al., 2003; Pickering, 1985). The content of the sesquioxides hematite, goethite and maghemite was highest in the Red Ferrosol and Red Vertosol, and the kaolinite content was highest in the Red and Brown Ferrosols and Red Vertosol. Consequently, the F sorption was greatest in Red Ferrosol.

The sorption of F was poorly predicted by other soil chemical parameters such as pH, salinity as measured by electrical conductivity (EC), organic matter (OM), and cation exchange capacity (CEC) (Table 10). Likewise, anions, exchangeable cations and surface areas were not correlated with F binding (data not shown). Therefore, comprehensive soil chemical analyses are not suitable as predictors of F sorption.

Determination of hydrous oxides of Al and Fe by the citrate dithionite method (Rayment and Higginson, 1992) gave good correlations with F sorption (r = 0.630 for Al-oxide and r = 0.638 for Fe oxide, Table 10) and supports the claim that ligand exchange with the OH groups is contributing to F binding (Harrington et al., 2003; Sujana et al., 2009). The amount of F bound to citrate-dithionate Fe and Al agreed very well with the amount of F bound to sesquioxides. Therefore, the Fe-OH and Al-OH method can be used to estimate F binding rather than having to rely on the XRD method for sesquioxides.

Table 9. Correlation coefficients (r) between soil mineralogy listed in Appendix 3 and the F sorption parameters K_L, Qmax and the calculated amount of F bound at an equilibrium concentration of free F of 1 mg/L.

	KL	Qmax	F bound
Quartz	0.324	-0.275	-0.519
Albite	-0.313	-0.066	-0.283
Orthoclase	0.361	-0.110	0.078
Hematite	-0.010	0.452	0.630
Goethite	0.279	0.160	0.558
Maghemite	-0.020	0.240	0.603
Anatase	-0.035	-0.014	0.117
Kaolin	0.156	0.457	0.703
Illite/Mica	0.220	-0.129	-0.532
Smectite	0.048	-0.146	-0.111

Table 10. Correlation coefficients (r) between physical and chemical properties of soil listed in Appendix 4, and the F sorption parameters K_L, Qmax and the calculated amount of F bound at an equilibrium concentration of free F of 1 mg/L.

correlation between	K_L	Qmax	F bound
pH water	-0.130	0.057	-0.256
pH CaCl	-0.014	0.102	-0.069
OM	0.097	-0.014	0.345
CEC	0.028	-0.126	-0.177
EC	0.108	-0.125	-0.281
Al-OH	0.062	0.287	0.630
Fe-OH	0.165	0.417	0.638

Since we were interested in identifying all soil parameters that may predict F sorption, we conducted stepwise linear regressions between the amount of F bound at a solution equilibrium concentration of 0.05 mM F (1 mg/L) and 0.26 mM F (5 mg/L) and soil parameters. For simplicity, only values calculated for 0.26 mM F are presented here. The equilibrium concentration was calculated from the adsorption parameters and this approach

has the benefit that it is an interpolated value, unlike Qmax with is an extrapolated value to high equilibrium concentrations, thereby avoiding undue influence from extreme values. For the soils in the first study (Part 1) (see "Final Report - Managing environmental risk of fluoride in coal seam water irrigation systems (2014)"), the sorption of F could be predicted with 92.5% of variability accounted for by the soil parameters using the following equation (Eq. 1):

Predicted F adsorbed at 0.26 mM = 14.831 + 2.226*Al hydrous oxide
+ 0.302*CEC
- 15.327*EC
- 0.022*Fe hydrous oxide
+ 0.226*kaolinite
- 0.184*OM
- 3.594*pH 1:5 $CaCl_2$
+ 0.358*sum M_2O_3 (XRD) (Eq 1)

The agreement between F adsorbed predicted from Eq 1 and the calculated sorption from Langmuir parameters (Table 5) was good for the soils with detailed soil characterisation (Figure 11).

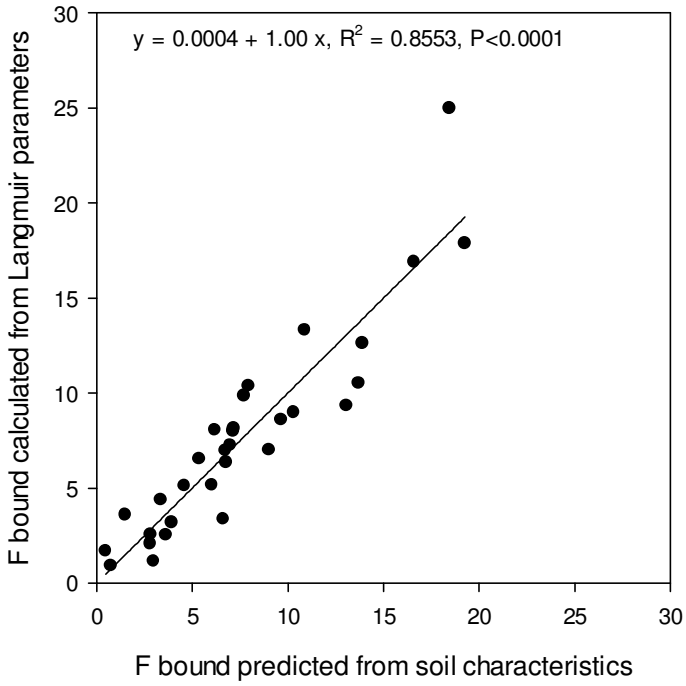


Figure 11. Correlation between F bound by the soils from Part I of the study predicted from soil characteristics using Eq 1 and the calculated amount F bound using the Langmuir parameters listed in Table 5.

However, in order to predict F sorption a complete soil analysis is required, including Al and Fe hydrous oxide content by citrate dithionite analysis, and mineralogical composition (kaolinite, sesquioxides) by X-ray diffraction. These are not routine chemical analyses and increase the cost of the soil analysis. Interestingly, phosphate buffer index (PBI) (Appendix 4) was not well correlated with F sorption (R = 0.4980), although PBI was highly correlated with Fe and Al hydrous oxide and kaolinite contents (R = 0.969). Therefore, determination of phosphate buffer index does not allow prediction of F sorption capacity. It is possible that the

mechanism of P and F sorption differ, with P binding via bidentate bonds, and F via mono-dentate inner-sphere complexes (Bia et al., 2012).

For the new soils (Part 2 soils, for which only basic soil analyses were available), correlation between soil parameters and F binding was poorer (R = 0.677) (Figure 12) when using the following relationship (Eq 2):

Predicted F adsorbed at 0.26 mM = 26.749 + 0.075*CEC
- 0.676*EC
+ 0.013*Fe extractable
- 0.043*kaolinite
+ 0.251*OM
- 3.104*pH 1:5 water (Eq. 2)

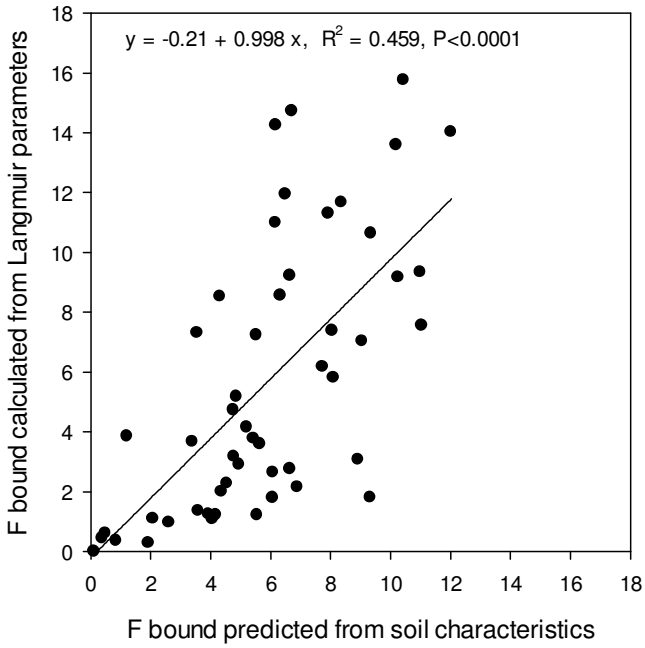


Figure 12. Correlation between F bound by the soils in Part 2 of the study, predicted from soil characteristics using Eq 2 and the calculated amount F bound using the Langmuir parameters listed in Table 6.

Correlation between F sorption on a single soil and soil pH, extractable Fe and clay percentage of a number of soil samples from Spain was also moderately poor (r = 0.68-0.77) (Gago et al., 2014).

Likewise, prediction of F bound from the soil characteristics of the combined Part I and Part II soils was poor (R = 0.664) (Figure 13) using equation 3:

Predicted F adsorbed at 0.26 mM = 26.749 + 0.075*CEC
- 0.676*EC
+ 0.013*Fe extractable/Fe hydrous oxide
- 0.043*kaolinite/clay
+ 0.251*OM
- 3.104*pH 1:5 water (Eq 3).

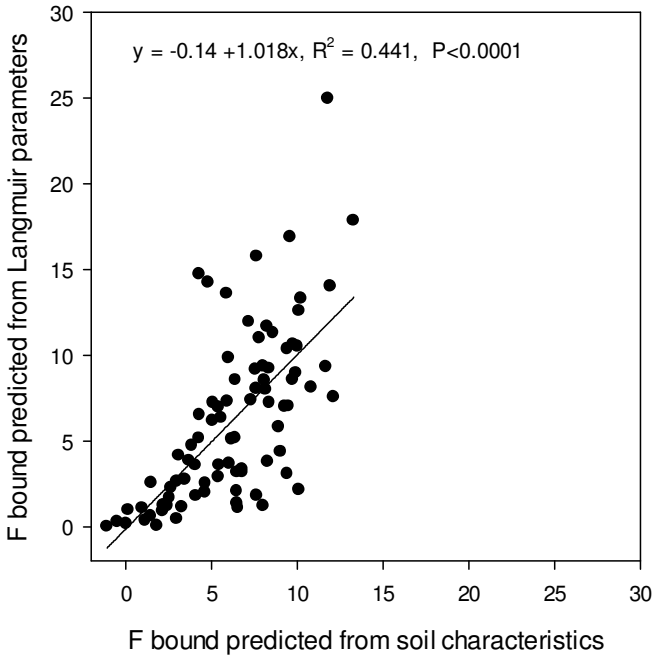


Figure 13. Correlation between F bound by the combined soils (Part I and Part II soils) predicted from soil characteristics using Eq 3 and the calculated amount F bound using the Langmuir parameters listed in Tables 5 and 6.

In summary, predicting amount of F bound by soils based on basic soil chemical analyses will not give reliable predictions. Rather than spending money on detailed chemical characterisation involving XRD determination of mineralogy and determinations of hydrous oxides of Fe and Al, adsorption isotherms will be more suitable. In addition, isotherms yield parameters which can then be used to accurately model and predict F retention in the soil.

Two point adsorption isotherms for determination of F binding have little advantage over full isotherms. The mathematical description of F sorption using the Langmuir or Freundlich models requires a minimum of three determinations (no F added, low concentration and high concentration of F added). In this case, the goodness of fit is 1.0 since there are zero degrees of freedom left when fitting three determinations to a two parameter model. To improve precision, more than three different concentration steps are required. Therefore, two-point adsorption isotherm cannot be recommended to describe F adsorption.

Desorption studies

Effect of pH on desorption

Desorption of F was influenced by pH and the response differed between soil types (Figure 6, 14). We consider these differences to be caused by differences in the point of zero net charge and presence of pH-variable charges on the soils. Desorption was lowest around pH 5.5, which corresponded to the pH at which maximum adsorption was observed.

The higher desorption at alkaline pH in all soils is due to the concentration of hydroxyl ions (i.e. higher pH), resulting in increased OH-F exchange (Kau et al., 1997). Likewise, lowering the pH below pH 5 increased desorption of F, due to protonation of binding sites and F ions (Figure 6).

Since application of alkaline untreated CS water to field soils can increase the pH to a maximum of pH 8.4, some F may desorb and become mobile. This underlines the importance

of pH control in land amendment irrigation. For instance, CS water irrigated field soils from IR6 have recorded pH 6.8-7.8 in the top 30 cm, and soils from IR5 recorded values of pH 6.3-8.3 in the top 30 cm (TCT Pty Ltd, 2013. *Report on Fairview IR4, IR5 and IR6 routine soil core monitoring 2013 Sampling Revised Report*).

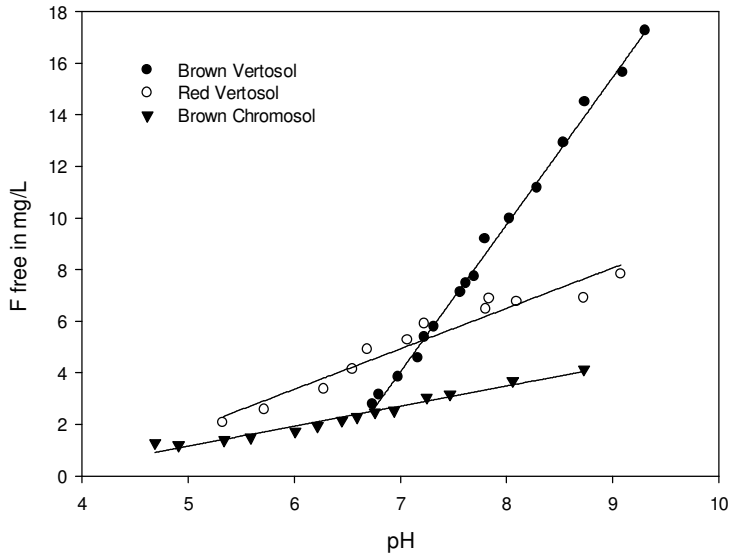


Figure 14. Effect of pH of 1:5 slurries on desorption of F from Red Vertosol IR6, Yellow Kandosol IR8 and Red Kandosol IR5. Values are the arithmetic mean of three replicates with the error bars shown.

Effect of temperature on desorption

The amount of F desorbed from soil depended on the soil type, irrespective of temperature. Brown and Red Vertosol had greater desorption than, for instance, Ferrosol (Figure 15) and these differences reflect soil mineralogy and pH. This is in agreement with results presented earlier. Interestingly, the effect of temperature on F desorption differed between soils. Significantly more F was desorbed from Brown and Red Vertosol at 65°C than at 25°C (Figure 15 and 16). Yet, temperature had no effect on F desorption from Ferrosol (Figure 15), Red Kandosol IR5 (Figure 16) and Yellow Kandosol IR8 (Figure 16). Thus, the assumption that increasing temperature increases anion desorption (Barrow, 1992) is not universally true.

High soil temperatures in the field would have little effect on F desorption and would not increase movement of F in the soil since F will be in contact with soil for a long time and be strongly adsorbed. Likewise, increasing the temperature in the lab did not affect desorption, and the desorption process was not accelerated by increasing the temperature. It is possible that differences in binding sites and mineralogy between the soil account for the differences in temperature sensitivity between soils (Barrow, 1992). Soil temperatures of 55°C at 2.5 cm depth have been measured in summer in Griffith (NSW) (Marshall and Holmes, 1988). Thus, the temperature of 65°C chosen in this study is realistic and unlikely to be exceeded in the field.

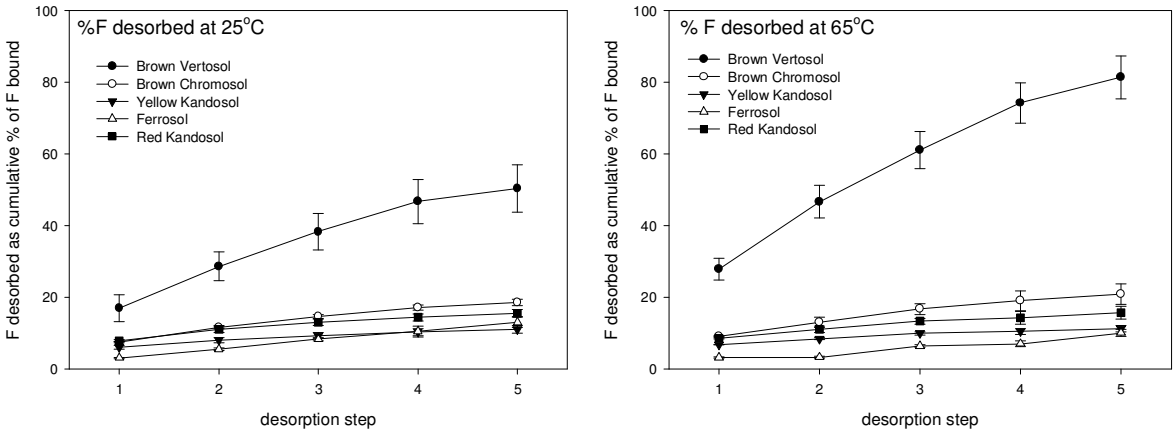


Figure 15. Desorption of F from five soils. Soils were incubated with F for 12 weeks, and the pellet resuspended with deionised water and incubated for 30 min at either 25°C (left panel) or 65°C (right panel). The concentration of F in the supernatant was determined and the desorption step repeated five times. Values are arithmetic means of four replicates (error bars are often obscured by the symbols).

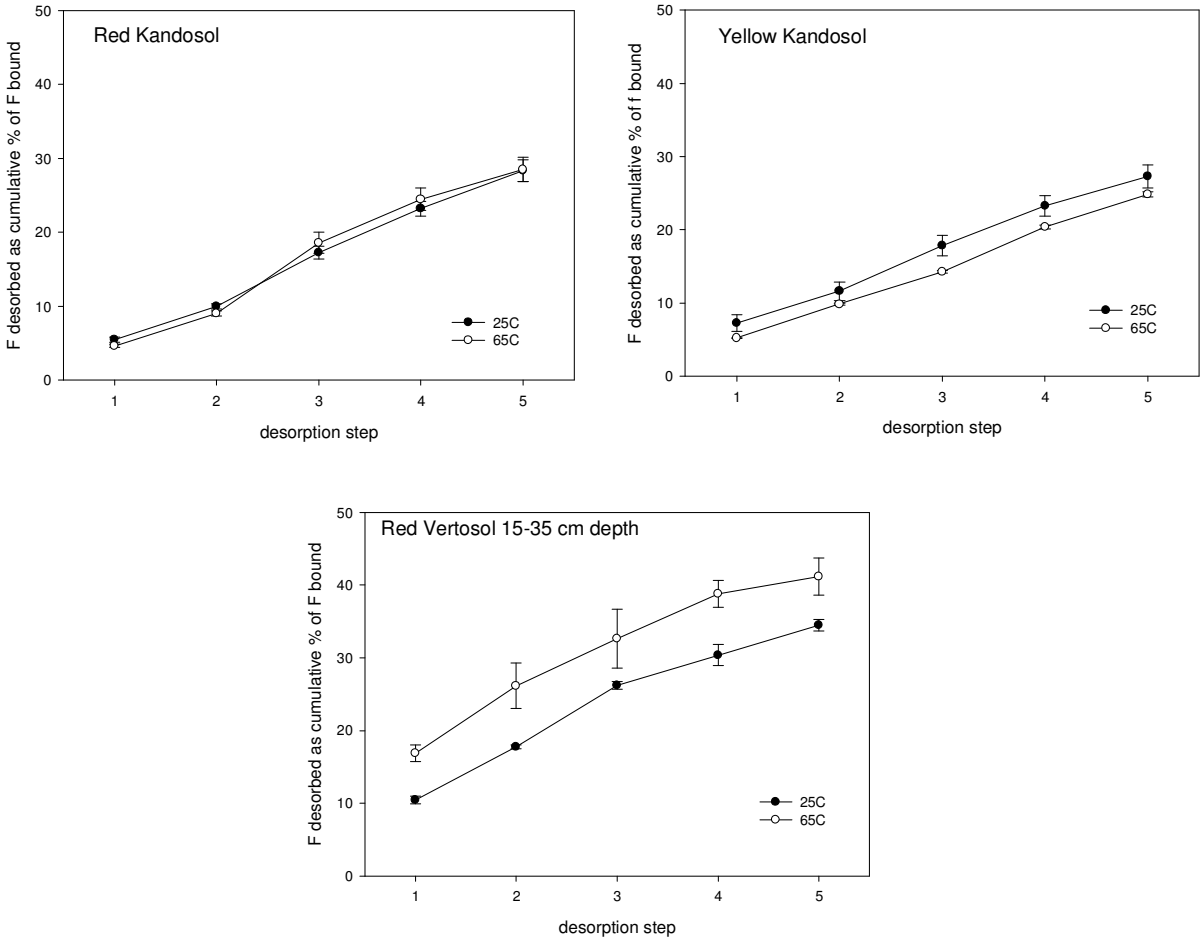


Figure 16. Desorption of F from Red Kandosol IR5, Yellow Kandosol IR8 and Red Vertosol (IR6) (15-35 cm depth). Soils were incubated for 14-19 h with F solution and pellets were resuspended in 10 mL DI water and incubated 14-19 h at either 25°C or 65°C. The amount of F desorbed was determined in the supernatant after centrifugation and expressed relative to the quantity of F adsorbed. The desorption step was repeated five times. Values are arithmetic means of four replicates (error bars are often obscured by the symbols).

Effect of water, salt, sulfate and buffer on F desorption

Anions such as Cl or sulfate may compete with F for anion exchange sites in soil colloids. Yet, unexpectedly, sulfate not only enhanced adsorption of F when no background electrolyte was added, but also decreased desorption of bound F (Figures 17 and 18). However, when background electrolyte (0.3 M NaCl) was used, no effect of sulfate on F desorption was observed (Figure 17). Comparing the desorption isotherms in salt-free solution and 0.3 M NaCl (top and bottom panel Figure 17) showed that desorption of F decreased at higher ionic strength. Therefore, desorption of F in the field will not increase due to CS water induced increases in soil solution salinity. Comparing F and sulfate concentrations in intact cores of IR6 old (which was irrigated with 18-20 ML of CS water with 250 kg S added per y/ha, S. Dalzell pers. comm.) with the new IR6 cores did not allow conclusions to be drawn regarding effect of sulfate on F movement since the S and F concentrations varied widely. In addition the new IR6 cores had much less F in the soil due to lower total irrigation volumes applied.

Overall, results show that sulfate does not affect adsorption or desorption of F (Figure 18), most likely due to the fact that sulfate and F have different sorption mechanisms with F being bound closer to the mineral surface than the larger sulfate anion (Zhang et al., 1987b). Thus, application of sulfur or sulfate to field soils is unlikely to affect F adsorption.

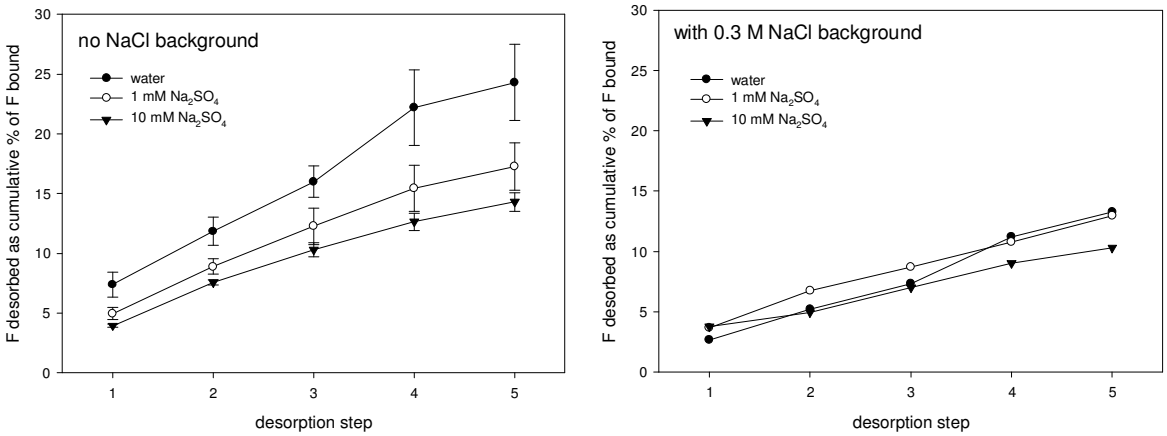


Figure 17. Desorption of F from Yellow Kandosol IR8 in the presence of 0-10 mM sulfate without added background electrolyte (top panel) or with 0.3 M NaCl background electrolyte (bottom panel). Values are means of four determinations with error bars shown in the top panel. Errors bars in the bottom graph have been omitted for clarity and treatment differences were not significantly different.

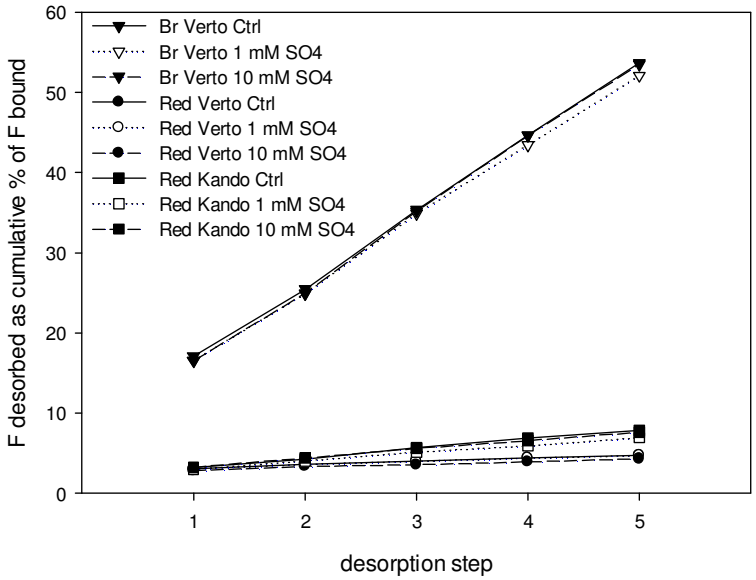


Figure 18. Desorption of F from four soils after 1-5 desorption steps using solution containing 0, 1, or 10 mM Na_2SO_4. Data points are means of three replicates.

A comparison between NH_4Cl and water as extractant showed that water was the most efficient extractant for Brown Vertosol, Ferrosol and Yellow Kandosol (Figure 19) treated with 50 mg F/kg soil for 42 days. In contrast, 0.2 M NH_4Cl was the better desorbent for Brown Chromosol and Red Kandosol (Figure 19). Since it was expected that buffer would be a better extractant than water, the study was repeated using soils treated with CS water and also using TISAB3b buffer as additional extractant. For, soils treated with F augmented CS water, water was again the most efficient F desorbent for the Brown Vertosol, Ferrosol and Yellow Kandosol, whereas 0.2 M NH_4Cl extracted significantly more F than water from the Brown Chromosol and Red Kandosol (Figure 19), irrespective of the concentration of F added to the soil. Interestingly, 0.2 M TISAB3b which preferentially complexes Ca, Al, Fe ions in soil solution, thereby demasking F ions, was not as effective as water (Figure 19). The effect of soil type on efficacy of desorbents observed in this study explains why a number of different desorbents have been suggested in the literature (Begin and Fortin, 2003; Loganathan et al., 2006; Rodriguez et al., 2001), with no single desorbent being the most suitable across all soil types.

It was considered that exchangeable F should be extractable with NH_4Cl since the chloride ion can replace adsorbed F. Furthermore, NH_4Cl is a common extractant widely used in soil fertility analyses. However, it does not appear to be the most suitable desorbent, and deionised water was selected as our preferred choice of F extractant. Furthermore, desorption isotherms determined with water can be easily extrapolated to the field since rainfall is similar to deionised water in composition. The results indicate that most F may be held in an easily exchangeable form rather than chemisorbed. The good efficacy of water suggests that ionic interaction may play a role in F binding since the buffers have a higher ionic strength and can mask repulsive forces between the negative charges of the CEC and F ions, and thereby decrease desorption.

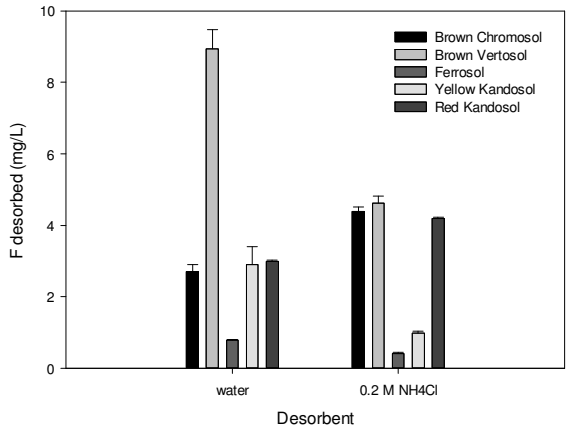


Figure 19. Effect of different desorbents (deionised water or 0.2 M NH_4Cl) on the cumulative amount of F desorbed from five soils following 5 desorption steps. Soil was incubated for 42 days with 50 mg F/kg soil. Bars are the means of three replicates, with standard error bars shown if not obscured by the bar.

Effect of soil:water ratio on F desorption

The desorption of F from soil at various soil:water ratios increased with dilution (Figure 20). The Brown Vertosol which had a high native F concentration (IR6 "Control 35-70 cm depth") showed greater desorption of F and F desorption clearly increased with increasing dilution. The results confirm the validity of Schofield ratio law when more monovalent ions are desorbed with increasing dilution (Barrow and Shaw, 1977; Tan, 2000). Thus, results obtained on 1:2 soil:water slurries represent a worst-case scenario in that the soil will reach saturation point. Since all research reported here was conducted with 1:5 soil:water slurries, the measured F concentration in the slurries are higher than would be observed in the field. Realistic soil:water ratios in the field are expected to remain below 1 : 0.5 (corresponding to saturation of a soil with porosity of 50%). However, desorption may increase if soil particles are eroded and suspended in a large volume of water (i.e. 1:20 soil:water ratio). Thus, soil erosion control is important to minimise movement of F in the environment in CS water irrigation systems. Yet, even for eroded sediments, the desorbed F will be diluted in a large volume of water and the actual concentration of F in water in the receiving environment will be very low.

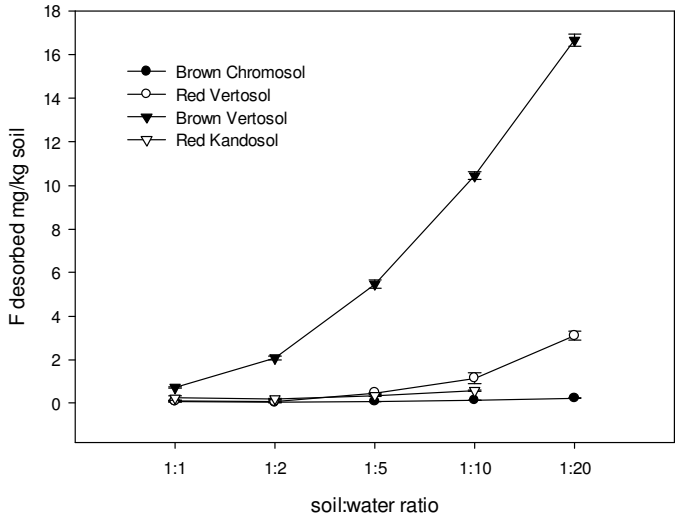
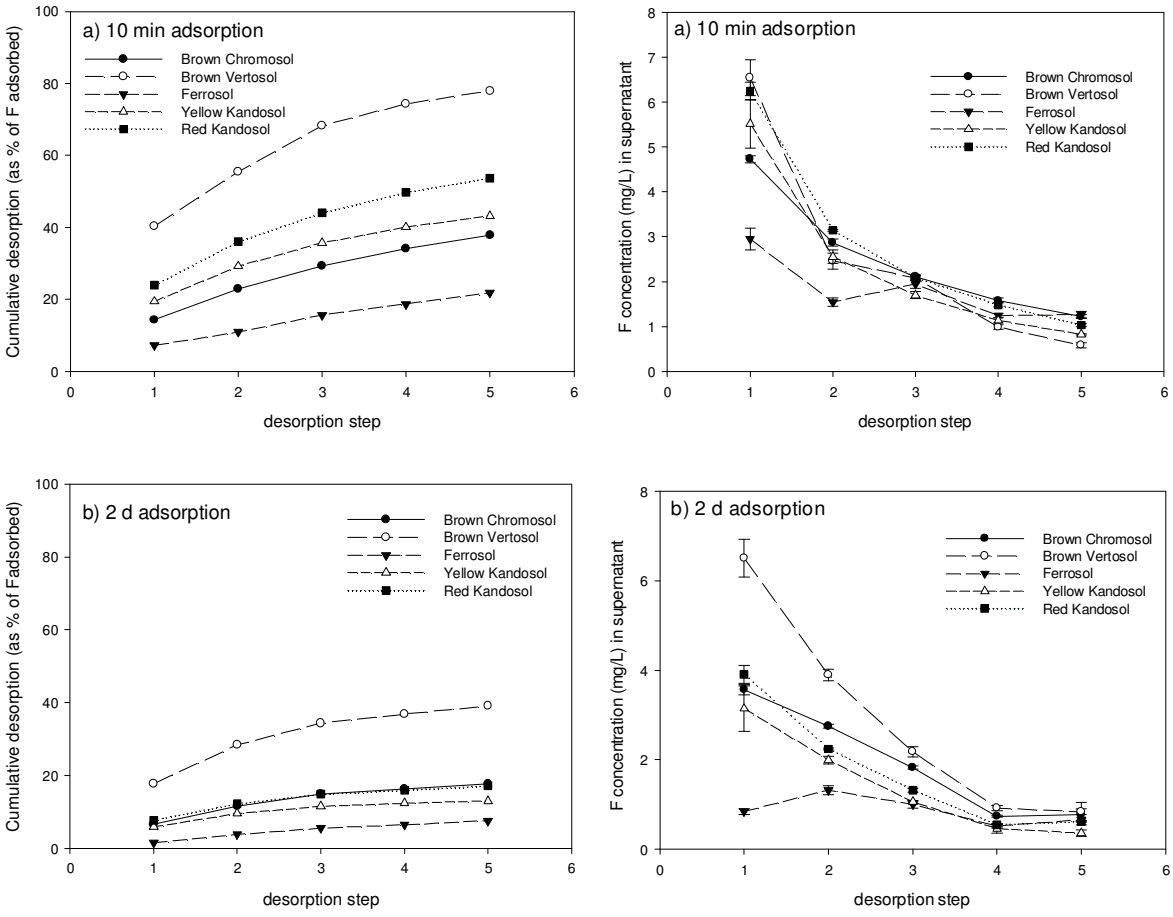


Figure 20. Effect of soil:water ratio on the amount of F desorbed. Soil slurries were shaken for approximately 16 h and the amount of F in the supernatant measured and expressed as mg F desorbed per kg of soil to account for differences in dilution. Values are means of three replicates with error bars shown if not obscured by the symbols.

Effect of ageing on desorption

The amount of F desorbed from soils was higher when the F adsorption was limited to only 10 min, but F desorption decreased substantially when soil was incubated for 2 days or more (Figure 21). For all soils except the Brown Vertosol, <10% of F adsorbed during an 8 week incubation was desorbed after 5 desorption steps. Thus, desorption of F decreased with increasing F adsorption incubation time. This could be caused by diffusion of F into interstices (micropores) of soil particles, which makes desorption of F a diffusion controlled process. Alternatively, F may have undergone chemical changes to poorly soluble F compounds (e.g. fluoroapatite), or formed Al-F or Fe-F bonds (chemisorption) (Barrow and Shaw, 1977). Therefore, bioavailability of F would be high immediately after application of F-containing water to soil, but F bioavailability would rapidly decrease with time. It is worthy to note that desorption of F was greatest from the Brown Vertosol and least from the Ferrosol, irrespective of time of adsorption. Since F saturation of Brown Vertosol is higher than in Ferrosol, and the Qmax value in Ferrosol being higher than in Brown Vertosol, ability of Brown Vertosol to adsorb F is lower than in Ferrosol. Extending the number of desorption steps revealed that more F was desorbed from the Brown Vertosol than was initially added (Figures 26 and 28), indicating that this soil naturally contains F, which was also desorbed during the desorption steps.



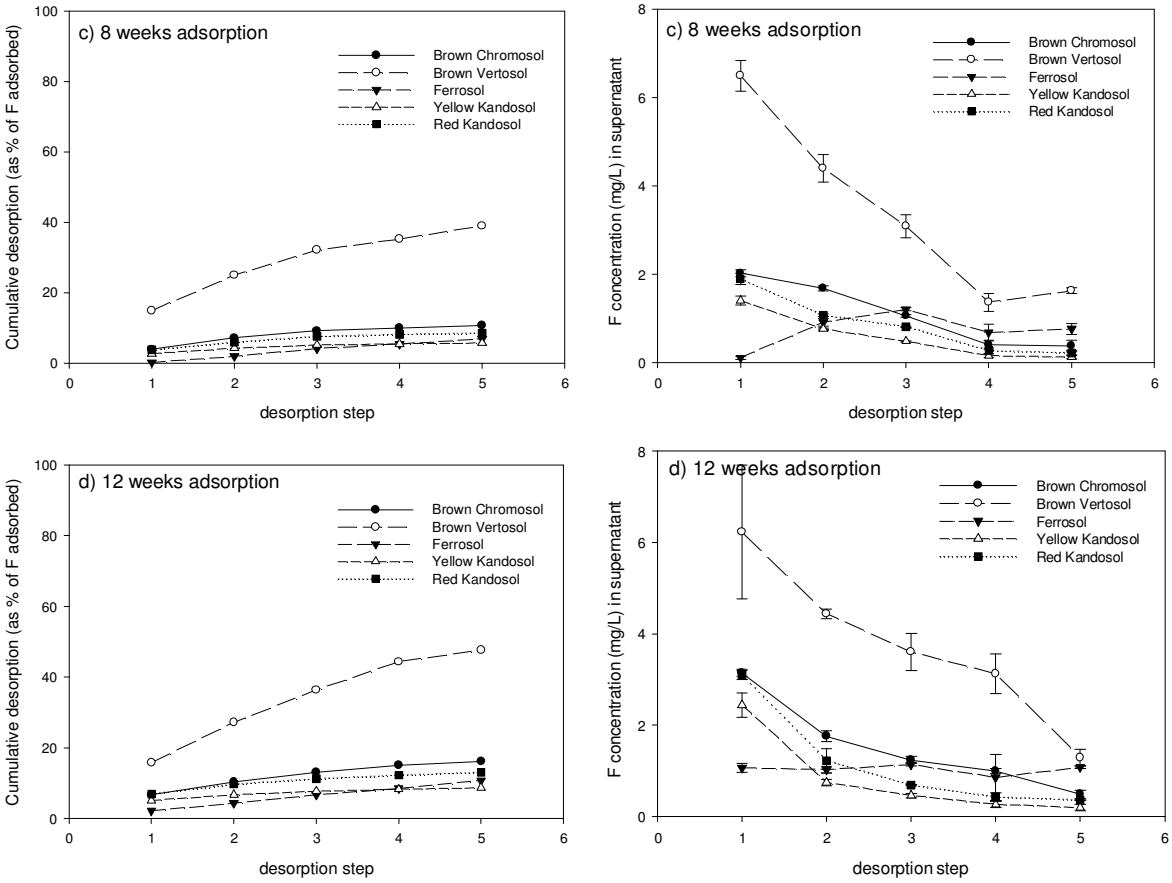


Figure 21. Effect of increasing adsorption duration on the desorption of F bound to five soil types. The panels on the left show cumulative F desorbed with increasing number of desorption steps, while the panels on the right show the F concentration in the supernatant of a 1:5 soil water slurry with increasing number of desorption steps.

Effect of soil drying

Drying of soil leads to changes in clay particle spacing and may also induce precipitation of F in minerals. Therefore, it is possible that drying of soil can decrease the amount of F that can be desorbed from soil. However, drying of soil was not observed to influence the amount of F desorbed, with only the Vertosol showing a significant increase in F desorption (Figure 22). While it is considered that drying of a Vertosol results in shrinkage of intermicellar spaces, it is possible that the high salt concentration during drying results in formation of F salts which go into solution after drying (i.e. during rewetting).

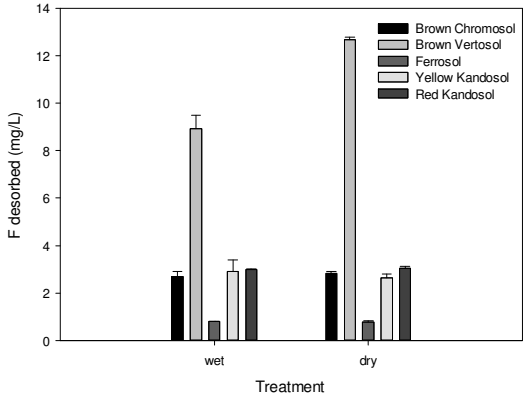


Figure 22: Effect of drying of five soils treated with 50 mg F/kg soil on the desorption of F. Soils were either stored moist or dried for 3 days at 60°C before resuspending the pellet with 10 mL

deionised water and measuring the F concentration in the supernatant of 1:5 slurries. Bars are the means of three replicates, with standard error bars shown if not obscured by the bar.

Desorption curves

The total amount of F desorbed was low in most soils treated with low F, and was typically in the range of ca. 20-40% of the total F adsorbed (Figures 23 to 29, Table 11). A notable exception was the Brown Vertosol which desorbed more F than was initially added in the 25-45 cm (188%) and 45-70 cm (159%) layers and 64% of that adsorbed in the top 0-25cm, thereby indicating that this soil already contained appreciable quantities of F (Figure 26, 28). The Aquic Podosol (low *K* value) also desorbed a substantial amount of F in the low treatment, up to 79% of initially adsorbed. When F adsorption occurred under high solution concentrations (125 mg F/kg soil) higher rates of F were subsequently desorbed for all soils (compare open and solid symbols in Figure 23-27). This could be attributed to the fact that all high affinity binding sites for F are occupied and part of the adsorbed F is more weakly held, resulting in greater desorption. In contrast, in soil treated with CS water containing 5 mg F/kg soil, all F is bound to high affinity binding sites and less F is desorbed.

The F adsorbed by the soils could progressively be desorbed with deionised water. The desorption of F was significantly inversely correlated to the *K* value estimated by the Langmuir equation for both low (5 mg F/L) and high (125 mg F/L) F treatments ($r = -0.54$ and -0.68 respectively, $p < 0.05$). This can also be seen from Figure 6, which shows that desorption is minimal when adsorption is high and vice versa. Consequently, desorption of F is low in soil with high K_L values. The results indicate that K_L is a useful measure for predicting the extent of F desorption from the soils examined.

The concentration of F in the supernatant of a 1:5 soil:water slurry was around 4 mg/L for the Brown Chromosol, Yellow and Red Kandosol, and 9 mg/L for the Brown Vertosol during the first desorption step (Figure 28). The concentration of F in the supernatant during desorption is dependent on the concentration of F added to soil; if high F concentrations (e.g. 125 mg/L) were added to soil, higher concentrations of F were measured during desorption than when using low F concentrations during the adsorption step (Figures 23-27 right hand panes). It needs to be highlighted that some of the F measured during the first desorption step is actually F in the entrained solution, rather than desorbed F. During the second and subsequent desorption steps, the measured F is true desorbed F. Thus, the desorbed F concentration decreased from 2 mg/L after the second desorption step from soil treated with 125 mg F/kg to less than 1 mg/L after the fifth desorption step. In the Brown Vertosol, the concentration of F decreased from 7 mg/L after the second desorption step to 4 mg/L after five desorption steps and to 1 mg/L after 11 desorption steps (Figure 28). Therefore, when F was desorbed, its concentration in the soil solution was low and diminished with increasing numbers of desorption steps.

In the field, the ratio of rainfall to soil is less (the water:soil ratio will be around 1:1 during heavy rainfall when the soil surface reaches saturation, and decreases with soil depth). The volume of deionised water used during five desorption steps (5x10 mL per 2 g soil) would be equivalent to 3250 mm of rainfall in the field. Therefore, the rates of F mobilisation in the field will be lower and will take longer until F concentrations in soil solution decrease to below 1 mg/L. Furthermore, in field soil, F movement through soil aggregates is probably more governed by diffusion than mass flow, unlike this study which used a 1:5 suspension. Therefore, desorption in the field will likely be much less, but at the same time, the

concentration of F in the soil solution will likely be lower. But, as mentioned earlier, the concentration of F in the soil solution also depend on the F loading; when high concentrations of F were adsorbed onto the soil, higher concentrations of F were measured in the supernatant during desorption.

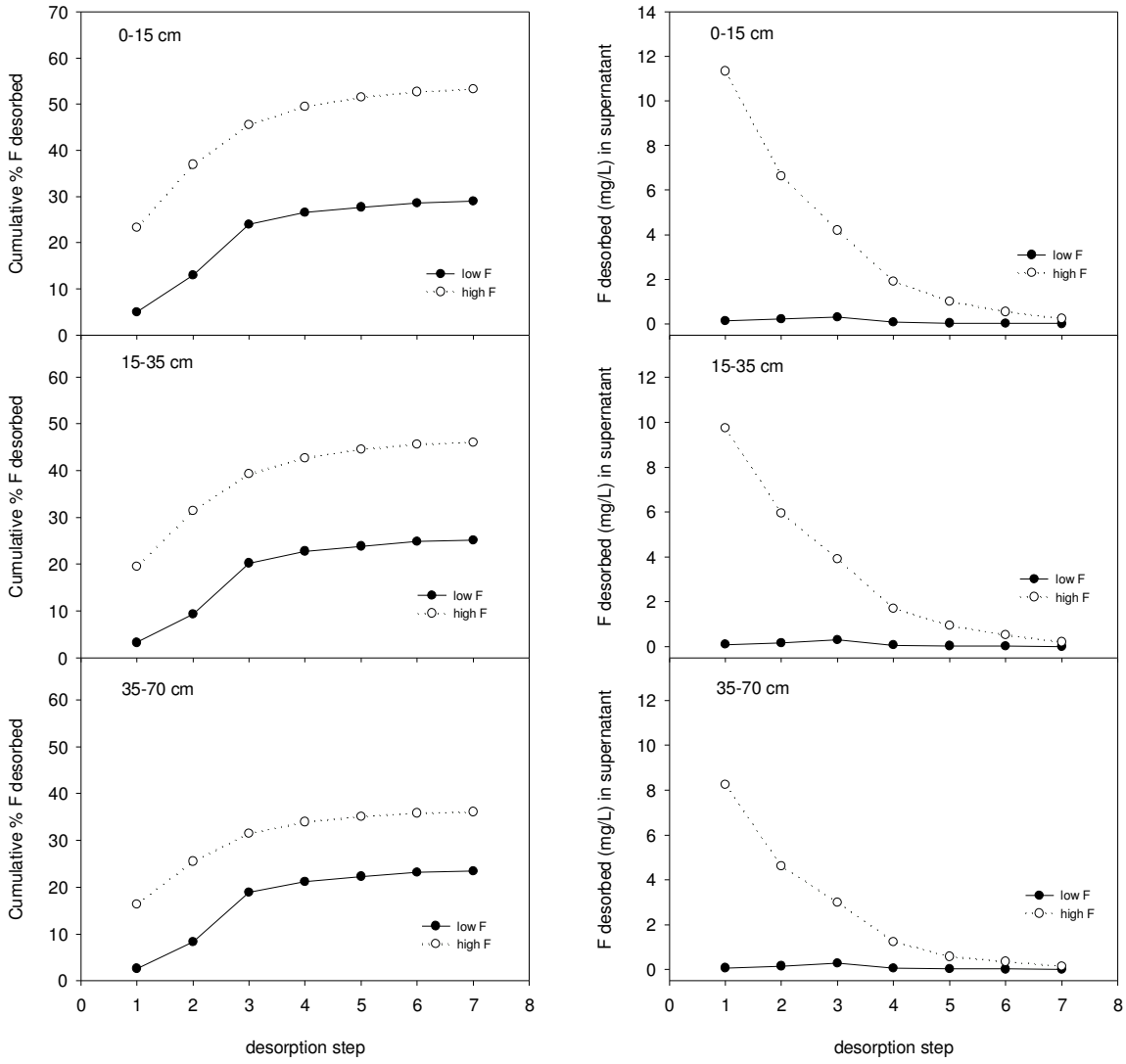


Figure 23. Cumulative % of F desorbed and concentration of F in supernatant of Yellow Kandosol mixed 1:5 with deionised water. Prior to desorption, soil was treated with 5 mg F/L (low F) or 125 mg F/L (high F) in CS water for 7 days. The desorption step was repeated seven times. F desorbed is expressed either as cumulative % of F bound (left column) or as concentration (right column) in the supernatant of 1:5 soil:water suspensions. No correction was made for F entrained in the pellet.

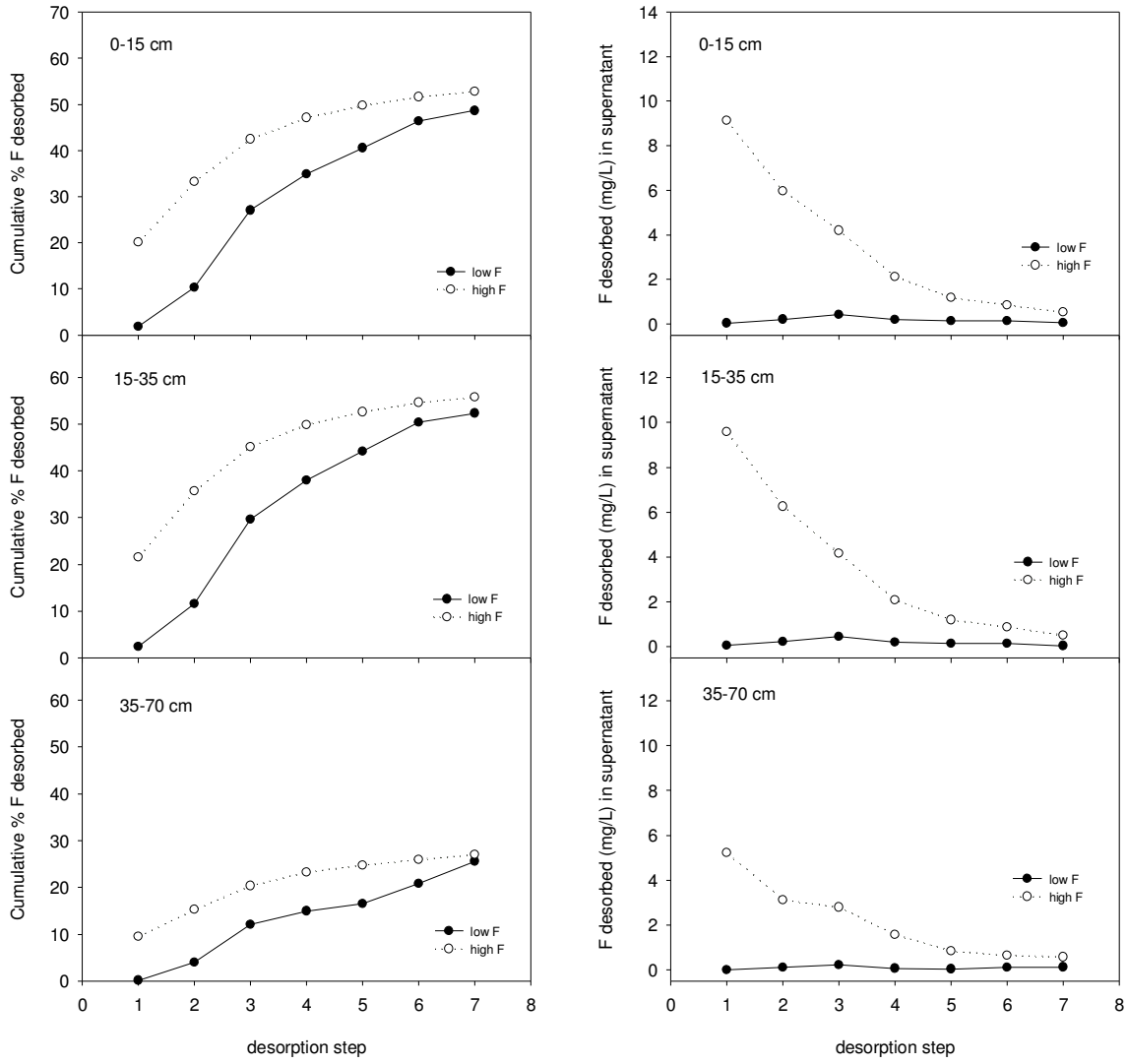


Figure 24. Cumulative % of F desorbed and concentration of F in supernatant of Red Vertosol mixed 1:5 with deionised water. Prior to desorption, soil was treated with 5 mg F/L (low F) or 125 mg F/L (high F) in CS water for 7 days. The desorption step was repeated seven times. F desorbed is expressed either as cumulative % of F bound (left column) or as concentration (right column) in the supernatant of 1:5 soil:water suspensions. No correction was made for F entrained in the pellet.

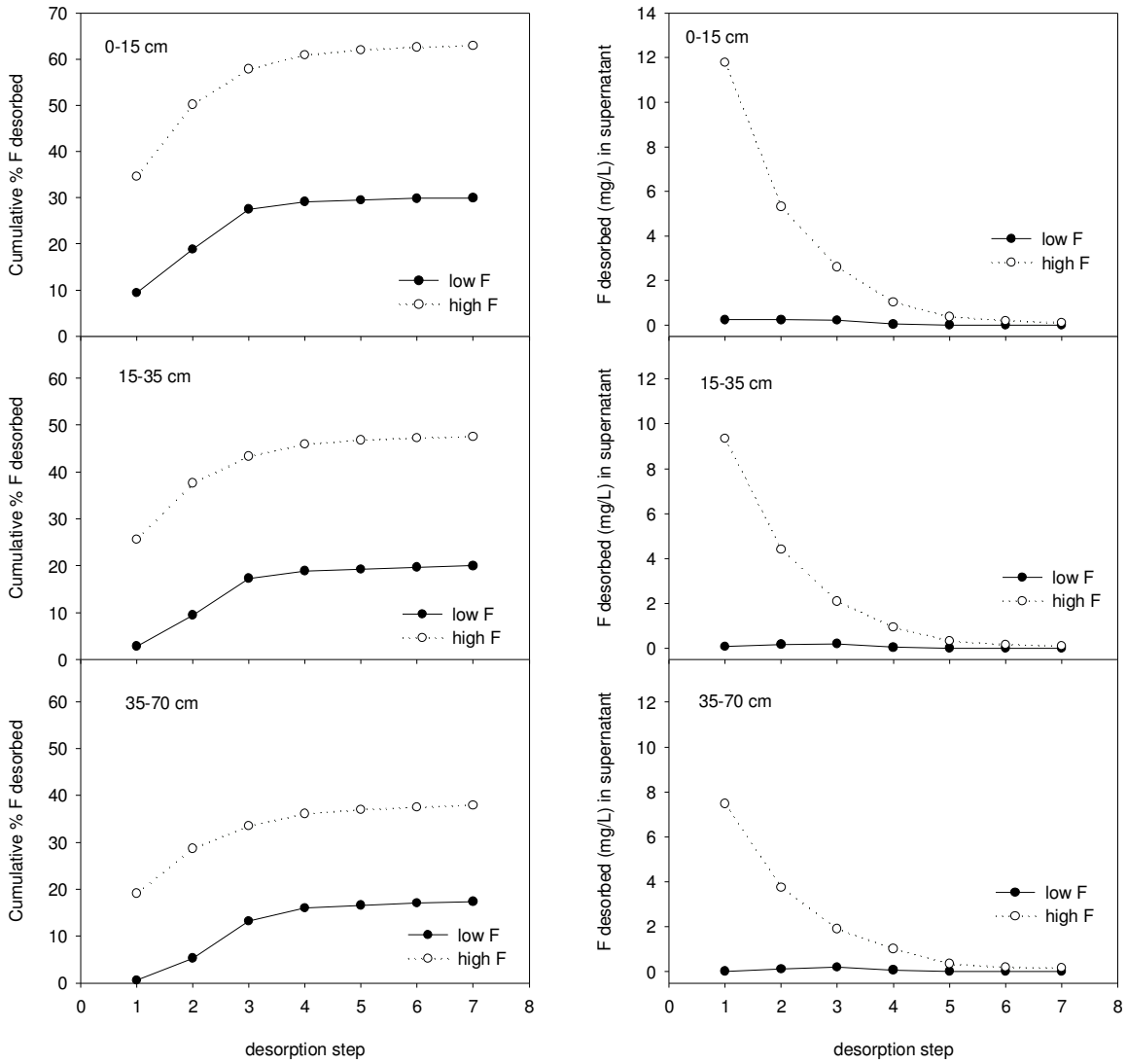


Figure 25. Cumulative % of F desorbed and concentration of F in supernatant of Red Kandosol mixed 1:5 with deionised water. Prior to desorption, soil was treated with 5 mg F/L (low F) or 125 mg F/L (high F) in CS water for 7 days. The desorption step was repeated seven times. F desorbed is expressed either as cumulative % of F bound (left column) or as concentration (right column) in the supernatant of 1:5 soil:water suspensions. No correction was made for F entrained in the pellet.

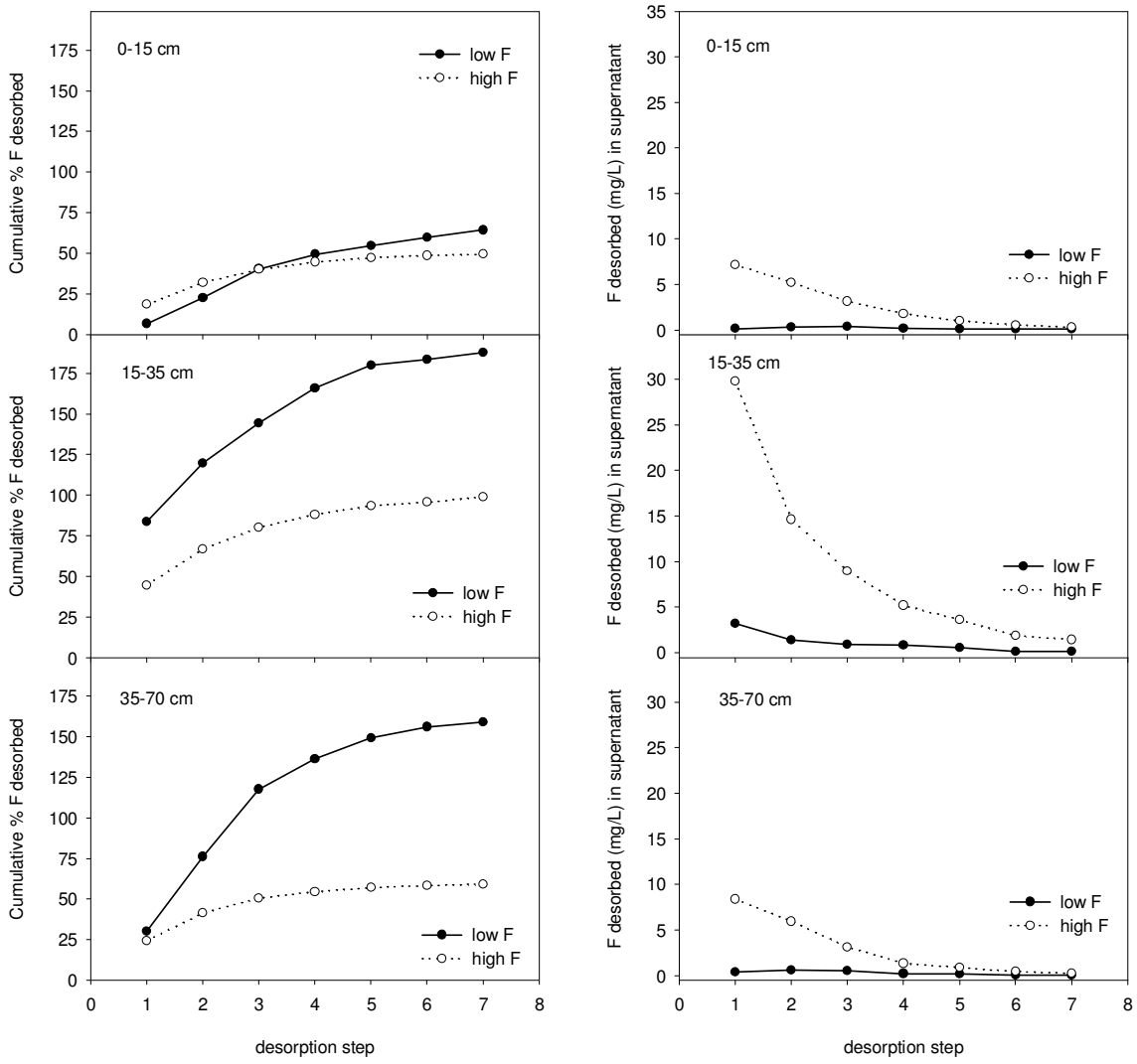


Figure 26. Cumulative % of F desorbed and concentration of F in supernatant of Brown Vertosol mixed 1:5 with deionised water. Prior to desorption, soil was treated with 5 mg F/L (low F) or 125 mg F/L (high F) in CS water for 7 days. The desorption step was repeated seven times. F desorbed is expressed either as cumulative % of F bound (left column) or as concentration (right column) in the supernatant of 1:5 soil:water suspensions. Note the changed y-axes scales. No correction was made for F entrained in the pellet.

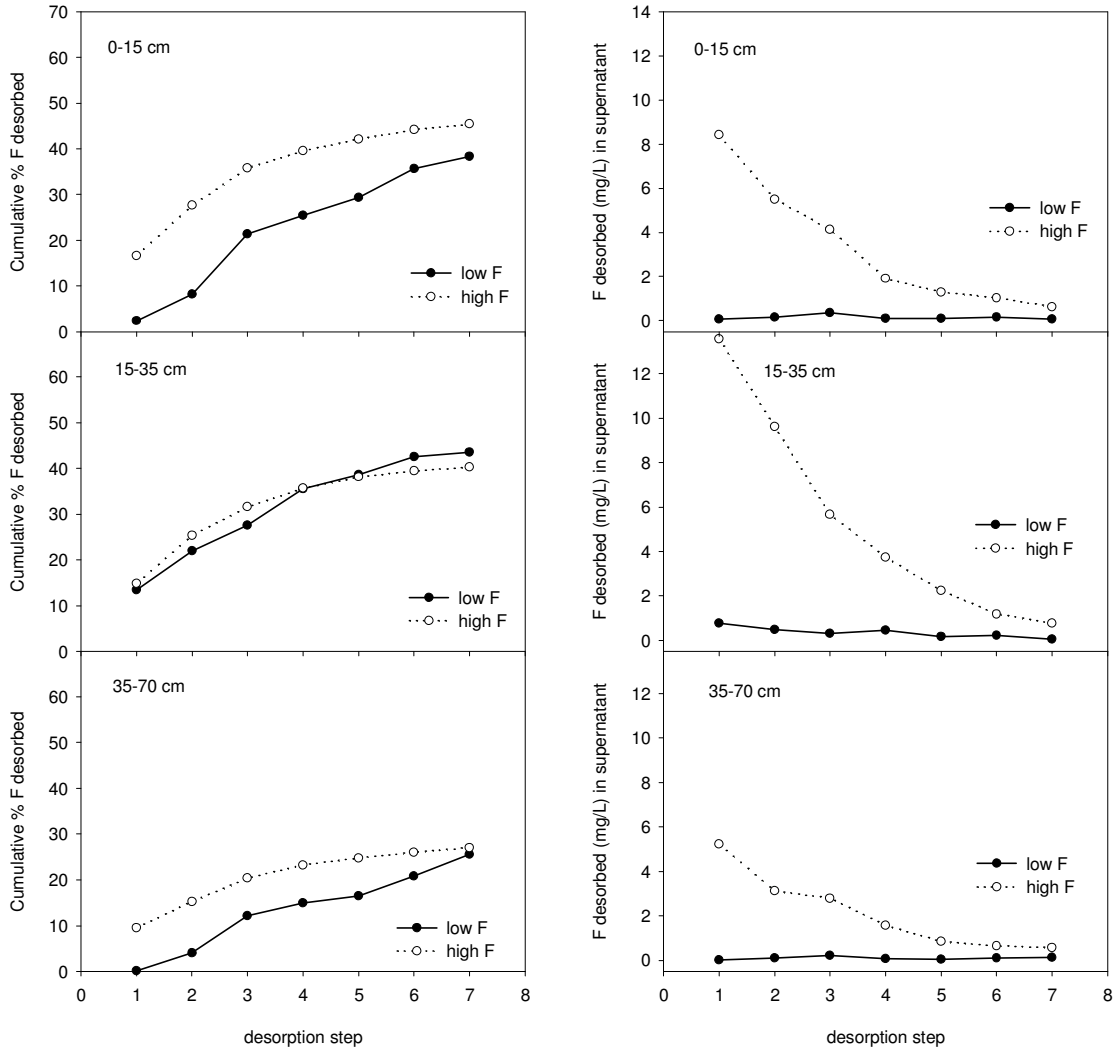


Figure 27. Cumulative % of F desorbed and concentration of F in supernatant of Brown Chromosol mixed 1:5 with deionised water. Prior to desorption, soil was treated with 5 mg F/L (low F) or 125 mg F/L (high F) in CS water for 7 days. The desorption step was repeated seven times and F desorbed is expressed either as cumulative % of F bound (left column) or as concentration (right column) in the supernatant of 1:5 soil:water suspensions. No correction was made for F entrained in the pellet.

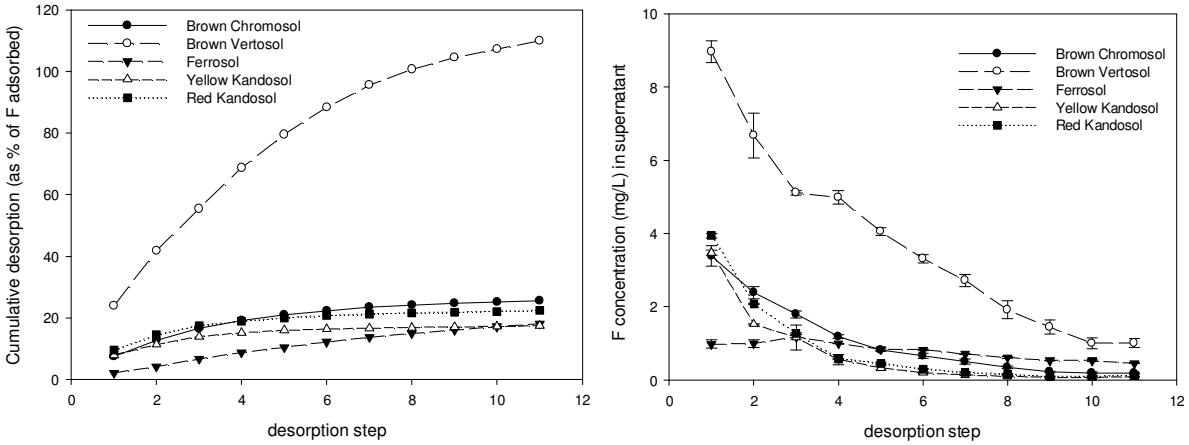
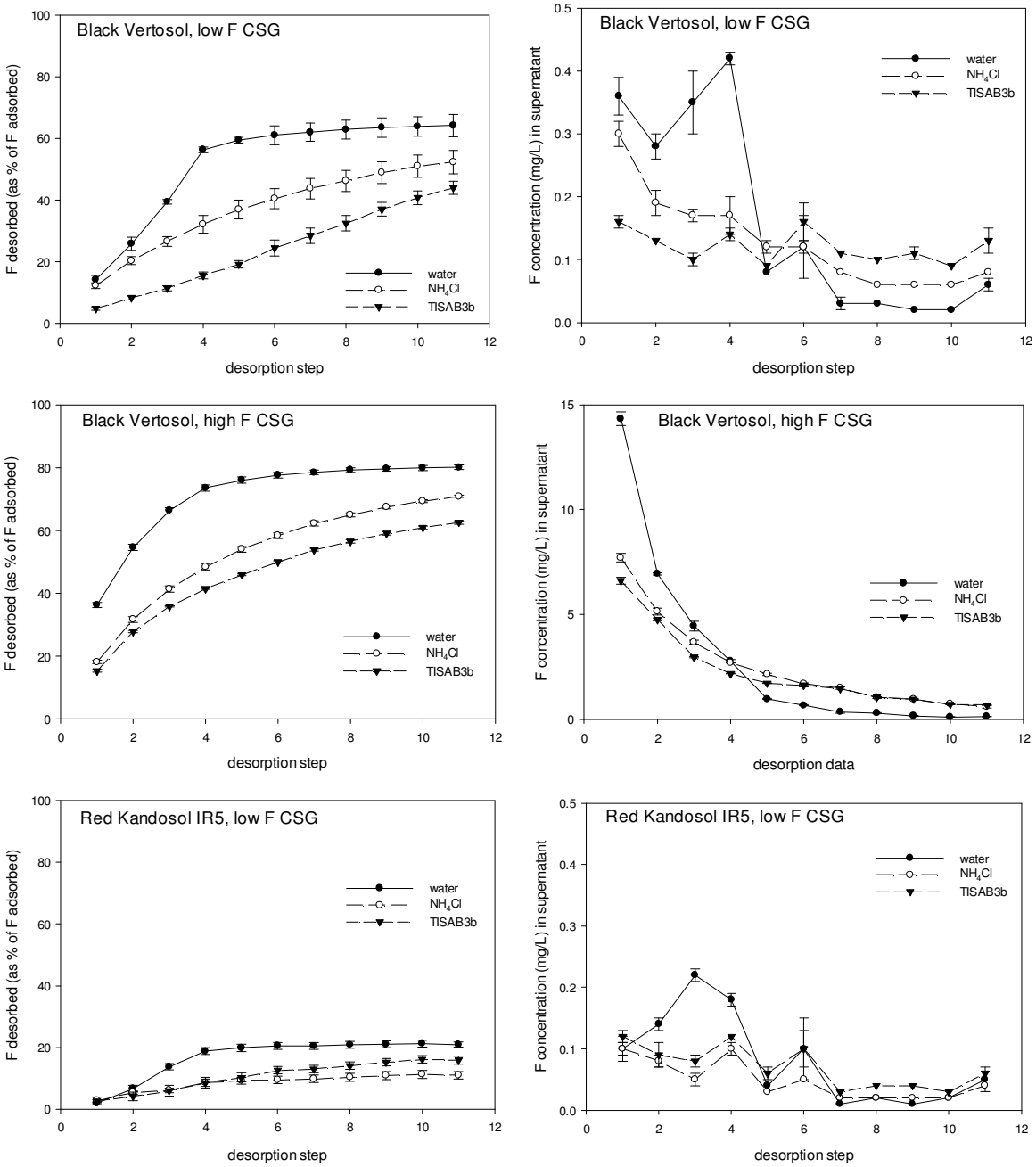


Figure 28. Desorption of F from five soils as affected by number of desorption steps. Soils were treated with 10 ml of 100 mg F/L in deionised water. After adsorption for 30 days, bound F was

desorbed with water and the desorption step repeated eleven times. Panel on left shows cumulative % F desorbed, panel on rights shows actual F concentration in the supernatant of 1:5 soil:water suspensions. No correction was made for F entrained in the pellet.

Desorption curves when different desorbents (water, 0.2 M NH_4Cl or TISAB3b buffer) were used are presented in Figure 29. Since it was found that ionic strength affects adsorption of F, the effect of different desorbents was expected. The amount of F desorbed from soil using water as desorbent reached a plateau after four desorption steps for the Black Vertosol and Red Kandosol (Figure 29). Desorption of F from Ferrosol with NH_4Cl and TISAB3b increased almost linearly with desorption steps. Consequently, the amount of F desorbed after extensive desorption steps differed little between desorbents because water desorbed more F initially, whereas F desorbed with NH_4Cl and TISAB3b remained constant with desorption steps and did not level off. The linear phase of the desorption isotherms observed after the fifth desorption step indicates that dissolution of a mineral in the soil controls the concentration of F in the supernatant.



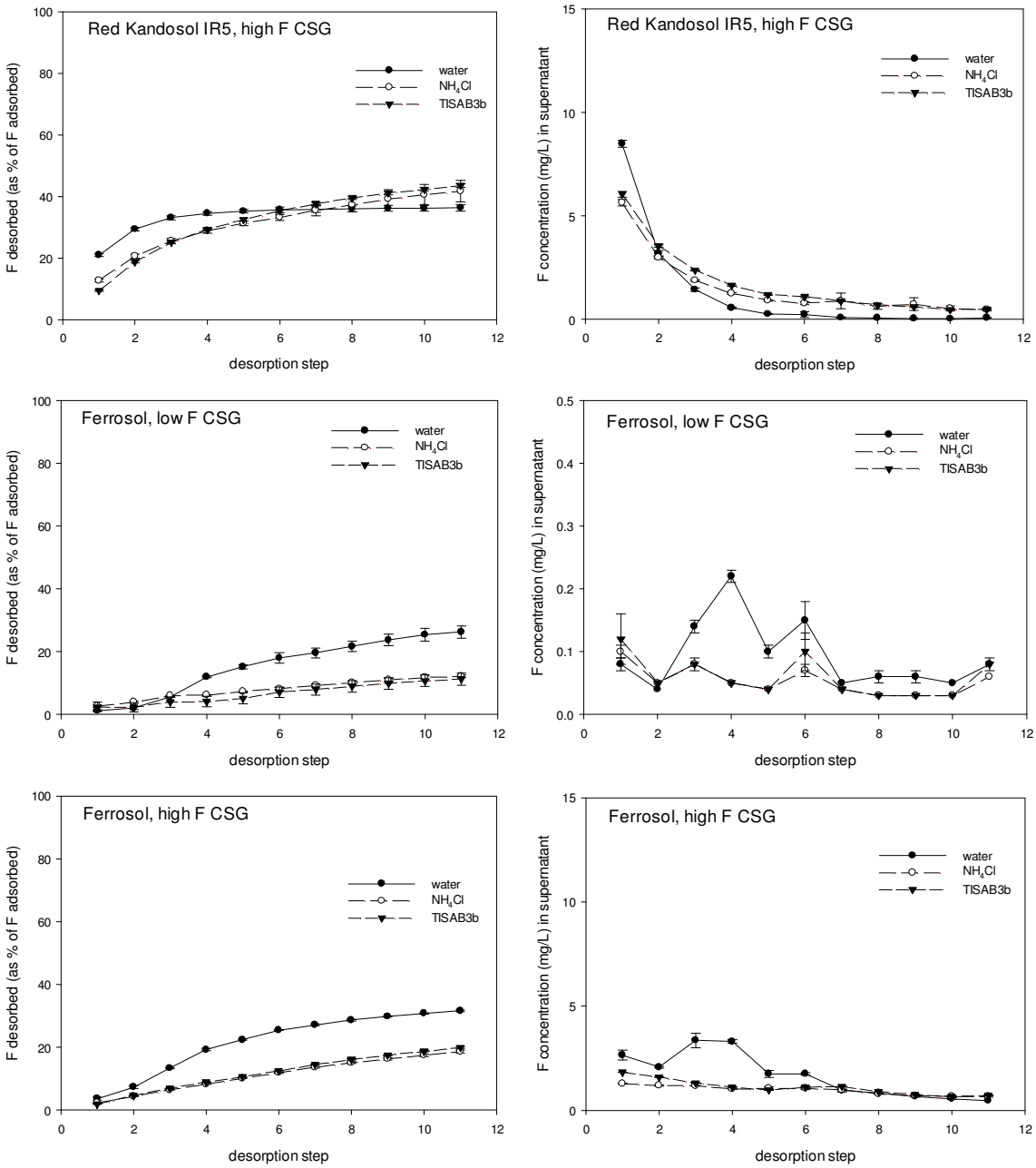


Figure 29. Desorption of F from the top 0-25cm of six soils treated with three desorbents (water, 0.2 M NH4Cl or 0.2 M TISAB3b). Cumulative percentage of desorption was calculated from observed initial F adsorption, following seven days in an end to end mixer. Error bars indicate the standard error. No correction was made for F entrained in the pellet.

Table 11. Cumulative desorption of F from topsoil in Part II of the study. Values are expressed as percentage of F desorbed relative to F bound. F was desorbed five times with water from soil loaded with 190 mg F/kg. The amount of F desorbed at the first desorption step includes desorbed and entrained F.

		Cumulative % F desorbed after desorption step				
Soil type	Site	1st	2nd	3rd	4th	5th
Red Chromosol	IR4-256	1	4	5	6	8
Brown Ferrosol	Kingaroy	2	3	6	6	8
Brown Kandosol	IR5	2	4	6	7	9
Brown Dermosol	Reuben Downs 17	-1	8	8	9	9
Brown Dermosol	Reuben Downs 3	9	12	14	13	14
Yellow Chromosol	Gatton	8	11	11	12	14
Grey Vertosol	Weemilah 1	2	10	12	13	15
Brown Chromosol	The Bend 30	9	12	15	16	18
Black Vertosol	Summerhills 5	8	7	13	15	18
Red Dermosol	Reuben Downs 8	7	11	17	19	22
Brown Dermosol	Broandah 1	7	12	18	21	23
Tenosol	The Bend 41	11	17	17	21	23
Black Vertosol	Summerhills 3	12	20	18	22	25
Brown Dermosol	Summerhills 10	12	18	23	22	26
Black Vertosol	Reuben Downs 6	10	15	21	25	27
Brown Sodosol	Pleasant Hills 63	11	18	25	25	28
Brown Dermosol	Mayfield	17	21	27	30	32
Red Chromosol	Pleasant Hills 88	17	23	29	30	33
Grey Vertosol	Moonie	38	33	37	35	33

In summary, the total amount of F desorbed, expressed as percentage of F bound initially, varied between soil types and was affected by the amount F added initially. The highest proportion of adsorbed F could be desorbed from the Black and Brown Vertosol (60-80%), but comparatively small quantities of F were desorbed from the Ferrosol (20-30%) after 5 desorption steps. Increasing the number of desorption steps increased the amount of F desorbed, indicating that eventually all bound F can be desorbed with infinite desorption steps. Soils with high binding strengths for F (e.g. Ferrosol) are also soils with low F desorption. The high initial desorption of F from all soils may be attributed to desorption of F either from exchange sites or from low affinity sites, whereas the low desorption during later stages of desorption may be due to dissolution of F-containing minerals, diffusion of F out of micropores or breakage of metal-F bonds. Thus, the concentration of F in the deep drainage will be low since F moves from layers with higher F saturation to layers with low F saturation, resulting in adsorption of F with little F (<1 mg/L) remaining in the leachate.

Relationship between total F and water soluble F in soil

There was a curvilinear relationship between F desorbed with water and total F in soil collected from the field by Santos personnel (Figure 30). Soils high in total F also had a high water extractable F, whereas soils with low total F had very low water soluble F. This indicates that some of the total F in soil is not available for plant uptake.

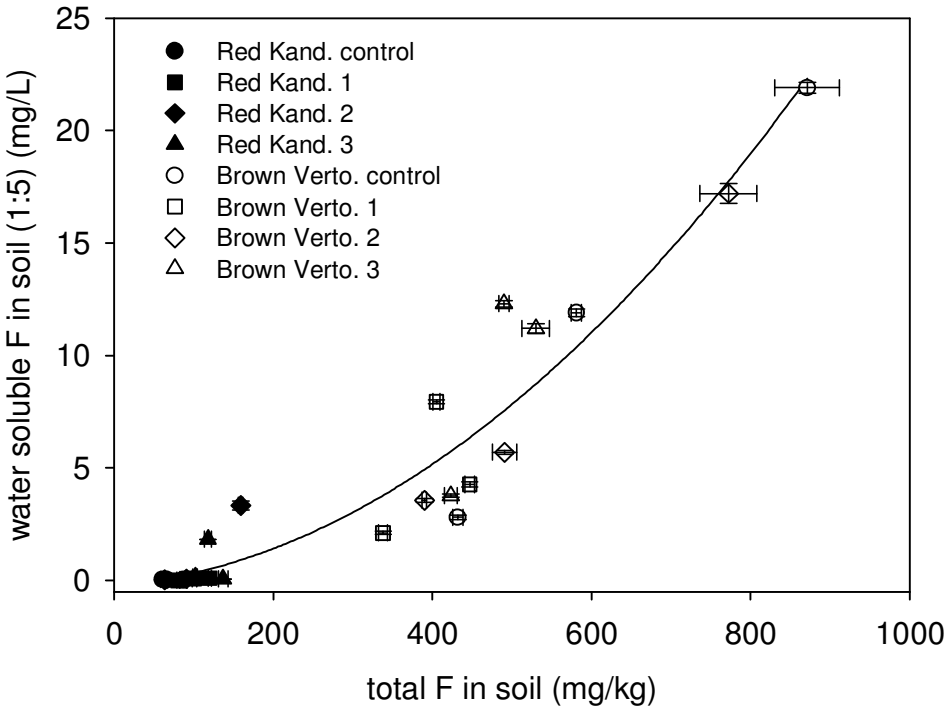


Figure 30. Relationship between water soluble F (measured on 1:5 soil: water slurries) and the total F, determined by NaOH fusion, of field soils treated with various volumes of F-containing CS water. Points represent different soils and soil horizons, the solid line represents the polynomial regression curve $y = 3.10^{-5} x^2 + 0.003x - 0.238$ ($R^2 = 0.914$).

The highest concentration of total F were found in the Brown Vertosol subsoils from the field (871 mg/kg), whereas Red Kandosol from the field had a subsoil F concentration of 87 mg/kg (see Appendix 6). It is worthy of note that the Brown Vertosol irrigated with CS water had lower total F than the non-irrigated control soil. Thus, the low F in CS water (around 3 mg/kg) can leach F from the Brown Vertosol since Brown Vertosol binds F only weakly. By contrast, application of CS water to the Red Kandosol, which has a higher affinity for F and a lower F concentration, results in immobilisation of the F from the CS water and accumulation of F in the Red Kandosol soil.

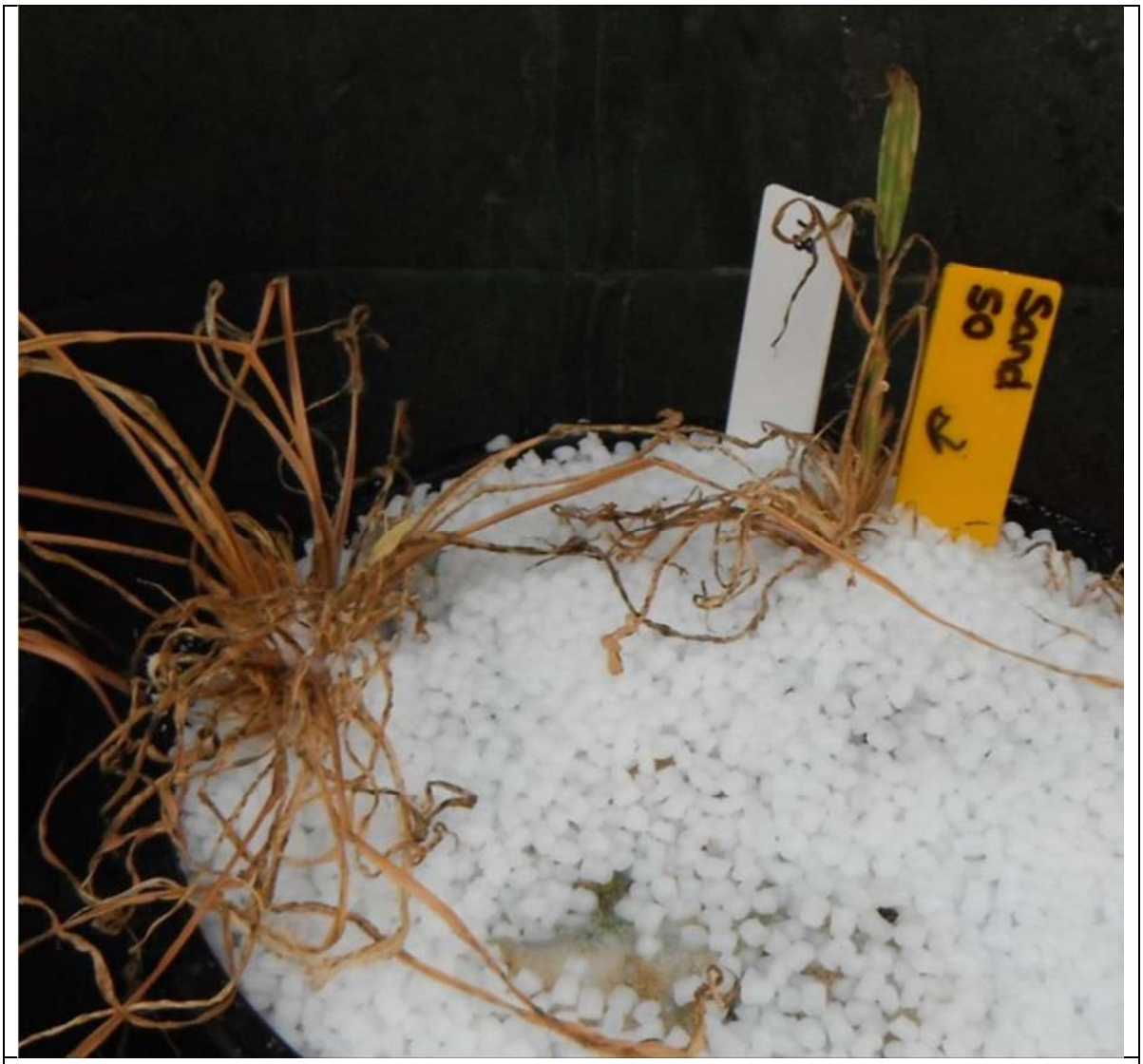
Plant uptake of F

Foliar concentrations of F in field grown pastures supplied by Santos

The foliar concentrations of F in buffel grass and panicum was below 25 mg/kg DM (Appendix 6), well below the maximum tolerable limit of 35 mg/kg DM for fodder for young beef cattle (Table 1). We do not have background information on the plant material supplied to us, so cannot comment on the irrigation regime the plants were subjected to, nor the soil F concentrations in which the plants were grown. Nevertheless, the data show that uptake of F into pasture species under field-conditions is unlikely to risk fluorosis in grazing animals.

Plant uptake of F from F treated soil

Red Kandosol, Yellow Kandosol, and Red Vertosol supplemented with 0-500 mg F/kg (as NaF) produced good growth of lucerne, leucaena and Rhodes grass (Appendix 7-9). However, growth was reduced substantially in the F-treatments for Sand, with complete mortality in Sand containing 50, 150 or 500 mg F/kg (Figure 31). In addition, the control plants in Sand exhibited nutrient deficiency symptoms (Figure 32). Some visual effects of F on plant growth in the sand are shown in Figure 31 and include necrosis of leaves and black-brown blotches on the leaves.



Sand with 50 mg/kg F and Rhodes grass

Sand with 150 mg/kg F and Rhodes grass

Sand with 150 mg/kg F and lucerne

Figure 31. Close-up images of lucerne and Rhodes grass seedling grown in sand with 50 or 150 mg/kg F as NaF. Plants were growing for less than 2 weeks on the F treated soil.

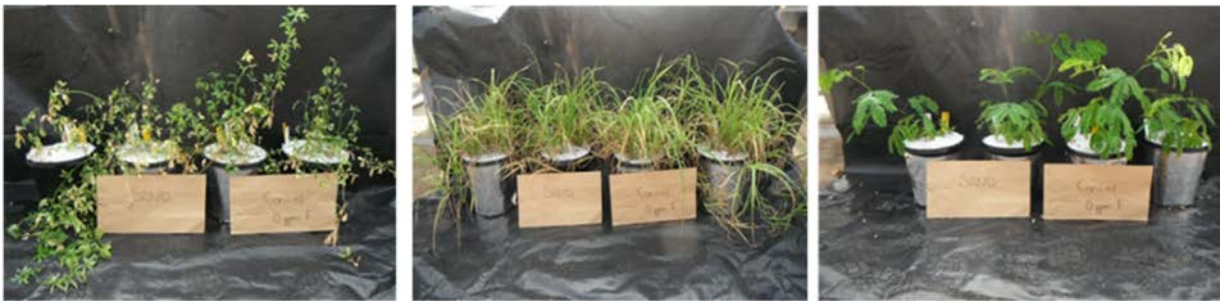


Figure 32. Obvious growth deficiencies in the control treatment of Sand and mortality observed in treatment pots in the control (0 mg/kg treatment).

For the foliar F concentrations, a significant interaction ($p<0.001$) was found between soil type and the rate of F addition, thereby indicating that whilst the addition of F to the soil significantly influenced the concentration of F in plant material, the pattern of this response varied for each soil (i.e. the soil type has an important influence on the uptake of F). The increase in foliar F was greatest in Sand (increasing from ca. 36 to 38,000 mg F/kg) and least for the Red Vertosol (increasing from ca. 12 to 14 mg F/kg) (Figure 33). In the 500 mg F/kg treatment, the average foliar F of plants grown in the Red Kandosol and Yellow Kandosol were similar, but was significantly higher than in plants grown on Red Vertosol. There were no visual differe ndix 7-9).

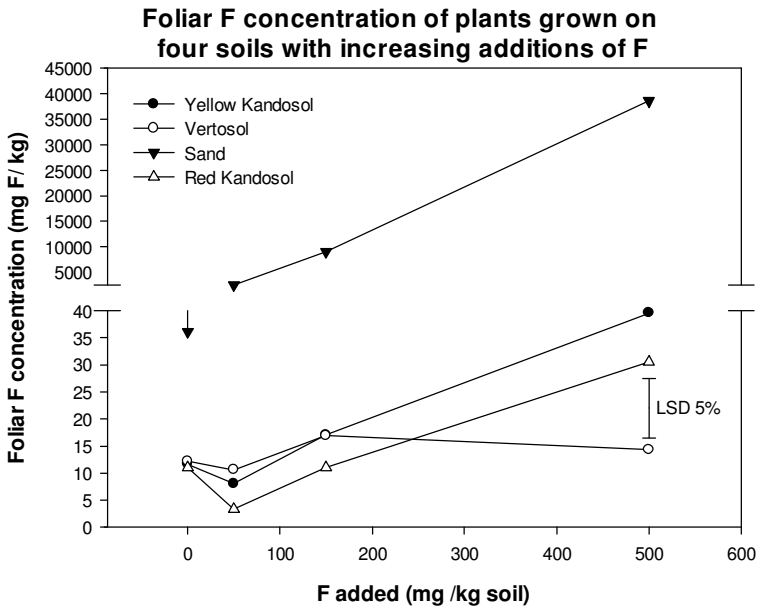


Figure 33. The concentration of F in dry plant foliar material (averaged across three species) grown on four soils treated with increasing concentrations of F (0, 50, 150 and 500 mg F/kg). LSD at 5% indicates significant differences.

Not only was the uptake of F influenced by soil type, but also by plant species. Analyses of individual plant species grown on each soil identified a significant interaction between F addition to the soil and plant species (for the Yellow Kandosol, Red Kandosol and Sand). Therefore, whilst the addition of F influences the accumulation of F in the foliage, the magnitude to which the F accumulates differs between the various plant species ($p<0.001$) (Figure 34). Specifically, lucerne accumulated significantly more F in the foliage than did Rhodes grass or leucaena in the 500 mg F/kg treatment of Sand, Yellow Kandosol and Red Kandosol soils ($p<0.05$). Interestingly, there were no significant differences in foliar F concentrations between plant species in the Red Vertosol (Figure 34).

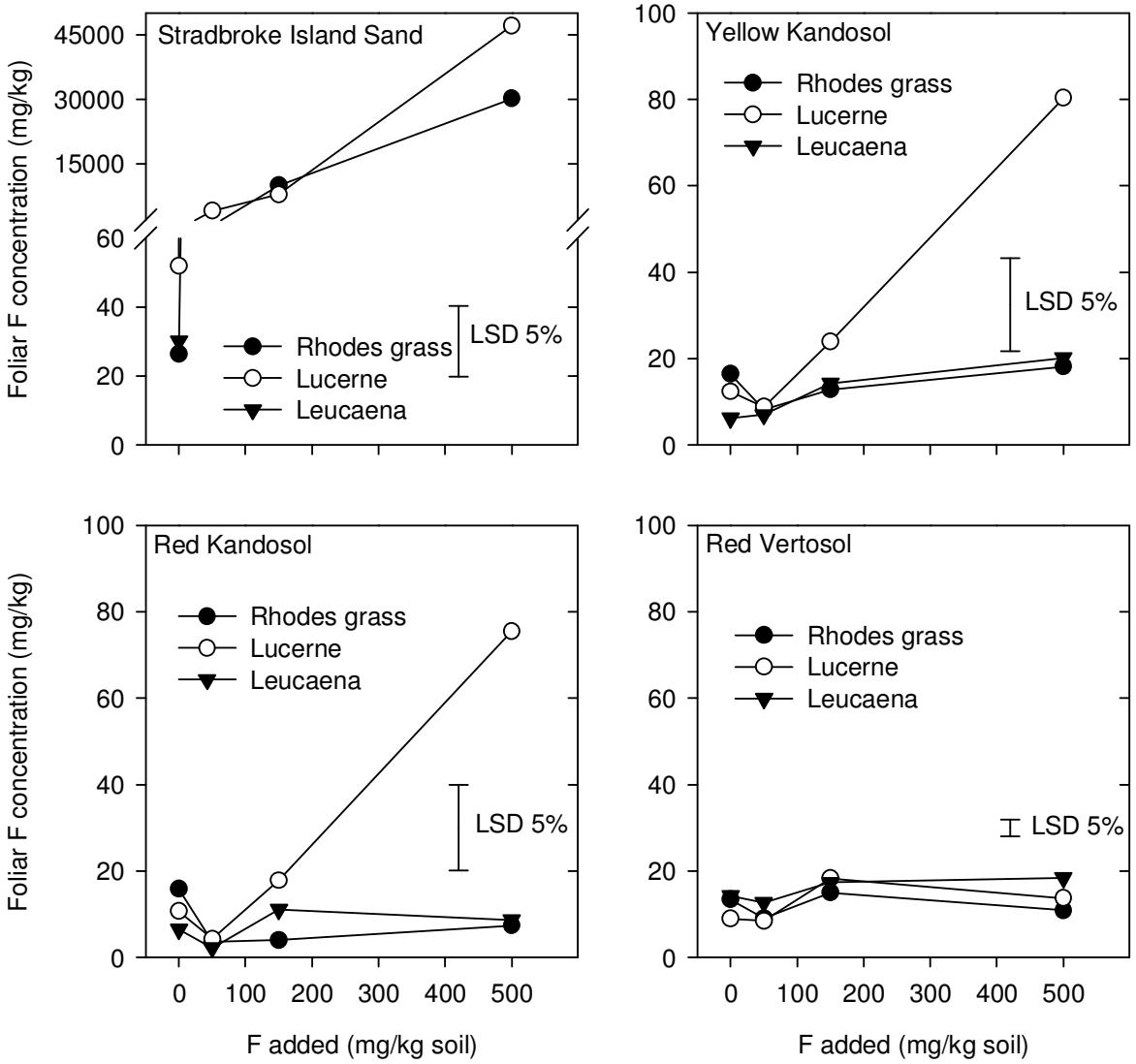


Figure 34. Foliar F concentrations (in mg F/kg DM) of Rhodes grass, lucerne and leucaena grown on four soils (Sand, Yellow Kandosol, Red Vertosol and Red Kandosol) treated with 0, 50, 150 and 500 mg F/ kg soil. Due to severe mortality, leucaena plants in the 50, 150 and 500 mg F/kg treatments could not be analysed due to insufficient volume of dry plant material.

For the Red Kandosol, the addition of F to soils increased the pH of soil solution by ca. 3 pH units, with the increase in the other soils being ca. 1 pH unit. Interestingly, the pH in the solutions of soils growing Rhodes grass was higher than those for lucerne and leucaena in Red Kandosol, Yellow Kandosol and Red Vertosol in every F treatment (excluding Red Kandosol 500 mg F/kg) (Figure 35). This suggests an effect of plant roots on rhizosphere pH in response to NaF addition.

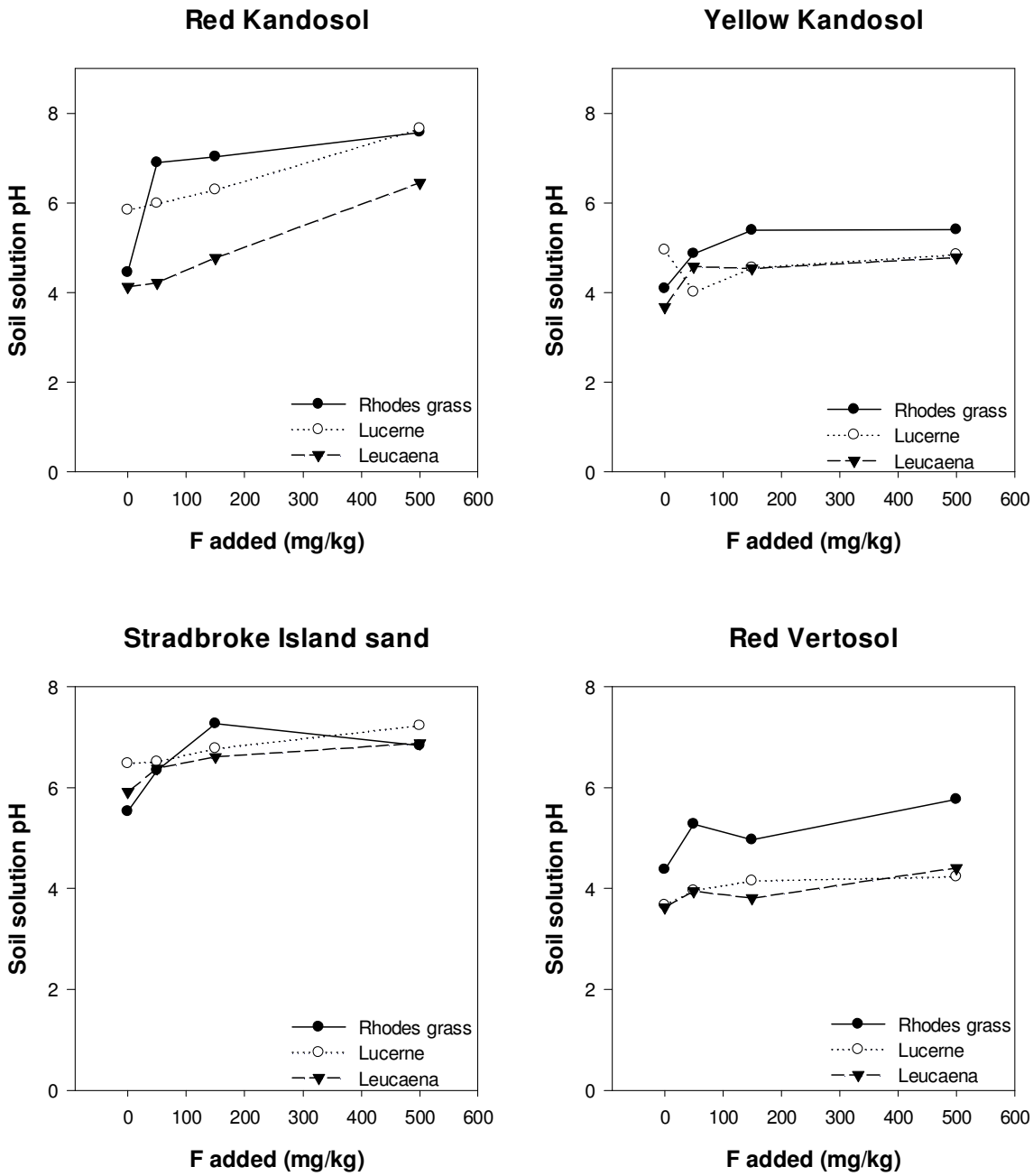


Figure 35. The pH of soil solutions extracted from the four soils (Red Kandosol, Yellow Kandosol, Sand and Red Vertosol) treated with four concentrations of F (0, 50, 150 and 500 mg F/kg), with plant species individually investigated.

The addition of F influenced plant growth to varying extent, depending upon the soil type. For lucerne and Rhodes grass, dry weights decreased significantly ($p<0.05$) from the control to 500 mg F/kg in the Yellow Kandosol, with a significant negative correlation found between F in plant material and dry weight ($p<0.05$) (Figure 36). The dry weight of leucaena was unaffected by all treatments of F across all soils and there was no correlation between F in plant material and dry weights of plants grown in Red Kandosol or Red Vertosol and there were no visual differences in plant growth between treatments (Appendix 7-9).

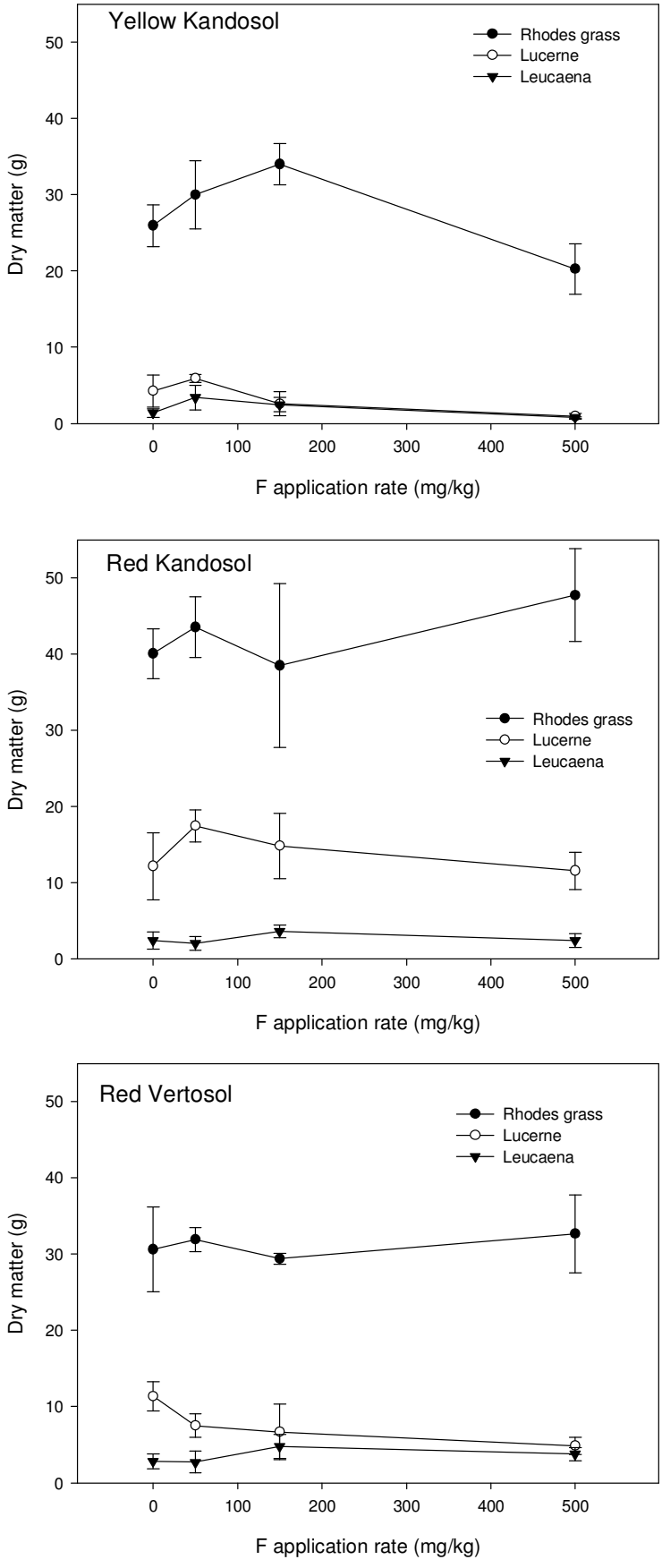


Figure 36. Effect of increasing soil F concentration on shoot dry matter of Rhodes grass, lucerne and leucaena grown on the three soils.

Soil solution concentrations increased with F addition, with the magnitude of increase varying between soils. This increase in the soil solution F concentration was related to the Qmax and K_L values, with Sand having negligible adsorption capacity and thus achieving the highest concentration of F in the soil solution. In contrast, the Red Vertosol which had the highest Qmax and high K_L values, had the lowest F present in soil solution (Figure 37). For the Sand, between 59.6 and 63% of the added F was present in the soil solution (2.2 mg F/L was also measured in the control, even though no F was added). For the three other soils, the Red Kandosol had significantly higher soil solution F concentrations than the Yellow Kandosol and Red Vertosol in both the 150 and 500 mg F/kg treatments, with no significant differences between the Yellow Kandosol and Red Vertosol across all treatments ($p<0.05$, Figure 37).

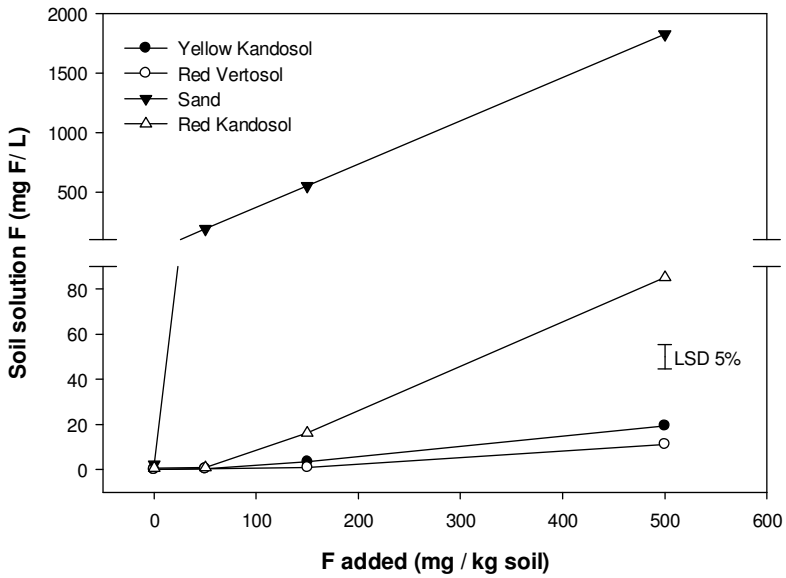


Figure 37. Soil solution F concentration (plant species averaged) of four soils (Yellow Kandosol, Red Vertosol, Sand and Red Kandosol) treated with increasing concentrations of F (0, 50, 150 and 500 mg F/kg). LSD at 5% indicates significant differences.

To determine the factor regulating the uptake of F from the soil solution, the foliar tissue concentrations were related to the soil solution properties. Firstly, foliar concentrations were related to total F concentrations in the soil solution. Due to extremely high F in the soil solution and foliar material of Sand treatments, there was a significant correlation between total F in the soil solution and plant foliar material ($r = 0.9$, $p<0.05$). For the Yellow Kandosol, significant correlations were present between the total F in soil solution and foliar concentrations in lucerne and leucaena ($r = 0.8$ and 0.8 respectively, $p<0.05$), but not Rhodes grass. Similarly, for the Red Kandosol, although a significant correlation was found between concentrations of F in the soil solution and in the foliar tissue for lucerne ($r =0.9$, $p<0.05$), there was no significant correlation for either Rhodes grass or leucaena. For the Red Vertosol, no significant relationship was found between the soil solution F concentration and the shoot tissue F concentration for any plant species.

Given the lack of relationship between plant uptake and total soluble F concentrations, F speciation in soil solution was modelled using the computer program PhreeqcI (Parkhurst and Appelo, 1999). Lucerne was selected for modelling as it was the only species to have a consistent significant increase in foliar F upon the addition of F to the soil. This modelling indicated that the speciation of F within the soil solution differed substantially between the

soils (Figure 38). For the Red Kandosol, F was predominantly present as the free F^- ion (accounting for 67% of total soluble F) with the various Al-F species accounting for ca. 8% of the total F. Similarly, in the Sand, F was dominated by the free F^- ion, accounting for ca. 98% of the total F. In contrast, the Yellow Kandosol had a much lower proportion present as F^-, accounting for only ca. 0.37% of the total soluble F in the 500 mg F/kg treatment. Rather, for the Yellow Kandosol, AlF^{2+} and AlF_2^+ species were the primary F species, contributing ca. 62% of the total soluble F in the 500 mg F/kg treatment. Finally, for the Red Vertosol (which had the lowest total soluble F in the soil solution of the four soils) Al-F complexes accounted for 29% in comparison to F^- (19%), with the remainder of F being present as small proportions of numerous F complexes, such as MgF^+ and NaF^0.

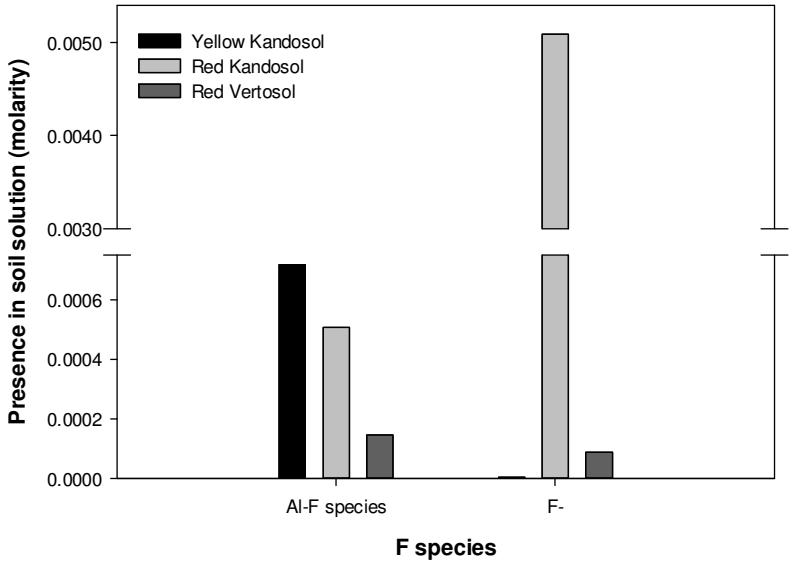


Figure 38. Presence of Al-F and F- species in the soil solution of three soils (Yellow Kandosol, Red Kandosol and Red Vertosol) treated with 500 mg F/kg, containing lucerne plants. Sand was excluded due to extremely high F^- concentrations, preventing visual analysis of graph.

Although various significant relationships were observed using this thermodynamic modelling, no consistent relationship was found across all four soils. For example, lucerne grown on Red Kandosol was found to have a highly significant correlation between F^- in the soil solution and F in foliar material ($r = 0.966$, $p<0.001$). Similarly, for the Sand, F^- in the soil solution was also highly correlated to F in foliar material. However, in contrast, lucerne foliar tissue F concentrations were most highly correlated with AlF^{2+} and AlF_2^+ species combined presence in the soil solution of Yellow Kandosol ($r = 0.8$, $p<0.001$). For the Red Vertosol, no significant relationship was found for either F^- or Al-F species in the soil solution. Investigation of the foliar Al concentration of plants grown in Red Kandosol and Yellow Kandosol, the two soils which concentrated the most F in lucerne foliar tissues (excluding Sand), found that lucerne contains more Al in foliar tissues than leucaena and Rhodes grass in both soils. Furthermore, all plants grown on Yellow Kandosol contained more Al in foliar tissues than those grown on Red Kandosol (Figure 39). The formation of Al-F complexes in leaves may serve as a detoxification mechanism for F or Al (Kinraide, 1997).

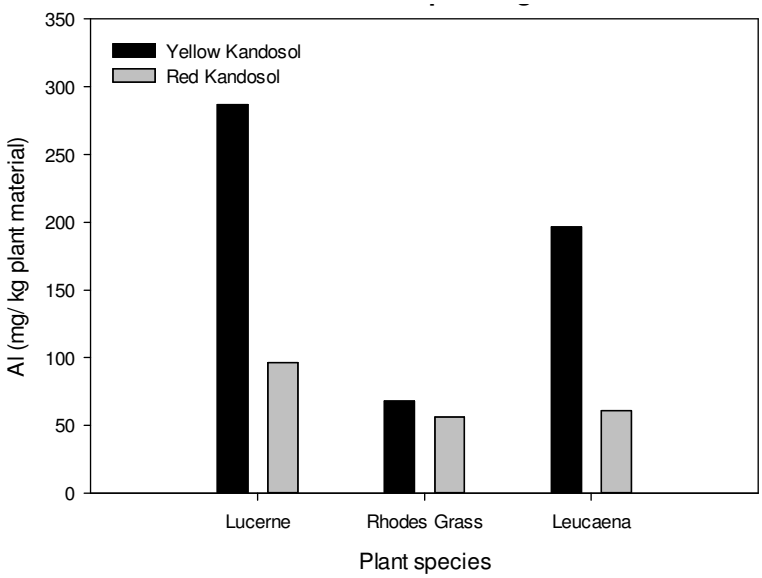


Figure 39. Concentration of Al in foliar tissues of lucerne, Rhodes grass and leucaena plants grown on either Yellow Kandosol or Red Kandosol treated with 500 mg F/kg.

Uptake of F from overhead irrigation

Overhead irrigation of F-containing CS water was found to influence the foliar F concentration. Indeed, a significant interaction was found between increasing irrigations of F-containing water and plant species ($p<0.001$), indicating that not only does the cumulative application of F in irrigation water increase foliar F concentrations, but also that the pattern of response differs between plant species.

The measured increase in foliar F can be attributed to overhead irrigation since the concentration of F within the soil solution of the Ferrosol averaged across all four treatments (five randomly selected pots sampled from each treatment) in Experiment 3 was <0.054 mg F/L. Thus, the strong F adsorption by Ferrosol prevented uptake of F from the soil.

Lucerne was found to retain the highest concentration of F in the foliar material; after four irrigations (second harvest) with ca. 5 mg F/L irrigation water, the concentration of F in lucerne foliar tissues increased from 7 to 32 mg F/kg DM, and following eight irrigations (third harvest) the plant material increased further to 44 mg F/kg DM, a ca. six-fold increase ($p<0.05$) (Figure 40). Conversely, increases in tissue concentrations were more modest for the other two plant species, increasing from 10 to 15 mg F/kg DM for Rhodes grass and 7 to 20 mg F/kg DM for leucaena after eight irrigations at ca. 5 mg F/L (Figure 40).

The concentration of F within the irrigation water also had a significant effect on foliar F concentrations; with a significant increase in tissue F concentrations when the F concentration of the water was raised from 0 to ca. 3 and 5 mg F/L irrigation water (Figure 41).

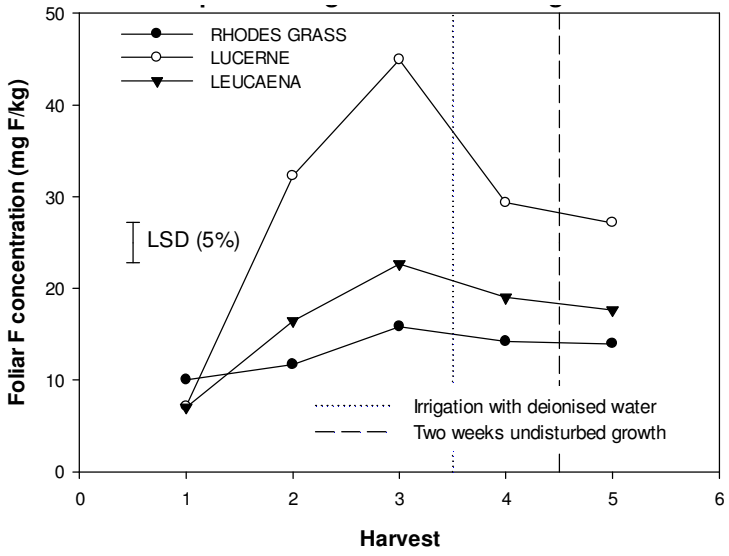


Figure 40. Rhodes grass, lucerne, and leucaena foliar F concentrations following four and eight irrigation with ca. 5 mg F/L (Harvest 2 and 3), one irrigation with deionised water (Harvest 4) and two weeks further undisturbed growth (Harvest 5). LSD (5%) bar indicates distance between data points required for significant difference at the 5% level.

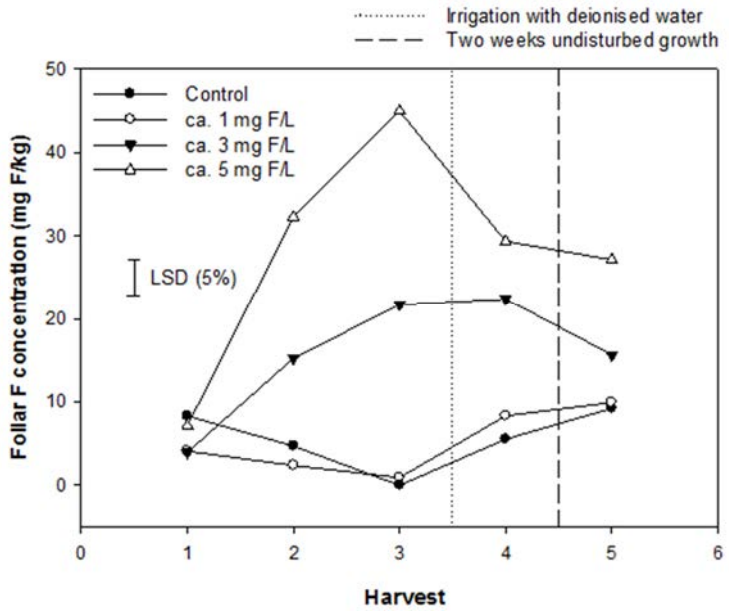


Figure 41. Lucerne foliar F concentration following 0, 4 and 8 irrigations (Harvest 1, 2 and 3) with either control or ca. 1, 3 or 5 mg F/L irrigation water, followed by irrigation with deionised water (Harvest 4) and following two weeks of undisturbed growth (Harvest 5). LSD (5%) bar indicates distance between data points required for significant difference at the 5% level. F concentrations of both the control and ca. 1 mg F/L treatments are all below the detection limit of 10 mg F/kg DM thus are unable to adequately detect reliable trends.

After eight irrigations with F-containing water, F-free deionised water was applied to simulate rainfall and to investigate the potential leaching of F from the foliage. Relative to tissue concentrations after eight irrigations with water containing ca. 5 mg/L, tissue concentrations decreased significantly (from 45 to 29 mg F/kg DM) for lucerne but there were no significant differences for the other two plant species (Figure 40). For water containing ca. 3 mg F/L, the

irrigation of F-free water had no significant effect for any plant species. Similarly, there were no significant differences for either the control or the ca. 1 mg F/L treatment for Rhodes grass and leucaena. Unexpectedly, tissue concentrations for lucerne increased significantly after irrigation with F-free water from 1 to 8 mg F/kg DM in the ca. 1 mg F/L treatment (Figure 41). Although statistically significant, the uncertainty of F concentrations under ca. 10 mg F/kg DM creates difficulty separating actual values from the background value, thus we are unable to ascertain if this observation is reflective of genuine concentrations.

Allowing the plants to grow undisturbed (i.e. no overhead irrigation) for a further two weeks after the simulated rainfall resulted in a decrease (although not significant, $p>0.05$) in foliar F concentration in all plants previously irrigated with water containing ca. 5 mg F/L (Figure 41). Following this two week period, a significant decrease was observed for lucerne in the ca. 3 mg F/L treatment (Figure 41), but no there was no significant difference in the Rhodes grass and leucaena plants of the same treatment.

Tissue concentrations in the control and ca. 1 mg F/ L treatment did not follow a clear trend, with all values again < 10 mg F/kg DM (i.e. the estimated detection limit).

Movement of F in repacked soil columns

Column leaching experiments are relatively time consuming to set up and can be slow to conduct (especially with soils having low hydraulic conductivity such as those considered here). A comparable understanding of the system can be obtained from batch adsorption experimentation, though the results may be less compelling for non-soil scientists. To provide a better link between the intuitive column data and the batch adsorption data, experiments using each approach were started in parallel. Two soils, Red Kandosol IR5 and a Yellow Kandosol IR8 were used either at their native pH, or amended with 15 t/ha limestone to mimic the effect of pH increase on sorption characteristics. The adsorption isotherm was determined for each 10 cm soil layer that made up the repacked columns of the IR5 Red Kandosol and IR8 Yellow Kandosol.

The pore volume of the columns was estimated from the weight difference of the air-dry columns and wetted up columns allowed to drain for several days. Thus the pore volume represents the maximum volume of water the soil can store at field capacity, and the values for the soils are shown in Table 12.

Table 12. Pore volumes and packed soil heights for the four soils.

Soil type	Pore volume (L) ± s.d. (n = 3)	Soil height (cm)
IR5 Red Kandosol	0.59 ± 0.01	69 ± 0
Lime amended IR5 Red Kandosol	0.62 ± 0.01	69 ± 0
IR8 Yellow Kandosol	0.85 ± 0.01	89 ± 0
Lime amended IR8 Yellow Kandosol	0.90 ± 0.01	88 ± 1

The Langmuir binding constant increased in the subsoil of IR5 Red Kandosol while the maximum binding capacity of the soil, Qmax, did not change with increasing soil depth (Figure 42 left). It is possible that the decrease in pH with soil depth may have increased the binding strength of F. It is noteworthy that the F concentration in native soils also increases with depth (Adriano, 2001b). Indeed, for the other soil types used in this study, differences in K_L and Qmax have been observed for the different depths layers (Table 5 and 6).

Amending the IR5 Red Kandosol with lime (15 t/ha) to increase the pH decreased the F binding strength, while having little effect of the F sorption capacity (Qmax) of the soil (Figure 42 right). The decrease in F binding strength was particularly noticeable for the more acidic subsoil where the increase in pH was greater. The effect of pH on binding strength was expected since Figure 6 shows that binding is decreased at higher pH.

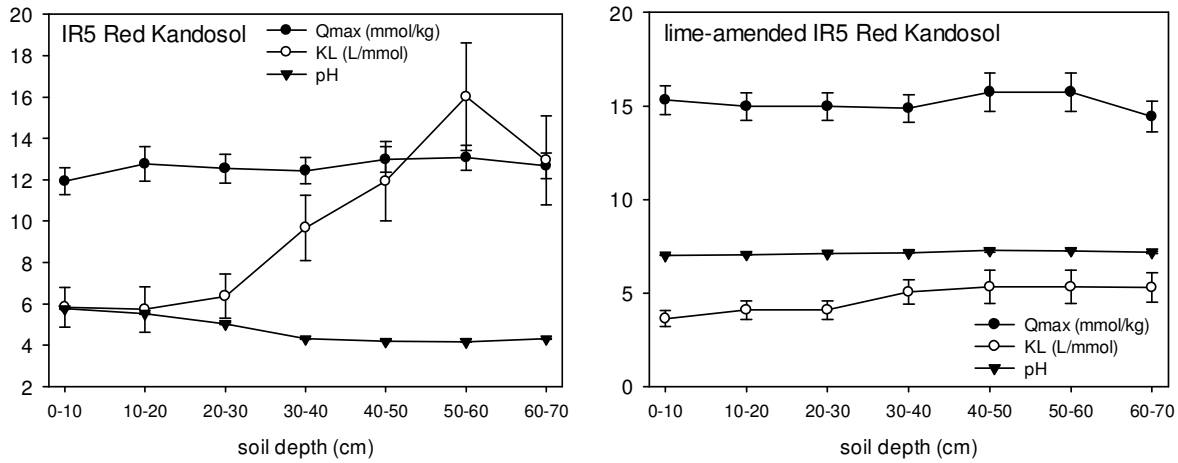


Figure 42. Langmuir adsorption parameters K_L and Qmax, and the pH, for different soil layers of the IR5 Red Kandosol without lime (left) or lime-amended (15 t/ha) (right). Values shown are the mean of triplicate samples with standard errors shown if not obscured by the symbols.

The binding strength K_L of F onto IR8 Yellow Kandosol increased with soil depth from 2 L/mmol in the topsoil to 16 L/mmol in the lowest soil layer (Figure 43). The increase in binding strength with soil depth is similar to that observed for the IR5 Red Kandosol and may be attributed to changes in soil mineralogy (e.g. clay content) but not pH since the pH also increased with depth.

The maximum sorption capacity Qmax decreased slightly with depth, ranging from 14 to 10 mmol/kg (Figure 43), and the sorption capacity of the IR8 Yellow Kandosol is similar to that of the IR5 Red Kandosol. Addition of lime to the IR8 Yellow Kandosol had little effect on the maximum sorption capacity Qmax but decreased the binding strength compared to the natural (not limed) IR8 Yellow Kandosol soil (Figure 43). There were no changes in sorption parameter with depth in the limed soil, most likely due to the fact that the pH was constant with depth.

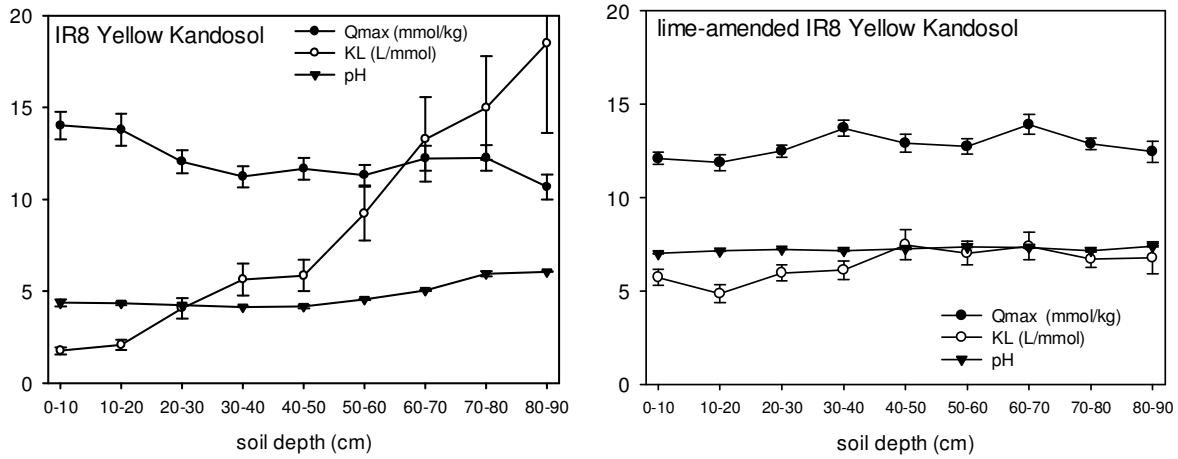


Figure 43. Langmuir adsorption parameters K_L and Qmax, and the pH, for different soil layers of the IR8 Yellow Kandosol without lime (left) and lime-amended (15 t/ha) (right). Values shown are the mean of triplicate samples.

The hydraulic conductivity of the IR8 Yellow Kandosol in the repacked columns was very low due to the high clay content and poor structure, whereas the IR5 Red Kandosol, which was sandier, maintained greater flow rates. Therefore, a larger volume of CS water could be applied to the IR5 Red Kandosol in the available timeframe of the study. After application of 2340 mm CS water (= 23.4 ML/ha), F movement occurred only in the top 10 cm of the IR5 Red Kandosol columns, but F had not increased above baseline levels at 20 cm depth and below (Figure 44). The lime amended IR5 Red Kandosol appeared to bind more F (hence lower soil solution F concentration) than the native Red Kandosol, but this may be an artefact of the higher Ca concentration of the lime-amended soil, which may react with F to form insoluble CaF_2 which would not be picked up with the solution samplers. In the IR5 Red Kandosol without and with lime amendment, the concentration of F in the soil solution at 10 cm depth after application of 2340 mm of CS was 2.5-2.7 mg/L, which is approaching the F concentration in the CS water (3.1-3.5 mg/L). Therefore, the ability of a 10 cm layer of Red Kandosol to adsorb F is exhausted if 2340 mm (= 23.4 ML/ha) CS water with a F concentration of 3 mg/L is applied. Since the soil columns were 70 cm long, it can be extrapolated that breakthrough of F could occur after application of 16400 mm CS water with 3 mg/L F, whereas application of 6 x 2340 mm = 14,000 mm (140 ML/ha) CS water would not exceed the F concentration in the drainage water of a 70 cm long column above the background (0.2 mg/L). The predicted value is in good agreement with the value calculated in the batch adsorption study (12,000 mm for CS water with 5 mg F/L, or 20,000 mm for CS water with 3 mg F/L) and confirms the validity of the batch adsorption approach to estimate the sorption capacity of a soil profile.

The movement of F in the IR8 Yellow Kandosol (Figure 45) columns was less due to the lower volumes of CS water applied. It can be suggested that between 12,000 and 13,000 mm CS water can be applied to columns with 90 cm length before the drainage water F concentration exceeds 1 mg/L. Again, these values are in good agreement with those determined from batch adsorption (14,000 mm for CS with 5 mg F/L).

Application of CS water to the soil columns resulted in a rapid alkalinisation of the soil (Figure 46) since no sulfur was added to the soil to offset the alkalinity in the CS water. For the IR5 Red Kandosol, 200 mm CS water (i.e. 1/3 of the pore volume) increased the pH in the top 10 cm to pH 7.2. It increased to pH 8.2 after 600 mm CS water and to pH 8.7 after 1800 mm CS water was applied. No further pH was observed due to the strong buffering of the soil, confirming results shown in Figure 7. In IR8 Yellow Kandosol, similar trends were observed. Thus, application of alkaline CS water in the field would increase soil pH of these two soils, and this may have negative effects on the uptake of nutrients, and decrease adsorption of F by soil (Figure 6). Therefore, pH adjustment of the CS water is recommended, alternatively, soil amendment with sulphur may be required on these two soils.

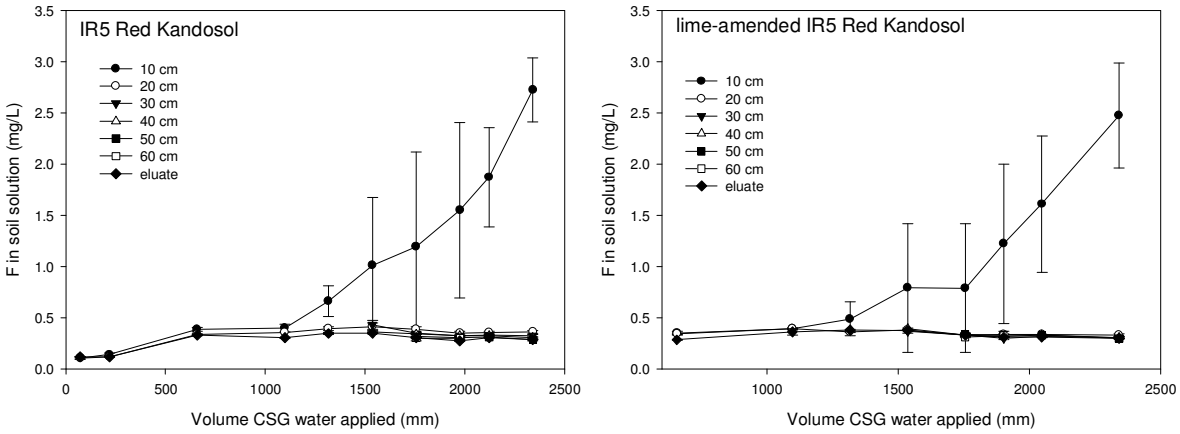


Figure 44. Concentration of F in soil solution at different soil depth in repacked columns containing Red Kandosol from IR5 without and with lime-amendment (15 t/ha). Error bars shown are standard deviations of the three columns.

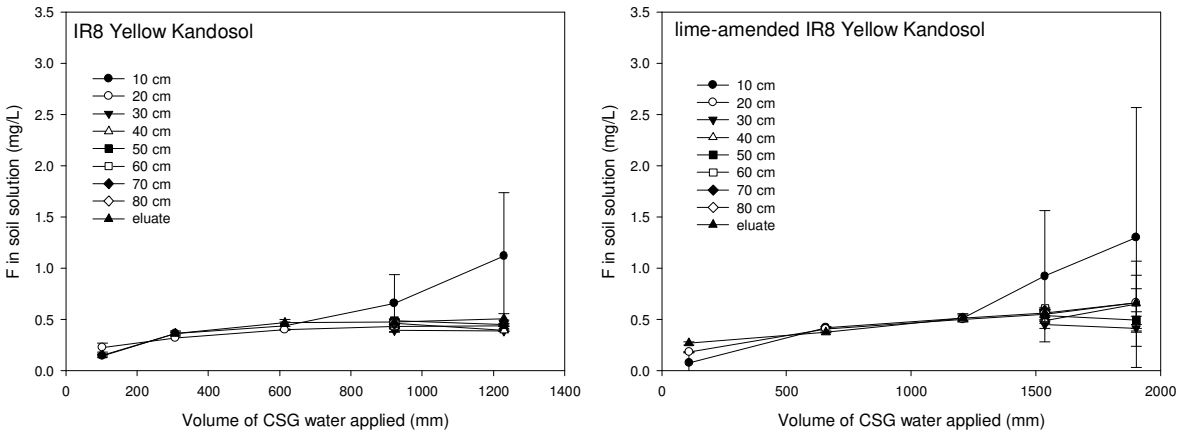


Figure 45. Concentration of F in soil solution at different soil depth in repacked columns containing Yellow Kandosol from IR8 without and with lime-amendment (15 t/ha). Error bars shown are standard deviations of the three columns.

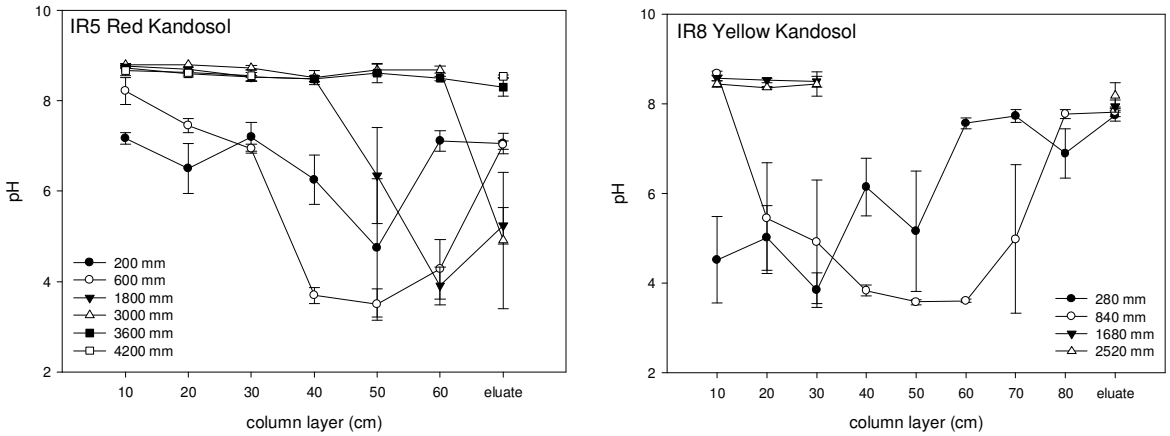


Figure 46. Effect of CS water application on changes in soil solution pH with depth in the repacked columns of the IR5 Red Kandosol and IR8 Yellow Kandosol. Values are means of three columns with the standard deviation shown.

Maximum safe volumes of CS water application

Depth of F sorption in soil assuming 0.105 mM F in soil solution

Since F may redistribute in soil (moving from areas of high concentration to areas of low concentration), the depth of soil at which the soil solution concentration is 0.105 mM (2 mg/L) was calculated (Table 13). The value of 0.105 mM F was chosen since this is the value currently considered to be environmentally safe in irrigation water for short term applications (ANZECC-ARMCANZ, 2000). The depth of soil required was calculated from the amount of F_{bound} using Q_{max} and K_L values shown in Table 5 and 6 as follows:

$F_{bound} = Q_{max} \times K_L \times F_{free} / (1 + K_L \times F_{free})$

For example, for the top layer of Yellow Kandosol (Table 5) and using a value of 0.105 mM for F_{free} (2 mg/L F):
$F_{bound} = 14.2 \times 3.7 \times 0.105 / (1 + 3.7 \times 0.105) = 3.96$ mmol/kg = 7720 mol/ha per 15 cm top layer.

Irrigation with 60 ML of water containing 0.237 mM F would add a total of 14,200 mol F/ha. However, the top layer (0-15 cm) can only adsorb 7720 mol F and the middle layer (15-35 cm) 11,000 mol F. Therefore, the middle layer would need to adsorb the remaining 6490 mol to maintain the free F concentration in soil solution at 0.105 mM.

Since the middle layer can adsorb 11,000 mol F per 20 cm, the remaining 6490 mol F would be adsorbed by 11.7 cm of the middle layer. Thus, the total profile depth contributing to F sorption is 15 cm + 11.7 cm = 26.7 cm.

In cases were the soil depth required to adsorb F exceeded 70 cm (e.g. Brown Vertosol), it was assumed that the F sorption characteristics at depth >70 cm were the same as at 70 cm depth (the deepest layer for which parameters were determined).

The calculations are based solely on the binding strength and capacity of the soils. As such, no information can be derived regarding the timeframe of F movement or the likelihood of such changes occurring. Thus, the calculated soil depth simply assumes equilibrium between 0.105 mM F in the soil solution and the soil particles has been attained. Whether it takes years or millennia to achieve equilibrium cannot be considered in the calculation. The calculations constitute a worst-case scenario regarding how deep F will move while resulting in drainage concentration of 0.105 mM F.

It can be concluded from results in Table 13 that movement of F below 70 cm will be minimal for most soils at these high application rates, apart from Brown Vertosol. In Brown Vertosol, F will move to a depth of 213 cm due to its high native F concentration. Considering that lucerne and Rhodes grass are deep rooted perennials, with roots extending to 200 cm depth if no soil constraints are present (acid or saline layer), movement of F beyond the root zone is unlikely.

Table 13. Depth of soil (expressed in cm) at which the soil solution F concentration is 0.105 mM (2 mg/L) in five Fairview soil with different irrigation volume sand concentrations of F in irrigation water. The calculations assumed a bulk density of the soil of 1.3 g/cm^3.

	Yellow Kandosol (IR8)		
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	4.6	6.9	9.2
25	7.7	11.5	15.3
30	9.2	13.8	18.2
35	10.7	16.0	21.0
40	12.3	18.2	23.9
45	13.8	20.3	26.7
50	15.3	22.5	29.6
55	16.7	24.6	32.5
60	18.2	26.7	35.3

	Red Vertosol (IR6)		
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	5.1	7.7	10.2
25	8.5	12.8	17.2
30	10.2	15.4	20.8
35	11.9	18.1	24.5
40	13.6	20.8	28.2
45	15.4	23.6	31.8
50	17.2	26.3	35.6
55	19.0	29.1	40.7
60	20.8	31.8	45.8

	Red Kandosol (IR5)		
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	10.4	15.7	21.1
25	17.5	26.5	35.4
30	21.1	31.9	40.3
35	24.7	36.6	45.2
40	28.3	40.3	50.1
45	31.9	44.0	55.1
50	35.4	47.7	60.0
55	37.8	51.4	64.9
60	40.3	55.1	69.8

	Brown Chromosol (IR8)		
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	2.9	4.3	5.8
25	4.8	7.2	9.7
30	5.8	8.7	11.6
35	6.8	10.1	13.5
40	7.7	11.6	15.5
45	8.7	13.0	17.7
50	9.7	14.5	19.9
55	10.6	16.1	22.1
60	11.6	17.7	24.3

	Brown Vertosol (IR6)		
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	16.5	33.3	47.4
25	38.2	61.3	84.3
30	47.4	75.1	103
35	56.7	88.9	121
40	65.9	103	140
45	75.1	117	158
50	84.3	130	177
55	93.5	144	195
60	103	158	213

Maximum volumes of irrigation water that can be applied safely to soil

Results shown in Table 5 and 6 were used to determine the maximum volume of irrigation water containing 0.158 mM to 0.316 mM F (3, 4.5 and 6 mg/L F) while still maintaining F in soil solution at 0.105 mM (2 mg/L) at 70 cm soil depth (Table 14). Since Brown Vertosol had a high native F concentration, little additional F can be applied to that soil. Soils from Summerhills site 5 and Reuben Downs site 8 could be irrigated with 348 ML/ha or 372 ML/ha, respectively before the soil solution concentration would exceed 2 mg/L. In contrast, soils from Mayfield South (Brown Dermosol) and The Bend site 41 (Tenosol) can only be

irrigated with 12, and 16 ML/ha, respectively. If the concentration of F in the irrigation water is lower, larger volumes of water can be applied before the threshold is reached. Likewise, increasing the threshold equilibrium concentration in the soil solution, a larger volume of water can be applied. For instance, with a threshold of 5 mg/L in soil solution, and a F concentration in irrigation water of 5 mg/L would allow to apply 734 ML/ha to Summerhills site 5 soils, or 32 ML to Mayfield South soil.

Table 14. Irrigation volumes (ML/ha) of CS water containing 3, 4.5 or 6 mg/L F that can be applied to soils studied in Part 1, while maintaining a soil solution concentration of 2 mg/L F at 70 cm depth in the soil profile.

Soil	F in CS water		
	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
Yellow Kandosol IR8	250	167	125
Red Vertosol IR6	168	112	84
Red Kandosol IR5	120	80	60
Brown Chromosol IR8	407	272	204
Brown Vertosol IR6	42	28	21

Table 15. Maximum volumes of irrigation water containing 2-6 mg/L F that can be applied to soils studied in Part 2, while maintaining a soil solution equilibrium concentration below 2 mg/L. The amount of F bound to depth of profile and the equilibrium solution concentration was calculated from the Langmuir adsorption parameters.

Site	Profile depth (cm)	F bound (mmol)	Concentration of F in irrigation water				
			2 mg/L	3 mg/L	4 mg/L	5 mg/L	6 mg/L
			Max. volume of irrigation water (ML/ha)				
Mayfield South	50	364	36	23	17	14	12
Broandah 1	150	3698	370	234	176	141	117
Summerhills 3	150	3295	329	209	157	125	104
Summerhills 5	140	10986	1099	695	523	418	348
Summerhills 10	150	1406	141	89	67	53	44
Reuben Downs 3	130	7686	769	486	366	292	243
Reuben Downs 6	130	5491	549	348	261	209	174
Reuben Downs 8	150	11769	1177	745	560	448	372
Reuben Downs 17	140	2297	230	145	109	87	73
Springwater IR4-256	70	7263	726	460	346	276	230
The Bend 30	90	2060	206	130	98	78	65
The Bend 41	120	492	49	31	23	19	16
Pleasant Hills 63	60	2052	205	130	98	78	65
Pleasant Hills 88	90	1264	126	80	60	48	40
Weemilah 1	90	2969	297	188	141	113	94

Given that around 25-50 ML/ha of CS water with a F concentration of 3 mg/L may be applied to irrigation areas in the Fairview, Roma and Scotia Project Areas, there is little risk that the F concentration in the drainage water will be greater than 2 mg/L. Brown Vertosol IR6, Mayfield South (Brown Dermosol) and The Bend site 41 (Tenosol) are the only sites were irrigation either needs to be limited or carefully monitored.

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Appendix 1. Risk assessment

Summary

Concentrations of fluoride (F) in raw CS water from the Fairview and Roma Project Areas suited to chemical amendment, or use in land amendment irrigation, currently exceed regulatory guidelines of 2 mg/L. To irrigate this water under a general beneficial use approval or the current Fairview environmental authority, Santos GLNG is required to undertake an environmental risk assessment in accordance with ANZECC (2000). We investigated adsorption and desorption of F using Red Kandosol IR5, Yellow Kandosol IR8, Red Vertosol IR6, Brown Vertosol IR6 and Brown Chromosol IR8 from Fairview. The results indicated that up to 60 ML/ha coal seam (CS) water with a concentration of 0.316 mM F (6 mg/L) could be applied before F exceeded the critical threshold concentration of 2 mg/L in drainage water at 0.7 m depth for all soils. Plant uptake of F from Red Vertosol, Red Kandosol, and Yellow Kandosol containing less than 6 mg/L F in the soil solution, resulted in tissue concentrations below 35 mg/kg dry matter (DM), considered the safe level for young beef cattle and horses. Soils with a high native F concentration (Brown Vertosol) or low F sorption capacity (sand) were less suitable for irrigation. In these soils, the mobile and plant available F concentration exceeded thresholds when water with a high F concentration or large irrigation volumes were applied. Of the three crop species tested (lucerne, Rhodes grass and leucaena), lucerne accumulated the most F in forage on Red and Yellow Kandosol but not on Red Vertosol. We suggest that the accumulation of F was due to plant root uptake of Al-F complexes by lucerne, but not by the other two crops. The highest risk of F moving from a CS water irrigation area into the broader environment is posed by eroded soil particles transporting adsorbed F.

Approach

The determined values for Qmax and K_L (Table A1) were used to determine the amount of F bound (F_b) at an equilibrium concentration of free F (F_f) of 0.0525 mM (corresponding to 1 mg/L F, the maximum recommended concentration of F in irrigation water (ANZECC-ARMCANZ, 2000)), using the Langmuir equation:

$$F_b = \frac{Q_{\max} K_L F_f}{1 + K_L F_f}$$

Next, it was calculated how much CS water with a theoretical F concentration of 0.26 mM/L (corresponding to 5 mg/L F) is needed to supply the calculated amount of F in the soil. The calculated volumes of CS water that can be applied were 13,000 L/m^2 (130 ML/ha) for the IR5 Red Kandosol (70 cm soil depth, bulk density of soil 1.3 g/cm^3), 10,500 L/m^2 (105 ML/ha) for the lime-amended IR5 Red Kandosol (70 cm soil depth, bulk density 1.3 g/cm^3). For the IR8 Yellow Kandosol, the calculated volume of CS water was 13,950 L/m^2 (139 ML/ha) to a soil depth of 0.9 and bulk density 1.3 g/cm^3. For the lime-amended IR8 Yellow Kandosol, 14,650 L/m^2 (146 ML/ha) could be applied, assuming a soil depth of 0.9 m and bulk density 1.3 g/cm^3. The volumes determined for individual soil layers added together is in good agreement with the values determined on a bulked soil sample (data not shown). Since soils in the field are likely to be deeper than 70-90 cm, the volume of water that can be applied to the soils in the field is higher, assuming that the sorption capacity of the deeper soil layers is similar to the tested soil layers. Should the soils in the field have different bulk densities than the values assumed for the calculation, the irrigation volumes need to be adjusted.

Adsorption isotherms were fitted to the measured data and the Langmuir isotherm gave the best fit. The Langmuir adsorption parameters K_L (a high K_L indicates that the soil has strong adsorption of F and a weak desorption of bound F) and Q_{max} (an indication of maximum sorption capacity for F) (Table A1) were then used to rank the soils according to their binding characteristics and to correlate binding parameters to soil chemical and physical properties. Furthermore, the Q_{max} and K_L values were used to model the maximum concentrations of F that can be bound by the soils and the corresponding equilibrium F concentrations in solution.

Table A1. Langmuir sorption characteristics of the Fairview soils. The top layer comprised 0-15 cm depth, the middle layer 15-35 cm depth and the bottom layer 35-70 cm depth.

	Layer	Qmax mmol/kg	s.d.	K_L L/mmol	s.d.
Brown Vertosol (IR6) (adjusted for desorption)	top	2.4	0.4	9.1	5.8
	middle	1.6	0.2	4.7	2.7
	bottom	2.2	0.2	4.0	1.2
Brown Chromosol (IR8)	top	18.1	3.0	5.0	1.7
	middle	13.4	1.6	6.7	2.1
	bottom	22.3	6.3	5.6	3.0
Red Kandosol (IR5)	top	11.7	1.1	1.7	0.3
	middle	3.8	0.2	7.7	1.6
	bottom	4.4	0.5	12.3	4.9
Red Vertosol (IR6)	top	18.9	2.3	2.2	0.5
	middle	16.0	1.5	2.5	0.5
	bottom	21.5	3.8	1.2	0.3
Yellow Kandosol (IR8)	top	14.2	1.4	3.7	0.9
	middle	13.6	1.3	4.3	1.1
	bottom	16.3	2.6	3.7	1.3

Build-up of fluoride in soil

Fluoride added to soil was rapidly and near-quantitatively adsorbed by soil as long as the maximum sorption capacity Q_{max} was not exceeded. The Q_{max} values shown in Table A1 and F loadings (calculated from projected irrigation volumes) were used to calculate the depth of F sorption assuming saturation of the available binding sites in the soils with F. The calculations show that theoretically only the top 12 cm of the soils would become saturated with F, apart from the Brown Vertosol where 81 cm would become saturated. Practically, however, F will move through the soil before all binding sites are saturated, because F becomes progressively less tightly bound as saturation increases, resulting in the typical levelling off of the Langmuir adsorption isotherms.

A similar outcome was observed in repacked columns containing Red and Yellow Kandosol which were irrigated with up to 2400 mm CS water. In these columns, F progressively moved down the soil profile when the sorption capacity of the 0-10 cm soil layer became exhausted (Figure A1).

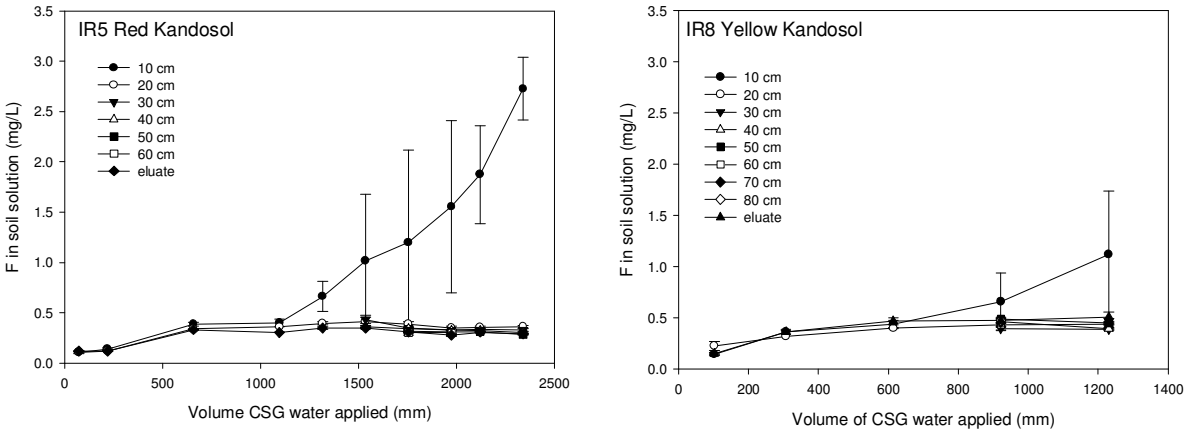


Figure A1. Concentration of F in soil solution at different soil depths in repacked columns containing Red Kandosol from IR5 or Yellow Kandosol from IR8. Error bars shown are standard deviations of the three columns.

It was considered that the addition of chloride (from CS water), sulfur from land amendment or treatment of CS water, and possible changes in soil pH due to application of alkaline CS water may affect the adsorption of F. Addition of sulfate did not compete with F for sorption and indeed F sorption was increased with increasing sulfate concentration due to the higher ionic strength. Overall, competing anions and ionic strength of the solution had no effect on F adsorption, but pH may decrease F adsorption. Since the soil pH would change little in a well-managed CS irrigation system, the effect on F adsorption is minimal.

The maximum permissible concentration of F in CS water was calculated from the maximum sorption capacity of the 70 cm soil profile and was far greater than the F concentration in Fairview or Roma irrigation water. For Brown Vertosol, the sorption capacity of the soil would be approached only if 60 ML/ha was applied and the irrigation water contained 0.31 mM F (6 mg/L F). With planned irrigation volumes of 25-50 ML/ha and concentrations of 0.15 mM F, the sorption capacity of the soils is not likely to be exhausted.

Release of fluoride from soil to crops

Although F adsorbs strongly to soil constituents, over time F may be taken up by plant roots, or leach from the soil in deep drainage, and pose a potential risk to grazing animals. To determine desorption of F from soils, soils were treated with CS water containing either 5 mg/L (0.24 mM) or 125 mg/L (6.58 mM) F. Soils treated with the high concentration of F in CS water showed greater desorption since F was less tightly held. In this case, between 30-60% of adsorbed F could be desorbed over seven desorption steps. In contrast, only 20-30% of F could be desorbed when these soils were treated with the low F concentration, because only high affinity sites were saturated with F and F was tightly bound. The amount of F desorbed increased with an increasing number of desorption steps. Interestingly, the native F concentration of the Brown Vertosol was high (data not shown) and more F could be desorbed than was added to the soil during the adsorption step.

The desorption curves indicate that the concentration of F in the soil solutions were below 0.5 mg/L (0.03 mM) when soils were treated with the low F concentration. Thus, the concentration of F leached from soil following the completion of a CS water irrigation scheme would be well below the critical threshold value of 2 mg/L (0.10 mM).

Other factors influencing desorption from soil are duration of adsorption (ageing), pH, temperature, competing anions and soil drying. Desorption gradually decreased the longer F could react with soils (data not shown), suggesting that F either becomes more strongly adsorbed, diffused into soil minerals or formed insoluble compounds. Therefore, F added over months or years in CS irrigation projects will be less likely to be desorbed than that observed under the current experimental conditions. The amount of F desorbed increased linearly with pH, and suggesting that hydroxyl ions control the desorption of F. Thus, pH of the soil used for CS irrigation needs to be controlled by applying sulphur to avoid increases in soil pH associated with the prolonged application of alkaline CS water.

Increasing the temperature had little effect on the desorption of F from Red Kandosol, Ferrosol, Yellow Kandosol, and Brown Chromosol. On the other hand, the amount of F desorbed from Red Vertosol and Brown Vertosol increased with temperature. It is possible that these differences are due to diffusion or kinetic processes, but are unlikely to be important for F desorption processes in the field where subsoil temperatures remain relatively constant. The effect of anions (Cl and sulfate) on F desorption showed that ionic strength plays some role but not sulfate anions. Increasing the ionic strength decreased the desorption of F. Similarly, using buffers rather than water to desorb F, showed that desorption was decreased when buffers were used, whereas maximum desorption was observed using water (data not shown). This is relevant since rainfall in the field will essentially be deionised water.

Plant yield

The growth of lucerne and Rhodes grass in the pot trials was affected by the soil type and F application rate. While it appeared that dry weights for lucerne and Rhodes grass decreased significantly ($p<0.05$) from the control to 500 mg F/kg in the Yellow Kandosol, the decrease in yield may not have been caused by the F addition because there was no relationship between biomass yield and F in plant DM. Therefore, yield differences do not appear to be due to F in plant material but may have been due to other undiagnosed nutritional constraints. The dry weight of leucaena was not affected by all treatments of F across all soils.

Product quality

Plant uptake of F from soil increased with F application rate, and lucerne accumulated more F in foliage than Rhodes grass and leucaena. Plant F concentration was also affected by soil type. As expected, plants grown on pure sand (for control) showed the highest F concentration because sand does not adsorb F. In contrast, foliar F concentrations of the plants grown on Red Vertosol were below 20 mg/kg DM (the detection limit of the method), irrespective of the concentration of added F. This is because most of the added F is strongly adsorbed by the soil and is not plant available. The foliar F concentration in lucerne grown on Red and Yellow Kandosol increased with F application rate and reached 80 mg/kg DM with the 500 mg/kg soil rate. In contrast, Rhodes grass and leucaena did not take up F despite the F concentration in soil solution at a water potential of -1 kPa being around 20 mg/L. The difference in F uptake between plant species can be attributed to ion exclusion mechanisms. Whilst lucerne readily took up F, the plants were not negatively affected by high tissue F concentrations since neither visual symptoms of toxicity nor biomass reductions were observed.

Application of F in CS water by overhead irrigation will deposit F on external leaf/stem surfaces and thereby add to the foliar F concentration. Therefore, the soil F load may need to be lowered to avoid tissue F concentrations exceeding animal diet MTL (Table 1) when using overhead irrigation. We do not have data on the interaction between soil and foliar applied F on the total tissue F concentration and possible foliar toxicity symptoms.

Based on the suggested MTL of 30-40 mg F/kg DM for forages (National Research Council (USA), 2005), lucerne would accumulate 35 mg F/kg DM when the soil solution F concentration is around 6 mg/L at a water potential of -1 kPa. In contrast, Rhodes grass and leucaena do not reach a tissue concentration of 35 mg F/kg DM even when the solution F concentration reached 20 mg/L. Lucerne grown on Yellow and Red Kandosol appeared to accumulate most F. Thus, of the three species examined, lucerne appears to represent the worst-case scenario and a soil solution F concentration of 6 mg/L is safe for lucerne on the three soils.

Overhead irrigation with artificial CS water increased the foliar concentration of F in lucerne, Rhodes grass and leucaena. Again, lucerne accumulated more F than Rhodes grass or leucaena and the foliar concentration reached 45 mg/kg DM after eight irrigations with artificial CS water containing 5 mg/L (0.26 mM) F. After one simulated rainfall event, the tissue concentration decreased to 28 mg/kg DM, which is below the MTL. Thus, the risk of F accumulation in forage from overhead irrigation in the field may be low if the foliage is rinsed with low F irrigation water (e.g. RO permeate) or rainfall prior to grazing/harvest.

The results on foliar F uptake obtained in this glasshouse study need to be confirmed by field trials. Field grown plants will differ in their cuticle thickness and F uptake rates. Insect damage or abrasion of the leaf surface during high wind may increase F uptake, while deposition of dust on the leaves may increase adsorption of F. On the other hand, rainfall may wash more F off the surface than observed in this study with simulated rainfall.

Specific ion tolerance

The plant F uptake data generated by this study is limited to only three soil types and three crop species, hence further work would be required to extend these data. Yet, we did not observe any foliar symptoms of F toxicity even at the highest F application rate of 500 mg F/kg soil. While lucerne did take up more F than Rhodes grass and leucaena, it appears that lucerne can take up F as Al-F complexes, whereas the other species only take up F as free F^- (Figure A2a,b). Therefore, soil conditions that may complex F and yield less-toxic F complexes may result in increased uptake by lucerne but not by the other two species. The fate of the F complexes present in forages during digestion in animals may determine the ultimate toxicity of bioaccumulated F to animals, but we have not investigated this aspect.

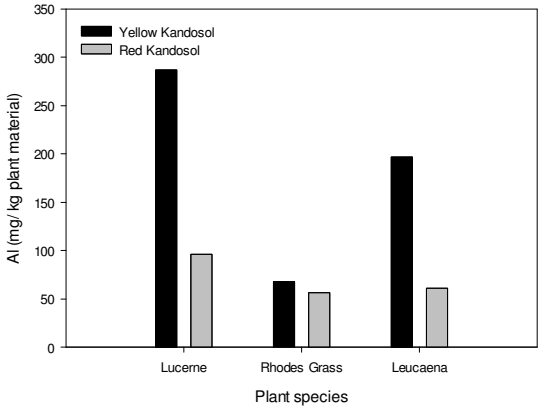


Figure A2a. Concentration of Al in foliar tissues of lucerne, Rhodes grass and leucaena plants grown on either Yellow Kandosol or Red Kandosol treated with 500 mg F/kg.

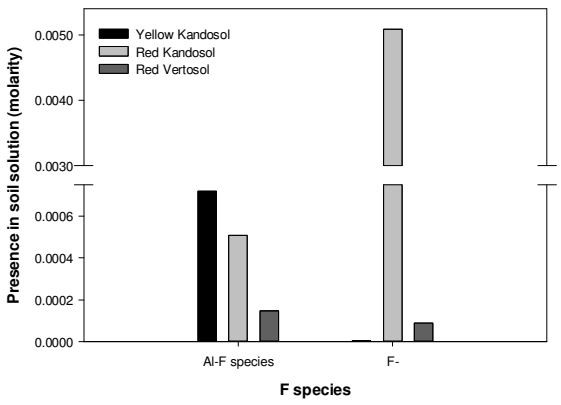


Figure A2b. Presence of Al-F and F^- species in the soil solution of three soils (Yellow Kandosol, Red Kandosol and Red Vertosol) treated with 500 mg F/kg, containing lucerne plants. Sand excluded due to extremely high F^- concentrations, preventing visual analysis of graph.

Foliar injury

We only observed F phytotoxicity symptoms (necrosis and plant death) in plants grown in sand. Since sand does not adsorb much F, most of the added F was plant available and plant tissue concentrations ranged up to 50,000 mg F/kg DM in the 500 mg F/kg soil addition. In contrast, most soils have strong sorption for F and little F would be available for plant uptake. Therefore, we have not observed any foliar toxicity symptoms in lucerne, Rhodes grass and leucaena when 500 mg F/kg soil was added to the Red and Yellow Kandosol and Red Vertosol. Likewise, foliar application of 5 mg/L (0.26 mM) F by overhead irrigation with artificial CS water did not produce symptoms of foliar injury. It may be necessary to conduct solution culture and foliar application studies at various stages of growth/regrowth to obtain foliar F toxicity symptoms for the three crops species for future use as a diagnostic tool.

Deep drainage and leaching below the root zone

Depth of F sorption in soil assuming 0.105 mM F in soil solution

Since F may redistribute in soil (moving from areas of high concentration to areas of low concentration), the depth of soil at which the soil solution concentration is 0.105 mM (2 mg/L) was calculated (Table A2). The value of 0.105 mM F was chosen since this is the value currently considered to be environmentally safe in drainage water for short term applications (ANZECC-ARMCANZ, 2000). The depth of soil required was calculated from the amount of F_{bound} using Q_{max} and K_L values shown in Table A1 as follows:

$$F_{bound} = Q_{max} \times K_L \times F_{free} / (1 + K_L \times F_{free})$$

For example, for the top layer of Yellow Kandosol (Table A1) and using a value of 0.105 mM for F_{free} (2 mg/L F):

F_{bound} = 14.2 x 3.7 x 0.105 / (1 + 3.7 x 0.105) = 3.96 mmol/kg = 7720 mol/ha per 15 cm top layer.

Irrigation with 60 ML of water containing 0.237 mM F would add a total of 14,200 mol F/ha. However, the top layer (0-15 cm) can only adsorb 7720 mol F and the middle layer (15-35 cm) 11,000 mol F. Therefore, the middle layer would need to adsorb the remaining 6490 mol to maintain the free F concentration in soil solution at 0.105 mM.

Since the middle layer can adsorb 11,000 mol F per 20 cm, the remaining 6490 mol F would be adsorbed by 11.7 cm of the middle layer. Thus, the total profile depth contributing to F sorption is 15 cm + 11.7 cm = 26.7 cm.

In cases where the soil depth required to adsorb F exceeded 70 cm (e.g. Brown Vertosol), it was assumed that the F sorption characteristics at depth >70 cm were the same as at 70 cm depth (i.e. the deepest layer for which parameters were determined).

The calculations were based solely on the binding strength and capacity of the soils. As such, no information can be derived regarding the timeframe of F movement or the likelihood of such changes occurring. Thus, the calculated soil depth simply assumes equilibrium between 0.105 mM F in the soil solution and the soil particles has been attained. Whether it takes years or millennia to achieve equilibrium cannot be considered in the calculation. The calculations constitute a worst-case scenario regarding how deep F will move while resulting in drainage concentration of 0.105 mM F.

It can be concluded from results in Table A2 that movement of F below 70 cm will be minimal for most soils at these high application rates, apart from Brown Vertosol. In Brown Vertosol, F will move to a depth of 213 cm due to its high native F concentration. Considering that lucerne and leucaena are deep rooted perennials, with roots extending to 200 cm depth if no soil constraints are present (e.g. acid, saline or compacted layers), movement of F beyond the root zone is unlikely.

Table A2. Depth of soil (expressed in cm) at which the soil solution F concentration is 0.105 mM (2 mg/L) in five Fairview soils with different irrigation volumes and concentrations of F in irrigation water. The calculations assumed a bulk density of the soil of 1.3 g/cm^3.

Yellow Kandosol (IR8)			
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	4.6	6.9	9.2
30	9.2	13.8	18.2
40	12.3	18.2	23.9
45	13.8	20.3	26.7
50	15.3	22.5	29.6
55	16.7	24.6	32.5
60	18.2	26.7	35.3

Red Vertosol (IR6)			
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	5.1	7.7	10.2
30	10.2	15.4	20.8
40	13.6	20.8	28.2
45	15.4	23.6	31.8
50	17.2	26.3	35.6
55	19.0	29.1	40.7
60	20.8	31.8	45.8

Red Kandosol (IR5)			
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	10.4	15.7	21.1
30	21.1	31.9	40.3
40	28.3	40.3	50.1
45	31.9	44.0	55.1
50	35.4	47.7	60.0
55	37.8	51.4	64.9
60	40.3	55.1	69.8

Brown Chromosol (IR8)			
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	2.9	4.3	5.8
30	5.8	8.7	11.6
40	7.7	11.6	15.5
45	8.7	13.0	17.7
50	9.7	14.5	19.9
55	10.6	16.1	22.1
60	11.6	17.7	24.3

Brown Vertosol (IR6)			
	F in CS water		
Volume (ML/ha)	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)
15	16.5	33.3	47.4
30	47.4	75.1	103
40	65.9	103	140
45	75.1	117	158
50	84.3	130	177
55	93.5	144	195
60	103	158	213

Maximum volumes of irrigation water that can be applied safely to soil

Results shown in Table A2 were used to determine the maximum volume of irrigation water containing 0.158 mM to 0.316 mM F (3, 4.5 and 6 mg/L F) while still maintaining F in soil solution at 0.105 mM (2 mg/L) at 70 cm soil depth (Table A3). Since Brown Vertosol had a high native F concentration, little additional F can be applied to that soil.

Table A3. Irrigation volumes (ML/ha) of CS water containing 3, 4.5 or 6 mg/L F that can be applied to soil while maintaining a soil solution concentration of 2 mg/L F at 70 cm depth in the soil profile.

Soil	F in CS water			Fairview field soil depth (m)
	0.158 mM (3 mg/L)	0.237 mM (4.5 mg/L)	0.316 mM (6 mg/L)	
Yellow Kandosol (IR8)	250	167	125	1.0-1.5
Red Vertosol (IR6)	168	112	84	1.5-4.5
Red Kandosol (IR5)	120	80	60	1.3-1.8
Brown Chromosol (IR8)	407	272	204	1.0-1.2
Brown Vertosol (IR6)	42	28	21	4.0-6.0

Given that around 25-50 ML of CS water with an F concentration of 3 mg/L may be applied to irrigation areas in the Fairview and Roma areas and that most soils have depths greater than 70 cm (Table A3), there is little risk that the F concentration in the drainage water will be greater than 2 mg/L, even for the Brown Vertosol.

Movement of F to groundwater and surface water

Risks of F moving below the root zone and into the groundwater appear negligible if the application rate and F concentration does not exceed 60 ML/ha and 0.316 mM F. We consider the main risk of F movement in the environment to be due to soil erosion since F strongly adsorbs to soil minerals. The desorption of F from soil at various soil:water ratios increased with dilution (Figure A3). Brown Vertosol (which had a higher native F concentration) desorbed more F than Red Vertosol or Brown Chromosol. The results confirm the validity of Schofield ratio law since more monovalent ion was desorbed as the dilution increased (Barrow and Shaw, 1977; Tan, 2000). Thus, results obtained on 1:5 soil:water slurries represent a worst-case scenario in that more F is desorbed than would occur in the field. In the field, the soil:water ratios are expected to remain below 1:0.5 (corresponding to saturation of a soil with porosity of 50%). However, desorption may increase if soil particles are eroded and suspended in a large volume of water. Thus, soil erosion control is important to minimise movement of F in the environment in CS water irrigation systems.

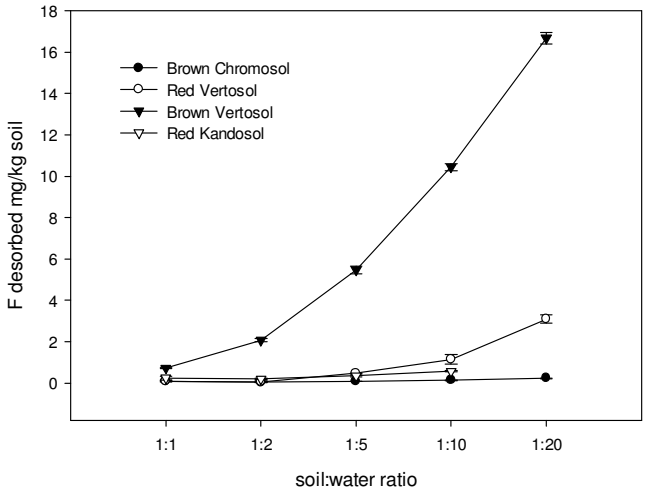


Figure A3. Effect of soil:water ratio on the amount of F desorbed from Brown Chromosol (IR8 top layer), Red Vertosol (IR6 top layer) and Brown Vertosol (IR6 top layer). Soil slurries were shaken for approximately 16 h and the amount of F in the supernatant measured and expressed

as mg F desorbed per kg of soil to account for differences in dilution. Values are means of three replicates with error bars shown (if not obscured by the symbols).

Increased F desorption may occur when eroded sediments become deposited in hypoxic environments (river/lake sediments) which results in reduction of ferric minerals to ferrous minerals and the release of adsorbed F. This scenario is only possible if F is adsorbed to iron sesquioxide minerals (hematite/goethite) which can undergo redox reactions, but not if F is adsorbed onto aluminium sesquioxide minerals (bayerite/gibbsite/boehmite) which are not redox reactive. Sediment transport is likely to involve highly diluted sediment concentrations and vigorous mixing under aerobic conditions. Therefore, we suggest that F concentrations measured in suspended sediments transported into rivers during erosion events will likely be lower than those measured here because of the dilution effect with large volumes of water. The risks posed by F desorbing from eroded sediments could be effectively mitigated by employing irrigation and land management practices that minimize runoff and soil erosion from irrigation areas.

Summary of recommendations

We investigated and modelled application of F to five soil types from Fairview that represent soils typical of CS irrigation systems in the Fairview, Roma and Scotia Project Areas. Up to 60 ML/ha CS water with a concentration of 0.316 mM F (6 mg/L) can be applied without drainage water or plant uptake exceeding critical concentrations of 2 mg/L (drainage water) or F in forage exceeding the MTL (35 mg/kg DM) for beef cattle. Soils with a high native F concentration (Brown Vertosol) or low F sorption capacity (sand) are less suitable for irrigation. In these soils, the mobile and plant available F concentration exceed thresholds when water with high F concentration (>6 mg/L) or large volumes (>60 ML/ha) are applied.

Of the three crop species tested, lucerne accumulated the most F on Red and Yellow Kandosol but not on Red Vertosol. We suggest that the accumulation is due to uptake of Al-F complexes by lucerne, but not by the other two crops. In soil where Al-F may form (acidic soils), Rhodes grass or leucaena are more suited than lucerne. Alternatively, irrigation volumes and foliar F concentrations need to be closely monitored when lucerne is grown on acidic soils (pH $\leq$5).

Foliar spraying of CS water containing 5 mg/L (0.26 mM) F did not result in foliar injury and tissue concentrations of 20-30 mg/kg DM were commonly observed in soil grown plants. Only lucerne accumulated up to 80 mg/kg DM from soil treated with 500 mg F/kg soil. Elevated foliar F concentrations did not result in plant yield losses or foliar F toxicity symptoms.

We consider the risk of F movement into deep drainage (>200 cm depth) as minimal when F concentrations and irrigation volumes do not exceed values investigated in this study. We suggest that the main F loss pathway from an irrigated pasture system could be via erosion of soil under poor irrigation and land management practices, but the capacity of soil erosion to remove F was not investigated in this study.

These studies indicate that 6 mg/L (0.31 mM) F could be adopted as a safe F concentration in CS irrigation water applied at up to 60 ML/ha for the Fairview soils tested without causing toxicity in the three plant species tested and without exceeding 35 mg F/kg DM in forage.

Appendix 2. CS water composition

Composition of coal seam (CS) water from Fairview AWAF1 used in this study

Parameter	unit	Batch 1	Batch 2
pH		9.04	9.02
H_2CO_3	mM	0.03	0.03
HCO_3	mM	19.19	15.22
CO_3^{2-}	mM	1.05	0.80
Total alk $CaCO_3$	mg/L	1064.76	840.72
Cl	mM	15.69	12.76
F	mM	0.18	0.13
Al	mM	0.00	0.00
B	mM	0.09	0.11
Ca	mM	0.08	0.05
Cu	mM		0.00
Fe	mM	0.02	0.00
K	mM	0.16	0.13
Mg	mM	0.06	0.19
Mn	mM		0.00
Na	mM	37.03	32.62
P	mM	0.03	0.02
S	mM	0.03	0.06
Zn	mM		0.00
EC	dS/m	3.01	2.72

Appendix 3. Surface area and mineralogy of some soils used in Part 1 of the study

Description	Depth (cm)	Surface area (m^2 g^{-1})			Mineral composition (%)													
		Single Point	BET	Langmuir	Quartz	Albite/ Anorthite	Microcline/ Orthoclase	Hematite	Goethite	Maghemite	Anatase	Apatite	Kaolinite	Illite/ Mica	Smecttie	Rutile	Gibbsite	Ilmenite
Red Ferrosol (Lakelands)	0-10	42	42	59	9			13	5	3	1		66			<1	2	1
	50-60	59	60	82	4			10	5	2	1		75			<1	3	<1
Brown Ferrosol (Lakelands)	0-10	26	27	37	42			2	4		2		42		7	1		<1
	50-60	60	61	84	9			2	13		2		73			<1		
Red Vertosol (Lakelands)	0-10	70	69	98	4		10	2	7	3			47		26			
	50-60	106	106	148	4		4	2	10	1			52		28			
Black Vertosol (Lakelands)	0-10	97	95	140	3	1		<1			3	1	4		88			
	50-60	105	103	149	2	1		<1			3	1	4		88			
Red Kandosol (IR5)		32	32	43	66			4		<1	<1		26		3	<1		
Yellow Kandosol (IR8)		26	26	36	58			<1	4		<1		34		4	<1		
Red Kandosol (IR8)		12	12	17	86			1			<1		12			<1		
Yellow Kand.(Beerburrum)		11	11	14	77			1			1		17		2	<1	1	
Black Vertosol (Gatton)		67	63	101	19	19		1			<1		14		46			1
Grey Kurosol (Mt Cotton)		4	5	7	86	<1					1		10		2			
Red Ferrosol (Toowoomba)		8	8	12	15	1		12	3	5	1		55		3	<1	4	1

Appendix 3 continued. Mineralogical composition of the soils as determined by quantitative XRD.

Field Name	Depth (cm)	Quartz	Albite/ Anorthite	Microcline/ Orthoclase/ Anorthoclase	Hematite	Goethite	Anatase	Kaolin	Illite/ Mica	Smecttie	Rutile	Calcite	sum M_2O_3
Red Kandosol (IR5)	0-15	70		2	3		<1	23	1		<1		3
	15-35	72		2	3		<1	22	1		<1		3
	35-70	67		2	4		1	26	1		<1		4
Yellow Kandosol (IR8)	0-15	71				2	1	25		<2	<1		2
	15-35	69				1	1	27		2	<1		1
	35-70	63				1	1	34		<2	<1		1
Brown Chromosol (IR8)	0-15	61			<1	2	1	35		<2	<1		2
	15-35	59			<1	2	1	37		<2	<1		2
	35-70	54			<1	2	1	42		<2	<1		2
Red Vertosol (IR6)	0-15	49	2	2	1	2	1	29		15			3
	15-35	50	2	2	2	2	1	28		14			4
	35-70	36	1	1	1	2	1	35		23			3
Brown Vertosol (IR6)	0-15	29	1	1	1	3	1	30		33			4
	15-35	31	1	1	1	3	1	30	2	30		<1	4
	35-70	30	1	1	1	3	1	30	2	31		<1	4
Podosol		88	<1	<1			1	11		<2	<1		0
Stradbroke Island Sand		99					<1				<1		0

Appendix 4. Soil chemical characteristics of soils

Soil order	Brown Chromosol (IR8)			Red Vertosol (IR6)			Brown Vertosol (IR6)		
Depth (cm)	0-15	15-35	35-70	0-15	15-35	35-70	0-15	15-35	35-70
pH (1:5 Water)	5.3	5.1	5.1	7	6.9	7.8	8.1	8.6	8.4
pH (1:5 $CaCl_2$)	4.5	4.2	4.2	5.5	5.5	6.6	7.4	7.9	7.7
EC (dS/m)	0.06	0.04	0.04	0.04	0.04	0.11	0.27	0.34	0.39
Chloride (ppm)	<10	<10	<10	<10	<10	53	<10	42	91
Nitrate N (ppm)	1.8	1.6	1.9	3	1.9	0.62	5.5	<0.50	3.4
Ammonium N (ppm)	12	7	7.3	2.1	2.7	1.2	5.6	6	9.4
P – Olsen (ppm)	<2.00	<2.00	<2.00	3.06	3.85	<2.00	2.04	<2.00	2.04
Calcium (meq/100g)	2	0.9	0.31	8	8.3	10	22	21	20
Potassium (meq/100g)	0.36	0.11	0.072	0.43	0.49	0.25	0.64	0.47	0.55
Magnesium (meq/100g)	2.5	2.1	2.6	7.1	6.6	12	11	13	13
Sodium (meq/100g)	0.061	0.083	0.1	0.61	0.59	2	1.4	2.7	2.8
Aluminium (meq/100g)	0.54	1.2	1.2	0	0	0	0	0	0
CEC (meq/100g)	5.46	4.39	4.28	16.1	16	24.2	35	37.2	36.4
Copper (ppm)	0.45	0.58	0.5	0.89	0.96	0.79	1.3	0.97	1.5
Iron (ppm)	120	64	32	41	42	23	34	31	32
Manganese (ppm)	12	2.2	0.61	110	120	33	20	12	16
Zinc (ppm)	0.54	2	0.41	1.8	2.2	0.51	1.6	3.8	1.2
Boron (ppm)	0.65	0.72	0.69	0.5	0.49	0.67	0.56	0.83	0.84
Sulfate – KCl (ppm)	8.4	5.8	5.7	1.5	2	1.3	8.9	8.9	12
Organic Carbon (%)	1.3	0.8	0.55	1.4	1.5	0.9	1.1	1.1	1.2
Al- hydrous oxide (%)	0.2	0.21	0.25	0.17	0.16	0.33	0.27	0.26	0.26
Fe hydrous oxide (%)	2.26	2.22	4.38	3.99	4.09	4.49	4.96	5.02	2.78

Appendix 4 continued. Soil chemical characteristics of soils used in Part 1 of the study

Soil order	Red Kandosol (IR5)			Yellow Kandosol (IR8)			Podosol	Sand
Depth (cm)	0-15	15-35	35-70	0-15	15-35	35-70		
pH (1:5 Water)	6.9	6.4	5.6	5.6	5.3	5.1	5.2	6.2
pH (1:5 $CaCl_2$)	5.7	5	4.5	4.4	4.2	4.1	4	5.4
EC (dS/m)	0.02	0.01	0.02	0.02	0.02	0.02	0.02	<0.01
Chloride (ppm)	<10	11	<10	<10	14	<10	<10	<10
Nitrate N (ppm)	4.1	1.7	0.76	3.7	3.8	2.1	4.6	3.1
Ammonium N (ppm)	1.4	0.74	0.84	1.7	1.5	1.4	9.4	<0.60
P – Olsen (ppm)	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	3.73	<2.00
Calcium (meq/100g)	3.1	1.9	1.4	2.5	1.8	0.9	0.19	0.035
Potassium (meq/100g)	0.48	0.41	0.28	0.16	0.12	0.052	0.045	<0.013
Magnesium (meq/100g)	0.91	0.51	0.72	0.91	0.82	0.63	0.35	0.041
Sodium (meq/100g)	<0.022	<0.022	<0.022	<0.022	<0.022	<0.022	0.031	<0.022
Aluminium (meq/100g)	0	0.1	0.5	0.78	1.3	2	1.3	0.1
CEC (meq/100g)	4.51	2.94	2.92	4.37	4.06	3.6	1.92	0.21
Copper (ppm)	0.51	0.52	0.74	0.93	0.66	0.14	0.21	<0.010
Iron (ppm)	8.9	5.5	2.8	96	90	29	50	0.7
Manganese (ppm)	13	9.9	3.6	3.2	2.9	0.25	0.44	0.037
Zinc (ppm)	0.51	0.17	0.59	0.6	3.1	2.3	3.8	0.025
Boron (ppm)	0.4	0.59	0.64	0.42	0.57	0.64	0.24	0.021
Sulfate – KCl (ppm)	<1.0	2.1	10	1.2	1.6	1.9	2	<1.0
Organic Carbon (%)	0.92	0.46	0.29	1.5	1.3	0.7	1.4	<0.15
Al- hydrous oxide (%)	0.1	0.1	0.12	0.15	0.16	0.17	0.04	0
Fe hydrous oxide (%)	3.15	2.92	3.44	0.95	1.01	1.11	0	0

Appendix 4 continued. Soil chemical characteristics of soils used in Part 1 of the study

Soil order	Ferrosol		Brown Ferrosol		Red Vertosol		Black Vertosol	
Location	Lakelands		Lakelands		Lakelands		Lakelands	
Depth (cm)	0-10	50-60	0-10	50-60	0-10	50-60	0-10	50-60
pH [1:5 H2O]	6.1	6.7	6.2	7.6	6.3	6.8	6.6	7.4
pH [1:5 CaCl2]	5.8	6.2	5.8	7.2	6	6.5	6.1	7.1
Organic Matter (%)	5.9	2.8	8.2	3.9	8	5	6.9	6.7
CEC (meq/100g)	9.9	4.6	12.1	8.8	23.0	21.1	52.1	55.3
EC [1:5 H2O] (dS/m)	0.17	0.02	0.11	0.04	0.07	0.04	0.09	0.07
NO3-N (ppm)	7.6	2.6	6.6	3.6	4.2	1.7	6.6	7.2
Phosphorus [Olsen] (ppm)	6	8	8	6	45	7	29	30
Potassium ex (meq/100g)	0.8	0.4	0.3	0.1	0.7	0.4	0.9	0.7
Calcium ex (meq/100g)	7.2	3.1	5.7	2.9	12.1	9.4	20.6	20.3
Magnesium ex (meq/100g)	1.7	0.8	5.0	5.0	10.0	10.9	30.1	32.9
Sulphur [MCP] (ppm)	6	5	6	1	7	2	6	3
Boron [CaCl2] (ppm)	0.3	0.3	0.3	0.3	0.1	< 0.1	< 0.1	0.2
Copper [DTPA] (ppm)	1.9	0.7	2.2	0.4	2.5	0.9	1.9	1.9
Iron [DTPA] (ppm)	16	8	74	13	111	40	105	113
Manganese [DTPA] (ppm)	51.3	26.3	32	11.1	24.6	5.2	6.3	1.6
Zinc [DTPA] (ppm)	0.3	< 0.1	0.3	0.1	1.9	0.2	0.9	0.7
Sodium ex (meq/100g)	< 0.1	< 0.1	0.9	0.6	0.1	0.2	0.4	1.4
Aluminium ex (meq/100g)	0.2	0.3	0.1	0.2	0.1	0.2	0.1	0.1
Chloride (ppm)	24	12	57	26	23	17	25	76
Ca base saturation (%)	72.1	66.1	47.6	33.3	52.4	44.6	39.5	36.7
K base saturation (%)	8.1	9.3	2.9	1.5	3.3	1.8	1.7	1.2
Mg base saturation (%)	17.4	17.3	41.5	56.6	43.4	51.9	57.9	59.5
Na base saturation (%)	0.8	1.5	7.1	6.3	0.5	1.0	0.7	2.5
Al base saturation (%)	1.6	5.8	0.9	2.3	0.4	0.8	0.2	0.1
Ca:Mg Ratio	4.1	3.8	1.2	0.6	1.2	0.9	0.7	0.6
Al hydrous oxides (%)	0.5	0.5	0.4	0.7	0.3	0.5	0.3	0.2
Fe hydrous oxides (%)	9.8	9.7	4.5	7.6	6.8	8.4	3.4	3.3

Appendix 4 continued. Soil chemical characteristics of soils used in Part 1 of the study

Soil order	Red Kandosol (IR 5)		Yellow Kandosol (IR 8)		Red Kandosol	Yellow Kandosol	Black Vertosol	Grey Kurosol	Ferrosol
Location	native	+lime	native	+lime	IR 8	Beerburrum	Gatton	Mt Cotton	Toowoomba
Depth (cm)					5-20	30-50	0-5	5-15	50-100
pH [1:5 H2O]	5	7.1	4.7	7.2	5	5.3	8.2	4.9	6.7
pH [1:5 CaCl2]	4.3	6.8	4.0	7.0	4.1	4.4	7.3	3.8	6.1
Organic Matter (%)	0.9	0.9	1.0	0.9	1.2	0.4	2.3	7.5	3.6
Org. Carbon (%)	0.5	0.5	0.5	0.5	0.6	0.2	1.2	4.0	1.9
CEC (meq/100g)	2.5	17.7	3.2	18.7	2.3	2.1	41.7	5.1	13.1
EC [1:5 H2O] (dS/m)	0.07	0.32	0.07	0.4	0.02	0.01	0.12	0.04	0.15
NO3-N (ppm)	2.4	2.7	5.9	6.2	3.5	<1	9.4	2.6	24
Phosphorus [Olsen] (ppm)	2.6	<2	2.2	<2	<2	<2	42.1	2.4	8.8
Potassium ex (meq/100g)	0.2	0.2	0.0	0.0	0.2	0.0	0.8	0.1	0.6
Calcium ex (meq/100g)	1.3	17	0.6	17.0	0.6	0.1	19.0	0.2	7.5
Magnesium ex (meq/100g)	0.3	0.3	1.6	1.5	0.3	0.5	21.0	0.6	4.7
Sulphur [MCP] (ppm)	21.0	33.0	9.5	15.0	2.3	8.5	7.0	1.5	52.0
Boron[CaCl2] (ppm)	0.6	0.4	0.8	0.5	0.4	0.2	1.0	0.8	1.3
Copper [DTPA] (ppm)	0.2	0.2	<0.10	<0.01	0.03	<0.01	1.6	0.1	0.7
Iron [DTPA] (ppm)	9.0	7.3	30.0	28.0	73.0	5.8	16.0	150	13.0
Manganese [DTPA] (ppm)	21	25	1.8	1.7	1.8	0.2	6.1	2.6	12
Zinc [DTPA] (ppm)	0.6	0.6	3.2	4.4	2.4	0.1	0.8	2.0	12
Sodium ex (meq/100g)	0.03	0.03	0.1	0.1	<0.02	0.04	0.8	0.1	0.3
Aluminium ex (meq/100g)	0.7	0.1	0.8	0.1	1.2	1.4	0.1	4.1	
Chloride (ppm)	<10	<10	<10	<10	10	<10	23	13	23
Ca base saturation (%)	51.6	96.0	20.4	90.9	25.8	6.2	45.6	4.1	57.3
K base saturation (%)	8.7	1.3	1.5	0.2	9.0	0.7	2.0	1.9	4.7
Mg base saturation (%)	11.9	1.7	50.3	8.0	12.9	24.8	50.4	12.2	35.9
Na base saturation (%)	1.1	0.1	2.9	0.5	<0.9	1.8	1.9	1.0	2.2
Al base saturation (%)	26.6	0.6	24.8	0.5	51.5	66.7	0.2	80.7	0
Ca:Mg Ratio	4.3	56.7	0.4	11.3	2.0	0.3	0.9	0.3	1.6
Al hydrous oxides (%)	0.1		0.2		0.1	0.1	0.2	0.2	0.7
Fe hydrous oxides (%)	3.9		1.2		0.9	0.3	1.6	1.0	8.6

Appendix 4 continued. Soil chemical characteristics of soils used in Part 2 of the study

Soil order	Vertosol (saline, sodic)				Black Vertosol (sodic)				Dermosol (saline sodic)			
Location	Summerhills3				Summerhills 5				Summerhills 10			
Depth (cm)	0-12	12-40	40-120	120-150	0-10	10-45	45-80	80-140	0-7	7-50	50-100	100-150
pH 1:5 water	7.6	8.4	4.9	4.8	6.2	5.9	4.8	4.5	6.2	8.3	9.1	8.6
pH 1:5 water (UQ)	7.6	7.3	7.1	5.4	6.5	7.8	5.2	5.5	7.5	8	8.4	8.8
SAR sat ext	5.9	16.2	30	41.4	5.8	7.6	21.7	29.1	1.1	13.6	22.6	35
EC 1:5 @ 25°C (dS/m)	0.06	0.14	0.79	0.87	0.06	0.09	0.66	0.88	0.02	0.07	0.47	0.45
EC 1:5 (UQ) (dS/m)	0.6	0.56	1.49	0.95	0.14	0.11	0.62	1.03	0.04	0.14	0.36	0.51
Clay (<2 µm) (%)	32	50	44	48	41	55	50	49	14	42	33	31
Sand (>75 µm) (%)	31	24	22	11	38	28	30	28	53	34	38	41
Silt (2-60 µm) (%)	35	23	33	41	20	16	19	18	32	23	26	27
CEC (meq/100g)	21.6	20	13.8	13.1	17.8	19.2	19.5	13.8	4	14.8	18.6	11.3
Aluminium ex (meq/100g)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1
Calcium ex (meq/100g)	12	9.9	3.2	2.2	9.2	8.2	5.8	3.2	2.2	4.4	7.6	1.8
Magnesium ex (meq/100g)	8.3	8.3	8	8.1	7.1	9.4	10.9	8	1.1	8.6	9.4	7.4
Potassium ex (meq/100g)	0.4	0.2	0.2	0.2	0.9	0.2	0.2	0.1	0.7	0.4	0.3	0.2
ESP	3.5	6.7	11.8	13	2.6	6.5	9.8	12.3	< 0.1	7.8	5.8	11.3
Extractable Iron (ppm)	22.7	9.15	123	45.1	86.3	159	165	86	26.9	5.55	5.45	4.6
Sulfate (ppm)	330	370	1030	1250	480	540	580	1450	160	180	510	510
Chloride 1:5 (ppm)	< 10	80	730	1020	30	40	930	1180	< 10	40	210	290
Fluoride 1:5 (ppm)	2	6	< 1	< 1	< 1	< 1	< 1	< 1	< 1	2	6	3
Fluoride 1:5 (UQ) (ppm)	1.5	13	6	1	1.5	1	0.5	0.5	1	1	10	9
Colwell P (ppm)	672	982	880	343	372	874	1530	497	272	500	56	392
Organic Matter (%)	4.3	1.6	2	0.8	3.7	2.8	1.5	1.3	4.2	< 0.5	< 0.5	0.6
Total alkal (as CaCO3) ppm	153	332	13	13	77	89	13	< 1	64	306	408	179

Appendix 4 continued. Soil chemical characteristics of soils used in Part 2 of the study

Soil order	Chromosol				Chromosol				Tenosol			
Location	IR4-256 (Springwater)				TBD30				TBD41			
Depth (cm)	0-10	10-20	20-30	50-60	0-10	20-30	50-60	80-90	0-10	20-30	80-90	110-120
pH 1:5 water	7.4	7.9	7.9	7.8	6.4	6.1	7.7	9.3	6.4	6.3	6.6	8.7
pH 1:5 water (UQ)	6.8	6.8	5.9	6.4	7.3	8	8.4	9	7.3	7.7	7.9	8.5
SAR sat ext	0.1	0.1	0.05	0.3	0.5	0.6	3	22	0.1	0.1	1.8	4.4
EC 1:5 @ 25°C (dS/m)	0.03	0.03	0.05	0.03	0.01	0.01	0.04	0.29	0.01	0.01	0.01	0.04
EC 1:5 (UQ) (dS/m)	0.16	0.08	0.04	0.03	0.03	0.1	0.22	0.43	0.03	0.02	0.02	0.09
Clay (<2 µm) (%)	20	24	36	38	17	18	39	31	11	12	11	16
Sand (>75 µm) (%)	42	38	38	32	74	73	54	61	82	82	80	73
Silt (2-60 µm) (%)	30	26	23	21	8	8	7	7	7	6	9	11
CEC (meq/100g)	15	12.7	12.8	10.9	3.7	4	12.2	20.3	2.2	2.1	1.4	5.1
Aluminium ex (meq/100g)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
Calcium ex (meq/100g)	10.8	10.1	10.2	7.3	2.2	2.5	6.5	13	1.3	1.3	0.9	1.5
Magnesium ex (meq/100g)	2.5	1.7	2	3.2	1.2	1.2	5	5.9	0.5	0.5	0.3	1.6
Potassium ex (meq/100g)	1.7	0.9	0.6	0.3	0.3	0.2	0.2	<0.1	0.4	0.3	<0.1	<0.1
ESP	<0.1	<0.1	<0.1	0.2	<0.1	0.4	4.6	6	<0.1	<0.1	3.6	38
Extractable Iron (ppm)	37.5	12.8	10.6	13.3	37.7	31	11.4	5.74	22	9.68	5.26	7.8
Sulfate (ppm)	340	260	240	140	100	110	<100	140	<100	<100	<100	<100
Chloride 1:5 (ppm)	30	10	<10	10	20	10	110	160	10	10	10	120
Fluoride 1:5 (ppm)	-	-	-	-	-	-	-	-	-	-	-	-
Fluoride 1:5 (UQ) (ppm)	<0.5	0.5	0.5	0.5	1	0.5	3	15	4	2	2	4
Colwell P (ppm)	<2	<2	<2	13	<2	<2	<2	<2	5	<2	<2	720
Organic Matter (%)	1.7	2	1.6	1.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Total alkal (as CaCO3) ppm	174	122	191	183	-	-	-	-	25	25	25	125

Appendix 4 continued. Soil chemical characteristics of soils used in Part 2 of the study

Soil order	Sodosol (non-saline)				Chromosol				Vertosol (gypsiferous)			
Location	PLH63				PLH88				Weemilah			
depth	0-10	10-20	20-30	50-60	0-10	20-30	50-60	80-90	0-20	20-50	50-80	80
pH 1:5 water	7.2	7.2	7.2	8.9	6.6	6.5	8.4	9.1	7.9	8.7	8.6	5.6
pH 1:5 water (UQ)	7.1	5.9	6.9	6.7	7.3	6.4	6.9	7.8	7.8	7.2	6.7	6.6
SAR sat ext	3.1	2.5	3.8	15.4	0.09	0.2	11.7	15.5	4.7	8.4	15.8	3.5
EC 1:5 @ 25°C (dS/m)	0.02	0.04	0.08	0.29	0.02	0.01	0.11	0.37	0.71	0.19	0.29	2
EC 1:5 (UQ) (dS/m)	0.36	0.16	0.07	0.08	0.07	0.02	0.03	0.06	0.11	0.25	0.33	3.08
Clay (<2 µm) (%)	20	31	32	33	18	15	16	22	43	50	55	40
Sand (>75 µm) (%)	65	56	57	56	65	68	45	43	48	40	37	48
Silt (2-60 µm) (%)	15	13	11	11	17	17	39	34	9	10	7	12
CEC (meq/100g)	8.3	11.4	12.2	14.1	4.5	4.2	18.5	31.2	25	30.8	33.4	94.1
Aluminium ex (meq/100g)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	< 0.1	< 0.1	< 0.1
Calcium ex (meq/100g)	6.2	6.4	5.6	4.4	2.9	3.3	9.3	24.2	16.9	20.6	20.1	86.4
Magnesium ex (meq/100g)	1.6	3.9	5	6.7	0.8	0.5	7.6	6	7	8.9	10.9	6.7
Potassium ex (meq/100g)	0.4	0.1	0.1	0.1	0.8	0.4	0.3	0.2	0.6	0.2	0.2	0.1
ESP	1.5	8.9	11.8	19.7	<0.1	<0.1	7.1	2.6	1.5	3.1	6.3	0.9
Extractable Iron (ppm)	42.1	93.9	54.3	8.66	15.1	8.31	5.15	2.82	27.3	18.2	11.2	23.1
Sulfate (ppm)	100	110	<100	250	100	<100	<100	1090	270	290	760	45000
Chloride 1:5 (ppm)	20	20	40	320	10	10	130	300	10	50	60	250
Fluoride 1:5 (ppm)	-	-	-	-	-	-	-	-	< 1	10	9	< 1
Fluoride 1:5 (UQ) (ppm)	1	1	1	1	1	<0.5	0.5	0.5	0.5	2	7	1
Colwell P (ppm)	<2	<2	3	<2	<2	<2	<2	<2	< 2	< 2	< 2	< 2
Organic Matter (%)	1.7	1	-	-	1.5	-	-	-	2.8	3.2	3.5	1.5
Total alkal (as CaCO3) ppm	-	-	-	-	-	-	-	-	198	466	443	11

Appendix 4 continued. Soil chemical characteristics of soils used in Part 2 of the study

Soil order	Dermosol		Dermosol (saline)				Dermosol (gypsiferous)				Br Kandosol
Location	Mayfield South		Broandah				Reuben Downs 17				IR5(2)
Depth (cm)	0-20	20-50	0-10	10-60	60-110	110-150	0-30	30-70	70-100	100-140	0-15
pH 1:5 water	8.4	8.5	6.4	8.4	6.9	4.8	6.9	8.4	6.2	8.5	4.5
pH 1:5 water (UQ)	7.3	6.2	7.3	6.9	5.9	5	8.5	6.4	7.8	7.6	4.0
SAR sat ext	-	-	2.1	21	7.7	36.1	8	40	-	22	-
EC 1:5 @ 25°C (dS/m)	0.33	0.82	0.05	0.57	0.17	0.79	0.06	1.38	1.93	1.76	0.12
EC 1:5 (UQ) (dS/m)	0.3	0.54	0.04	0.57	1.57	0.87	0.79	4.18	3.07	0.89	-
Clay (<2 µm) (%)	-	-	24	52	55	56	62	60	53	52	-
Sand (>75 µm) (%)	-	-	54	34	24	24	12	19	13	14	-
Silt (2-60 µm) (%)	-	-	14	13	20	20	26	20	33	34	-
CEC (meq/100g)	25.5	44	10.4	31	49.4	23.8	23.1	50.6	63	36.5	3.3
Aluminium ex (meq/100g)	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	2
Calcium ex (meq/100g)	18	30	5.8	17	36.1	8.7	7.6	34	53.7	14.8	0.8
Magnesium ex (meq/100g)	4.6	9.9	3.7	11.1	11.5	10.5	11.8	14	7.9	18.2	0.2
Potassium ex (meq/100g)	1.9	0.4	0.8	0.1	0.1	0.1	0.4	0.2	0.2	0.2	0.3
ESP	3.4	8.2	0.6	7.2	3	12.5	14.2	4.7	2	9.2	0.8
Extractable Iron (ppm)	8.1	9.4	31	10.5	5.52	59.1	20.2	9.31	21.4	9.11	31
Sulfate (ppm)	12	390	230	710	880	890	250	1640	3300	3040	50
Chloride 1:5 (ppm)	72	290	< 10	650	970	1050	40	980	620	960	<10
Fluoride 1:5 (ppm)	-	-	< 1	13	7	< 1	< 1	< 1	2	3	-
Fluoride 1:5 (UQ) (ppm)	1.5	7.5	0.5	11	7	0.5	6	7	4	4	-
Colwell P (ppm)	19	<5.0	415	433	1060	1030	< 2	< 2	< 2	< 2	<5
Organic Matter (%)	1.3	0.8	2.2	1.5	0.5	1	1.7	1	< 0.5	0.7	0.9
Total alkal (as CaCO3) ppm	-	-	153	391	64	13	166	319	38	306	-

Appendix 4 continued. Soil chemical characteristics of soils used in Part 2 of the study

Soil order	Dermosol (saline)				Dermosol/Vertosol (saline sodic)				Dermosol (saline sodic)			
Location	Reuben Downs 3				Reuben Downs 6				Reuben Downs 8			
Depth (cm)	0-25	25-50	50-100	100-150	0-5	5-50	50-90	90-130	0-5	5-50	50-100	100
pH 1:5 water	7.6	5.2	4.9	7.6	6.1	8.4	7.8	5	5.6	5	5	5.6
pH 1:5 water (UQ)	7.1	7.3	6.2	5.9	7.4	8.1	5.4	6.1	6.4	5.2	5.3	5.2
SAR sat ext	23.6	44.5	53.1	33.7	6.1	32.9	38.2	36.3	3.5	32.6	42.2	7.9
EC 1:5 @ 25°C (dS/m)	0.15	0.5	0.53	0.44	0.13	0.58	1.49	0.95	0.07	0.39	0.33	0.09
EC 1:5 (UQ) (dS/m)	0.23	0.47	0.57	0.59	0.14	0.73	2.98	1.72	0.03	0.3	0.53	0.52
Clay (<2 µm) (%)	44	48	49	44	38	57	52	55	17	27	28	28
Sand (>75 µm) (%)	29	21	24	21	31	19	16	17	39	41	39	36
Silt (2-60 µm) (%)	27	31	27	35	30	22	31	27	35	31	32	34
CEC (meq/100g)	19.2	12.3	11.9	14.1	14.2	32.7	26.2	17.5	5.2	8.7	8.1	10.2
Aluminium ex (meq/100g)	0.2	0.2	0.2	0.2	< 0.1	0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	0.2
Calcium ex (meq/100g)	5.3	1.5	0.8	2.7	8	14.6	8.3	4.8	1.9	1.1	0.5	3.4
Magnesium ex (meq/100g)	11	7.7	7.5	8.5	4.9	13.5	12.9	9	1.9	5.8	5.4	6
Potassium ex (meq/100g)	0.1	< 0.1	< 0.1	< 0.1	1	0.2	0.2	0.2	1.2	< 0.1	< 0.1	< 0.1
ESP	14.6	24.6	28.8	19.4	2.2	13.5	18.2	20	1.4	19.3	26.9	6.4
Extractable Iron (ppm)	13.5	39.3	42.2	26.6	54.9	13	11.9	28.2	37.3	40.1	54.3	74.9
Sulfate (ppm)	150	< 100	< 100	< 100	310	490	1410	1270	140	340	200	150
Chloride 1:5 (ppm)	180	910	980	770	80	960	1590	1440	40	570	420	100
Fluoride 1:5 (ppm)	< 1	< 1	< 1	1	< 1	3	< 1	< 1	< 1	< 1	< 1	< 1
Fluoride 1:5 (UQ) (ppm)	0.5	0.5	0.5	< 0.5	1	14	2	1	1	0.5	1	< 0.5
Colwell P (ppm)	< 2	< 2	< 2	< 2	14	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Organic Matter (%)	2	1	0.8	1.5	4.1	3.2	0.8	0.8	2.9	< 0.5	0.8	0.8
Total alkal (as CaCO3) ppm	319	13	13	536	89	166	38	< 1	51	26	13	26

Appendix 5. Technical note on total F determination

The method for total F determination by alkaline fusion was based on the method by McQuaker and Gurney (1977). For foliar samples, we tested other methods for total F analysis as well, notably the AOAC First action procedure (method 975.04) using a nitric acid digestion, the sodium carbonate-sodium tetraborate fusion method (Oliver and Clayton, 1970) and compared results to the NaOH fusion method (McQuaker and Guerney 1977) using reference plant material containing "bush branches and leaves" (NCS DC 73349, F: 23 ± 4 mg/kg), with results shown in Table A5.

Table A5. Foliar F determined in certified reference material NCS DC 73349 using three methods

Method	Avg F (mg/kg)	s.d.	CV (%)	% deviation
AOAC First action	6.01	0.41	6.9	-74
NaCO3/NaB4O7	11.94	2.45	20.5	-48
NaOH fusion	28.51	0.78	2.7	+24

The first two methods significantly underestimated F in the reference plant sample and the coefficients of determination on quadruple determinations was higher than for the alkaline fusion method. While the alkaline fusion method slightly overestimated the F in reference sample, the measured values were not significantly different from the stated concentration.

Replacing the NaOH in the alkaline fusion method with KOH gave significantly lower recoveries of F and, thus, underestimated foliar F levels (data not shown).

Microwave digestion (Keerthisinghe et al 1991) was also conducted but due to the fact that the Teflon bombs were in the past used for HF digestion of soil, the background F concentration in controls were high, which precluded the use of Teflon bombs.

The following method was adopted:
Either 0.5 g of soil sample or 0.25 g foliar samples were transferred to a 100 mL nickel crucible and moistened with a small amount of water (1-2 mL). Thereafter, 5 mL of 16.7 M NaOH was added, mixed with the plant material, and placed in an oven at 155°C for 4 h. During this time, the crucibles were swirled 1-2 times to ensure complete wetting of the sample. We used a 4 h incubation at 155°C to dry the sample and prevent boiling-over of the sample when placed in the muffle furnace. The crucibles were then transferred to a furnace at 200°C for ca. 30 min, the temperature raised to 300°C, then raised to 570°C. Once this temperature had been achieved, the furnace was kept at 570°C for 30 min to fuse the sample in the crucible. It was found that slow heating resulted in less sample losses. Using smaller crucibles also increased sample loss when the sample boiled over, therefore a 100 mL crucible was optimal. Thereafter the crucible was placed in a fume-hood, allowed to cool, 15 mL deionised water added, and transferred to an oven at 155°C for 20 min to dissolve the sample. After cooling, the contents of each crucible were transferred quantitatively by rinsing with deionised water to a 50 mL plastic tube. Then, 7 mL of fuming HCl (37%) was added slowly to change the solution to neutral pH. Solutions were finally adjusted to between pH 5 and 6 with HCl, and made up to 50 mL with deionized water. Prior to measurement of F, 10 volumes of the solution was mixed with 4 volumes of concentrated TISABII buffer to ensure pH 5.4 and to prevent the F from forming complexes that would interfere with the measurement of F.

It was not possible to increase the buffer concentration and lower the volume of buffer to lower detection limits because the buffer would precipitate.

Using the fusion process, the minimum detectable concentration of F in the foliar tissue was estimated to be ca. 10 mg F/kg DM (but may be lowered if large sample mass is used). Using a larger sample mass may result in lowered detection limits, but this was not tested in more detail.

Appendix 6. F concentrations in soil and plant material

Total F in soils by NaOH fusion*: 0.5 g of soil sample was transferred to a 100 mL nickel crucible and moistened with a small amount of water. Five mL of 16.75 N NaOH was added and the crucible was placed in an oven (160°C) for 3.0-3.5 h until NaOH was completely solidified. The crucibles were placed in a muffle furnace set at 300°C, then raised to 600°C and kept at 600°C for 30 min in order to fuse the sample in the crucible. The crucible was placed in a hood and allowed to cool, and 15 mL of distilled water was added to dissolve the residue by heating with a hotplate. The crucibles were washed with 20 mL of water and 37% HCl solution (7.5 mL) was added slowly to adjust the pH to 9-10 to precipitate the interfering ions (Fe and Al). The sample solution was diluted with DI water to 50 mL and filtered. For measurement of F, the extract was mixed 1:1 with TISABII buffer.*

Soil samples	Calculated F in soils (mg/kg)	Standard deviation	Certified F level (mg/kg)
Reference soil NCS DC 73309	1770	17.7	1650±82
Reference soil NCS ZC 73001	415	10.4	452±16
RK control 0-15 cm	60.8	2.08	
RK control 15-30 cm	66.2	0.86	
RK-control 35-70 cm	87.3	4.27	
RK-1 10-15 cm Drip	80.6	1.71	
RK-1 15-30 cm Drip	120	2.09	
RK-1 35-70 cm Drip	101	2.58	
RK-2 0-15 cm Drip	63.5	1.18	
RK-2 15-30 cm Drip	90.7	1.19	
RK-2 35-70 cm Drip	159	3.01	
RK-3 0-15 cm Drip	118	4.70	
RK-3 15-30 cm Drip	102	2.63	
RK-3 35-70 cm Drip	137	6.06	
BV-control 0-15 cm	432	6.85	
BV-control 15-30 cm	581	6.32	
BV-control 35-70 cm	871	40.6	
BV-1 0-15 cm Drip	405	4.39	
BV1 15-30 cm Drip	338	5.46	
BV1 35-70 cm Drip	447	5.92	
BV-2 0-15 cm	772	35.6	
BV-2 15-30 cm	390	2.89	
BV-2 30-70 cm	491	15.1	
BV-3 0-15 cm	490	6.62	
BV-3 15-30 cm	423	7.84	
BV-3 35-70 cm	530	17.1	

Water-extractable F: *Fluoride was extracted by shaking 2 g of soil sample in 10 mL of water for 1 h. For measurement of F, extract was mixed 1:1 with TISABII buffer.*

Soil samples	Soluble F in soils (mg/kg)	Standard deviation
RK control 0-15 cm	0.030	0.003
RK control 15-30 cm	0.017	0.002
RK-control 35-70 cm	0.012	0.002
RK-1 10-15 cm Drip	0.002	0.001
RK-1 15-30 cm Drip	0.094	0.003
RK-1 35-70 cm Drip	0.077	0.001
RK-2 0-15 cm Drip	0.018	0.004
RK-2 15-30 cm Drip	0.066	0.0005
RK-2 35-70 cm Drip	3.33	0.193
RK-3 0-15 cm Drip	1.82	0.007
RK-3 15-30 cm Drip	0.14	0.016
RK-3 35-70 cm Drip	0.061	0.005
BV-control 0-15 cm	2.80	0.107
BV-control 15-30 cm	11.9	0.165
BV-control 35-70 cm	21.9	0.248
BV-1 0-15 cm Drip	7.94	0.095
BV1 15-30 cm Drip	2.11	0.063
BV1 35-70 cm Drip	4.26	0.120
BV-2 0-15 cm	17.2	0.433
BV-2 15-30 cm	3.56	0.083
BV-2 30-70 cm	5.69	0.073
BV-3 0-15 cm	12.3	0.138
BV-3 15-30 cm	3.76	0.073
BV-3 35-70 cm	11.2	0.225

Plant tissue analysis by NaOH fusion*: 0.25 g of plant sample was transferred to a 100 mL nickel crucible and moistened with a small amount of de-ionized water. 5 mL of 16.75 N NaOH was added and the crucible was placed in an oven (150°C) for 3-3.5 h until the NaOH was solidified. The crucible was placed in a muffle furnace set at 300°C, then raised to 600°C and kept at 600°C for 30 min in order to fuse the sample in the crucible. The crucible was placed in a hood and allowed to cool, and 20 mL distilled water was added to dissolve the sample. The crucibles were washed twice with 10 mL of water and 37% HCl solution (about 7.5 mL) was added slowly to adjust the pH to 5.4. The sample solution was transferred to a 50 mL plastic tubes, diluted with distilled water to the volume. For measurement of F, the extract*

was mixed 1:1 with TISABII buffer containing 0.2 mg/L F. The presence of a low background of fluoride is to reduce the response time of the electrode.

Plant samples	Calculated F in plants (mg/kg)	Standard deviation	Certified F level (mg/kg)
Reference plant NCS DC 73349	28.5	2.74	23±4
RK Buffel Control	23.8	1.62	
RK1 E.Ag Old	15.6	2.20	
RK1 E.Ag New	19.7	1.82	
RK2 E.Ag Old	20.3	1.20	
RK2 E.Ag New	22.0	1.38	
RK3 E.Ag Old	27.5	3.69	
RK3 E.Ag New	21.9	1.82	
RK4 E.Ag Old	21.0	2.20	
RK4 E.Ag New	22.2	2.12	
RK5 E.Ag Old	15.2	2.06	
RK5 E.Ag New	15.1	2.38	
RK6 E.Ag Old	18.0	1.42	
RK6 E.Ag New	16.6	1.23	
RK1-3 Drip Buffel	23.4	2.22	
RK4-6 Drip Buffel	23.0	3.04	
BV Panic Control	21.1	3.19	
BV1 E.Ag Old	20.1	1.62	
BV1 E.Ag New	15.0	2.86	
BV2 E.Ag Old	17.6	2.14	
BV2 E.Ag New Drip	17.2	2.65	
BV3 E.Ag Old Drip	12.6	1.79	
BV3 E.Ag New	14.2	2.20	
BV4 E.Ag Old	13.0	0.917	
BV4 E.Ag New Drip	12.0	0.736	
BV5 E.Ag Old Drip	14.2	1.35	
BV5 E.Ag New	13.1	2.29	
BV6 E.Ag Old	9.81	2.09	
BV6 E.Ag New	14.3	3.32	
BV1-3 Panic Drip	13.3	1.44	
BV4-6 Panic Drip	12.9	2.75	

Appendix 7. Visible effects of increasing soil F concentration on Leucaena

Leucaena grown in Yellow Kandosol

Yellow Kandosol 0 mg/kg F

Yellow Kandosol 50 mg/kg F

Yellow Kandosol 150 mg/kg F

Yellow Kandosol 500 mg/kg F

Appendix 7 continued. Visible effects of increasing soil F concentration on leucaena

Leucaena grown in Red Kandosol

Red Kandosol 0 mg/kg F

Red Kandosol 50 mg/kg F

Red Kandosol 150 mg/kg F

Red Kandosol 500 mg/kg F

Appendix 7 continued. Visible effects of increasing soil F concentration on leucaena

Leucaena grown in Red Vertosol

Red Vertosol 0 mg/kg F

Red Vertosol 50 mg/kg F

Red Vertosol 150 mg/kg F

Red Vertosol 500 mg/kg F

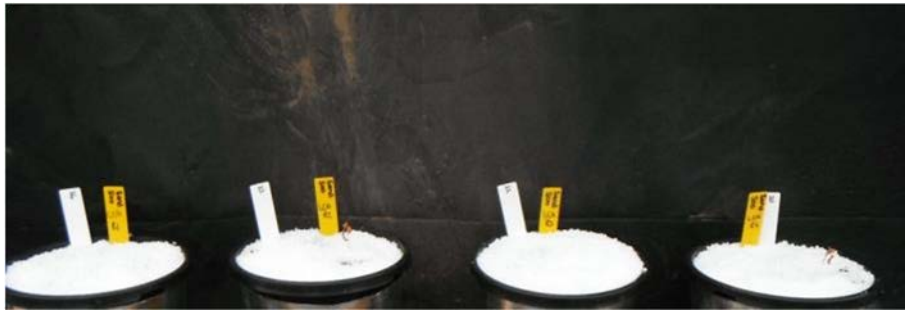
Appendix 7 continued. Visible effects of increasing soil F concentration on leucaena

Leucaena grown in Sand

Sand 0 mg/kg F

Sand 50 mg/kg F

Sand 150 mg/kg F

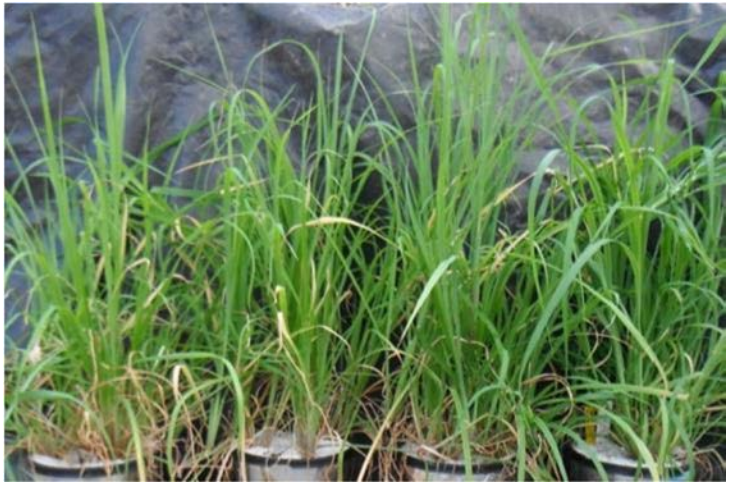


Sand 500 mg/kg F

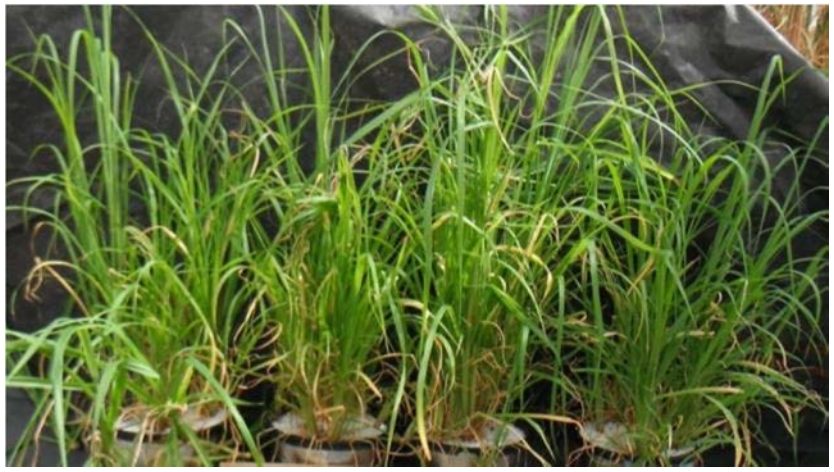
Appendix 8. Visible effects of increasing soil F concentration on Rhodes grass

Rhodes grass grown in Yellow Kandosol

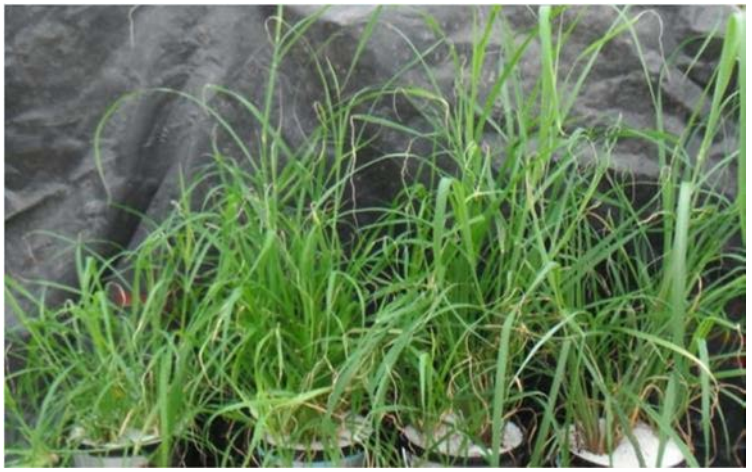
Yellow Kandosol 0 mg/kg F



Yellow Kandosol 50 mg/kg F



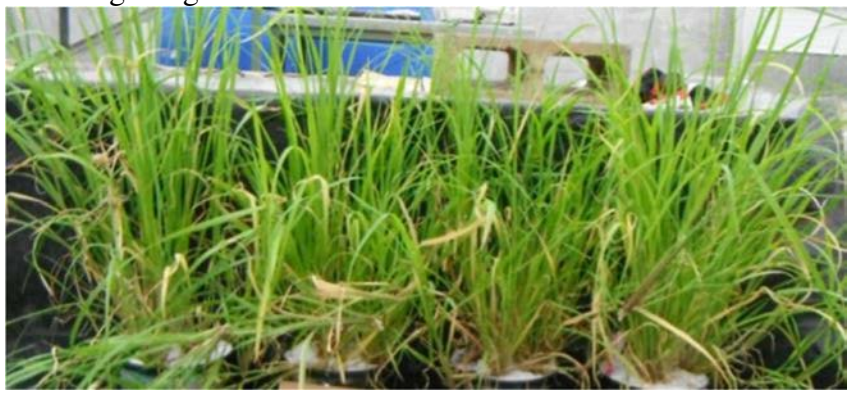
Yellow Kandosol 150 mg/kg F



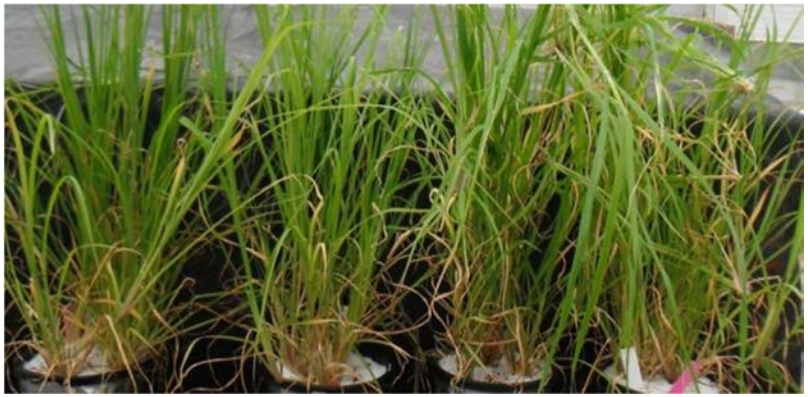
Yellow Kandosol 500 mg/kg F

Appendix 8 continued. Visible effects of increasing soil F concentration on Rhodes grass

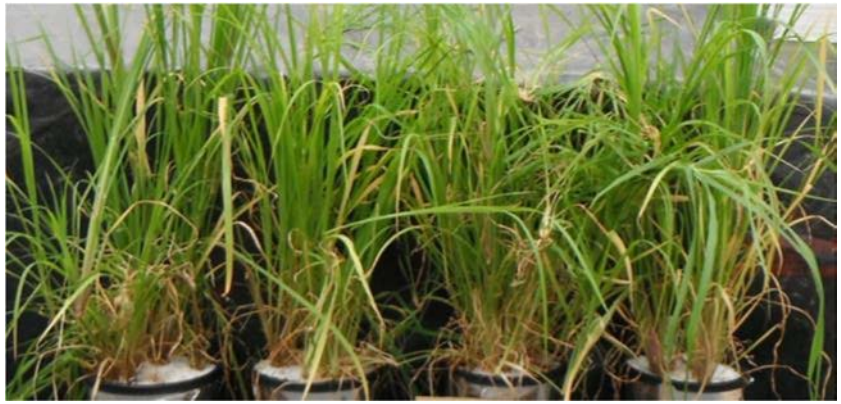
Rhodes grass grown in Red Kandosol



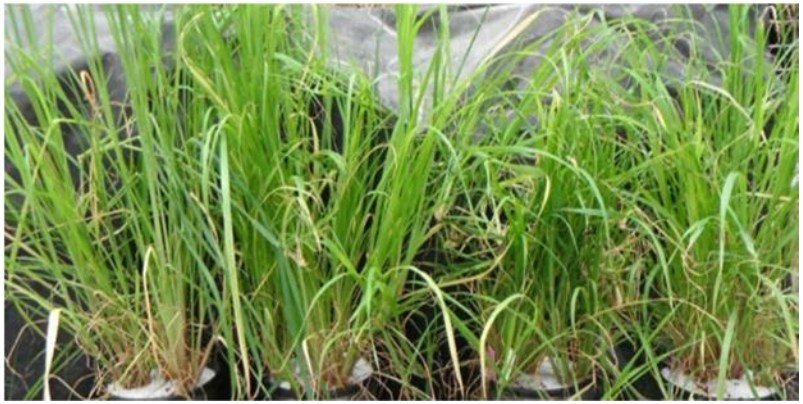
Red Kandosol 0 mg/kg



Red Kandosol 50 mg/kg



Red Kandosol 150mg/kg F

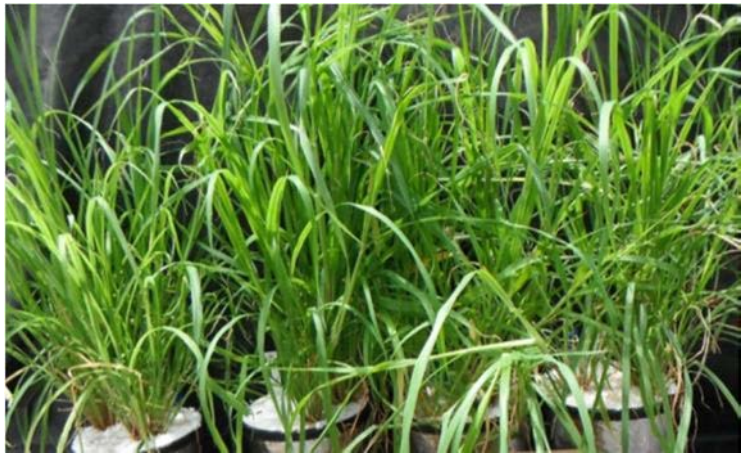


Red Kandosol 500 mg/kg F

Appendix 8 continued. Visible effects of increasing soil F concentration on Rhodes grass

Rhodes grass grown in Red Vertosol

Red Vertosol 0 mg/kg F



Red Vertosol 50 mg/kg F

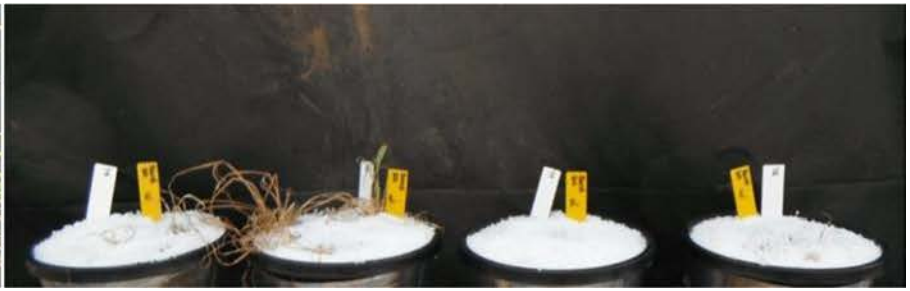
Red Vertosol 150 mg/kg F

Red Vertosol 500 mg/kg F

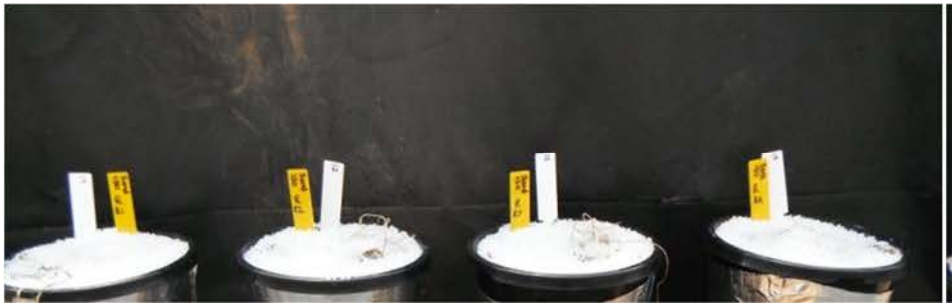
Appendix 8 continued. Visible effects of increasing soil F concentration on Rhodes grass

Rhodes grass grown in Sand

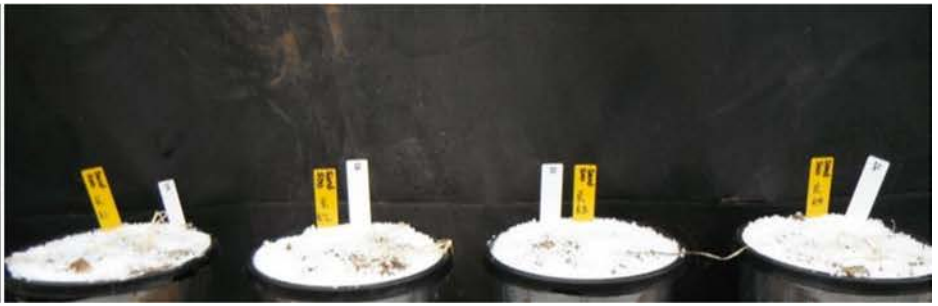
Sand 0 mg/kg F



Sand 50 mg/kg F



Sand 150 mg/kg F



Sand 500 mg/kg F

Appendix 9. Visible effects of increasing soil F concentration on lucerne

Lucerne grown in Yellow Kandosol

Yellow Kandosol 0 mg/kg F

Yellow Kandosol 50 mg/kg F

Yellow Kandosol 150 mg/kg F

Yellow Kandosol 500 mg/kg F

Appendix 9 continued. Visible effects of increasing soil F concentration on lucerne

Lucerne grown in Red Kandosol

Red Kandosol 0 mg/kg F

Red Kandosol 50 mg/kg F

Red Kandosol 150 mg/kg F

Red Kandosol 500 mg/kg F

Appendix 9 continued. Visible effects of increasing soil F concentration on lucerne

Lucerne grown in Red Vertosol

Red Vertosol 0 mg/kg F

Red Vertosol 50 mg/kg F

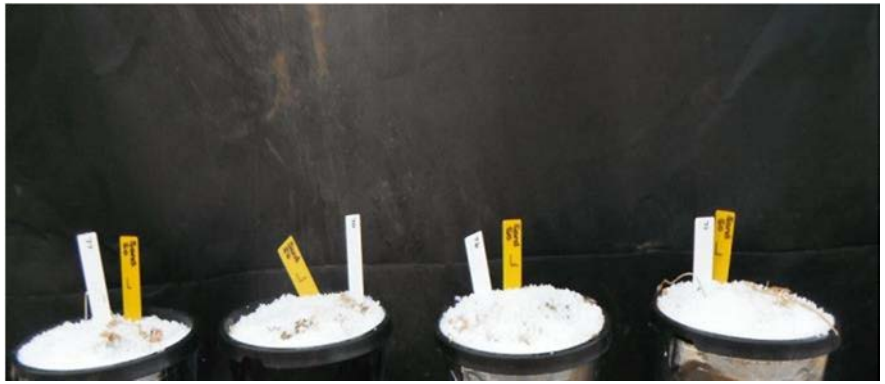
Red Vertosol 150 mg/kg F

Red Vertosol 500 mg/kg F

Appendix 9 continued. Visible effects of increasing soil F concentration on lucerne

Lucerne grown in Sand

Sand 0 mg/kg F



Sand 50 mg/kg F

Sand 150 mg/kg F

Sand 500 mg/kg F

Appendix 10. Paper published in Journal of Agricultural and Food Chemistry

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

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Use of Fluoride-Containing Water for the Irrigation of Soil–Plant Systems

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Supporting Information

ABSTRACT: Many groundwaters used for irrigation contain elevated concentrations of F, but much remains unknown regarding how this F behaves within soils and plants. The present study investigated the adsorption and desorption of F from several soils in short- to medium-term irrigation systems and related foliar F concentrations in three forage plant species to the maximum tolerable level (MTL) in the diets of grazing animals (being 1.8 μmol/g for young cattle, for example). Although adsorption isotherms could be successfully used to predict the behavior (adsorption and desorption) of F within the soil, this was not related to the subsequent accumulation of F in plant foliage. In addition, the extent to which F accumulated in the foliage depended on the plant species. Regardless, F generally did not accumulate in plant foliage to levels exceeding the MTL when used at rates equivalent to irrigation for 25 years. In addition to uptake by roots, F may accumulate in foliar tissues directly due to retention from overhead irrigation. The data presented here regarding the behavior of F in soils and plants will assist in the rigorous regulation of F-containing irrigation water to ensure maximum plant growth while simultaneously minimizing potential harm.

KEYWORDS: *adsorption and desorption, fluoride toxicity, fluoride uptake, lucerne, leucaena, Rhodes grass*

INTRODUCTION

Fluoride (F) is present naturally in the environment and is a common constituent of groundwater. However, agricultural activities, particularly the use of phosphatic fertilizers,[1] and industrial activities can also result in its accumulation to levels which are of concern in both soils and waters. At a concentration of ca. 0.053 mM (1 mg/L), F can mitigate against dental decay and is often added to potable water supplies. However, consumption of excess F can cause dental fluorosis or, in extreme cases, skeletal fluorosis. The concentration of F in groundwater is typically <0.053 mM, but concentrations of 0.25−1.0 mM are not uncommon.[2] The maximum concentration of F permitted in groundwater used for irrigation varies substantially depending upon the country and the conditions under which the water is to be irrigated (for example, soil type), ranging from 0.053 mM (1 mg/L) to 0.79 mM (15 mg/L).[3] In irrigated areas, the use of groundwater containing elevated levels of F is of concern not only due to direct ingestion of water by livestock but also due to its consumption in plant matter following its plant uptake from irrigated soils. The maximum tolerable level (MTL) of F in plant material has been developed as a guideline for the upper limit of F that different classes of animals may consume without a high risk of developing fluorosis, with the MTL for F ranging from 1.8 μmol/g (35 mg/kg) for young beef calves and heifers to >5.3 μmol/g (100 mg/kg) for swine and poultry.[4]

Given the worldwide problem regarding the irrigation of waters containing elevated F, the focus of this study was the Great Artesian Basin (Australia) which is the largest artesian basin in the world, containing an estimated 65000 million ML of groundwater.[5] The groundwater and coal seam water in this basin can be used for agriculture, and concentrations of F are typically <0.26 mM (5 mg/L).[6,7] Of particular interest to this study, the coal seam water, which is released during production of coal seam gas (also termed coal bed methane) can be used beneficially to increase agricultural production, although production of coal seam water only lasts for 10−15 years, after which no further irrigation is possible. Although the general irrigation of groundwater for agricultural production would typically exceed these timeframes, these traditional agricultural systems are not the focus of the present study.

In order to understand the risk of F uptake into forages, three factors are of interest: (i) adsorption and desorption of F by soils, (ii) uptake of F from soils by plant roots, and (iii) retention of F on the foliage of plants grown using overhead irrigation. Although numerous studies have investigated the F adsorption capacities of soils,[8−15] few have investigated desorption of F from soil surfaces back into the soil solution (as required for subsequent plant uptake).[9−12] The accumulation of F in foliar tissues resulting from irrigation with water containing F has also received comparatively little investigation.[16−22] Singh et al.[23] found that irrigation with 6.3 mM F will not harm okra (*Abelmorchus esculentus*) plants and that irrigation with 0.53 mM F resulted in fruit containing F at a concentration of 0.11 μmol/g. Another study investigating

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uptake and concentration of F in rice (*Oryza sativa* L.) irrigated with water containing up to 0.21 mM F found the concentration of F in the leaves to be >2.6 μmol/g.[24] Unfortunately, these studies do not differentiate between F taken up by plant roots and that accumulated by foliar tissues through direct contact with irrigation water. Indeed, we are aware of only one study examining the retention of F by foliar tissues as a result of direct contact between F in irrigation water and foliar surfaces.[25] These authors found that the accumulation of F on the foliar surfaces of bush beans (*Phaseolus vulgaris* L.) increased with increased F concentration of irrigation water and increases in irrigation frequency.

The aim of the present study was to investigate the risk of F accumulation above the lowest recommended MTL (young beef calves and heifers, 1.8 μmol F/g) in three forage plant species grown on a range of soils irrigated with groundwater containing concentrations of F above the current conservative regulated limit of 0.053 mM, as used in Australia, the USA, and Canada.[3] In doing so, three key factors were examined: (i) adsorption/desorption of F in soils (and hence concentrations of plant-available F in the soil solution), (ii) plant root uptake of F from the soil solution and translocation to foliar tissues, and (iii) the accumulation of F in foliar tissues from direct contact between F in irrigation water and foliar surfaces. Of particular interest were irrigated systems of short- to medium-term duration (i.e., < 20 years where water resources are limited), such as irrigation of coal seam water, irrigation to establish forestry/grazing systems, or irrigation to supplement the water supply in variable rainfall environments.

MATERIALS AND METHODS

Selection and Preparation of soils. Three experiments were conducted to investigate the movement of F within soils and plants. Experiment 1 was conducted in the laboratory and investigated the adsorption and desorption of F by soils. Experiment 2 was conducted in the greenhouse and investigated the uptake of F from F-loaded soils, and experiment 3 investigated the retention of F due to overhead irrigation. Six soils were used for these experiments: an alfisol, a red vertisol, a brown vertisol, a red ultisol, a yellow ultisol, and a spodosol. These soils were collected from various regions within the Great Artesian Basin and were representative of typical soils used for agricultural production (Table S1, Supporting Information), with the mineralogy being examined using quantitative X-ray diffraction (Table S2, Supporting Information).[26] A washed white quartz sand from North Stradbroke Island (Australia) was included as a control (the sand treatment is referred to as a "soil" for brevity). These soils had not previously been irrigated with groundwater and were selected as they were expected to vary in their F adsorption capacities. All soils were collected, air-dried, mixed, and ground to pass a 1 mm sieve.

Experiment 1: Soil F Adsorption and Desorption. First, a laboratory experiment was conducted to investigate the adsorption of F by soils. The NaF was added to the soil at seven rates, with seven soils (five soils had three separate layers and two soils had only a single layer; Tables S1 and S2, Supporting Information), and three replicates per treatment, yielding a total of 357 experimental units. Triplicate blanks (controls) containing no soil were also included and measured in the same manner as that for the soil samples. Soil subsamples (2 g) were weighed into 15 mL tubes, and 8 mL of deionized water and 2 mL of F solution was added. The solutions added contained F at concentrations of 0, 0.26, 1.1, 2.6, 6.6, 13, and 26 mM, yielding final nominal F concentrations of 0, 0.053, 0.22, 0.52, 1.3, 2.6, and 5.2 mM (0, 1, 4, 10, 25, 50, and 100 mg/L) with corresponding pH values ranging from 6.5 to 7.3. The lower F concentrations used were similar to those of irrigation waters, but much higher values were also used because preliminary experiments showed that these concentrations were required in order to reach maximum sorption. For each soil, a control (i.e., without soil) was included to allow for the measurement of the F added. Samples were shaken for 24 h on an end-over-end mixer[13] and centrifuged for 5 min. Then, 2 mL of the supernatant was mixed with 2 mL of total ionic strength adjusting buffer (TISAB, containing 1 M acetic acid, 1 M NaCl, and 4 g/L CDTA),[27] and the activity of the F^- was measured using an F^- ion selective electrode (TPS IONODE IJ-F, Australia). The pH of the supernatant was measured following shaking, with the pH increasing an average of 0.64 unit following addition of F (Figure S1, Supporting Information).

Second, following its adsorption to the soil matrix, desorption of F was investigated. Subsamples of untreated soils (2 g) were weighed into 15 mL tubes, and 10 mL of artificial groundwater was added containing F at a concentration of either 0.26 or 6.6 mM. Thus, the desorption study consisted of two F concentrations with seven soils (some with three layers), each with three replicates, and with triplicate blanks (controls, with no soil). Soils were allowed to equilibrate with F solution in an end-over-end mixer for 7 days and the samples centrifuged. The supernatant was removed, and the F^- activity was measured following the same procedure outlined above. The supernatant was replaced with 10 mL of deionized water, the sample was resuspended, and the tube was shaken for 1 h before the supernatant was again removed for the measurement of F^-, determining the F desorbed. This desorption process (i.e., addition of water, resuspension, and subsequent removal of supernatant) was repeated a total of seven times.

For statistical analysis of adsorption and desorption, the free F^- (mM) and bound F (mmol/kg) of the adsorption experiment were fitted by nonlinear regression to the Langmuir adsorption isotherm (SigmaPlot 12.3, Systat Software Inc., Chicago, IL, USA) given as

$$Q = Q_{max}\frac{K[A]}{1 + K[A]} \quad (1)$$

where Q is the adsorption capacity, Q_{max} is the maximum adsorption capacity, K is the binding strength, and A is the concentration of F at equilibrium (or free F). Relationships between K and Q_{max} were investigated using Pearson's correlation coefficient (Minitab 16, Minitab Inc., State College, PA, USA).

Experiment 2: Uptake of F by Roots. This experiment aimed to investigate the root uptake of F from four F-loaded soils using leucaena (*Leucaena leucocephala* (Lam.) de Wit ssp. *glabrata* cv. Tarramba), lucerne (*Medicago sativa* L. cv. L91), and Rhodes grass (*Chloris gayana* cv. Top Cut). The three plant species were grown on four of the soils used in experiment 1 (red Ultisol (0−15 cm), yellow Ultisol (0−15 cm), red Vertisol (0−15 cm), and sand) which were loaded with four levels of F: control (0), 2.6, 7.9, and 26 mmol of F/kg of soil (0, 50, 150, and 500 mg of F/kg). The maximum concentration used (26 mmol of F/kg soil) was equivalent to the application of 200 ML/ha water containing 0.26 mM F (5 mg/L F) to the top 20 cm of the soil (assuming an annual irrigation rate of 8 ML/ha, this a loading for ca. 25 years). Thus, there were 12 treatments per soil type (three species and four F concentrations) with four replicates. In addition, there were also three pots of each treatment with no plants. This gave a total of 51 pots per soil and 204 pots across the entire study, which were arranged in a completely randomized design.

In order to incorporate the F, each soil (excluding sand) was weighed and divided into four samples. For three of these samples, F (as NaF) was dissolved into 5 L of deionized water and sprayed evenly across the surface of the soil. The soil was mixed thoroughly while the 5 L of F solution was being applied. Due to its low adsorption capacity, F was added to sand by adding the F to the amount of water required for each pot to reach field capacity (1 L). The soil was placed in pots (200 mm, holding ca. 6 kg of soil per pot), and the pot was wrapped in reflective insulation foil and positioned on a capillary watering bench to reduce leaching through the pot and maintain constant water content within the soil. White polypropylene beads were placed on the top of the soil to reduce evaporation, and a basal application of "Flowfeed EX7" (21 N:3.3 P:17.4 K + trace elements) fertilizer (1 g/L) was added every 2−3 weeks.

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Approximately 20 seeds were sown in each pot, and germination was good for all treatments other than the F-containing sand treatments, where no seeds were observed to germinate in the 7.9 and 26 mmol F/kg treatments (and only low germination took place in the 2.6 mmol of F/kg treatment). For these sand treatments, seeds of all species were germinated in the laboratory before transplanting; however, there was again 100% mortality. Following their establishment, seedlings were thinned to three plants per pot and grown for 8 weeks during summer. During this growth period, average minimum temperatures were 22 °C with average maximum temperatures of 33 °C, with typical photosynthetically active radiation levels during the middle of the day of 1500 μmol of photons m^{-2} s^{-1}. The above-ground plant material was harvested, weighed, and dried in an oven at 60 °C for 4 days.

Soil solution was extracted from the soil using centrifugation.[28] The solution was analyzed for pH and F (1:1 with TISAB). To determine the concentration of F within the plant tissues, samples were prepared for NaOH fusion.[29] Prior to the measurement of F, the solution was mixed 10:4 with concentrated TISAB buffer to ensure pH 5.4 and to prevent the F from forming complexes that would interfere with the measurement of F. Our calculations indicate a 10-fold excess of CDTA over Al ions in the assays, with CDTA effectively complexing all soluble Al in soil solution. Activities of the free F^- ion in the solutions were determined by a F ion selective electrode.

The data were analyzed using a two-way analysis of variance (ANOVA) to investigate the relationships between F additions to soils, soil types, and plant species. The F concentration of soil solutions of the four soils was also investigated by conducting a two-way ANOVA, although sand treatments were removed for the soil F concentrations, as the variance did not conform to the normal distribution. Statistical analysis was conducted using Genstat (VSN International, Hemel Hempstead, U.K.) and Minitab 16.

Experiment 3: Foliar Retention of F. This experiment aimed to investigate foliar retention of F from direct contact between foliar surfaces and groundwater containing F. In systems irrigated with coal seam water (as with other systems), foliage will also occasionally be rinsed with low-F water (for example, rainfall). This would potentially remove much of the F previously accumulated on the foliage. To separate the effect of root uptake from foliar adsorption, we grew plants in an oxisol (Table S2, Supporting Information), since this soil had a very high F adsorption capacity and limited plant uptake of F from the soil. Furthermore, the soil surface of the pots was covered with plastic sheets to minimize the infiltration of irrigation water into the soil.

This experiment consisted of the three plant species utilized in experiment 2 and four F concentrations in artificial groundwater (0, 0.053, 0.16, or 0.26 mM, added using NaF and verified by measurement using an ion-selective electrode), each with three replicates arranged in a randomized block design totaling 36 pots (each pot containing three plants). The highest concentration of F utilized for experiment 3 (0.26 mM) represents the highest concentration of F generally found in the groundwater of the Great Artesian Basin (95% of groundwater wells having ≤0.26 mM F).[6] After an initial growing period of ca. 8 weeks, plants were overhead-irrigated twice weekly using irrigation chambers connected to a pump and a 100 L drum containing one of the four F treatments. The 100 L of water was irrigated per treatment, taking around 30 min. Plants were irrigated with the F-containing solutions a total of eight times. To investigate whether any F retained on the leaf surface could be subsequently leached by application of good-quality water following these eight F irrigations, the plants were irrigated with deionized water for 10 min to simulate a rainfall event, allowed to dry overnight, and harvested. Plants were allowed to grow for a further 2 weeks to see if any F remaining in the plant foliage was volatilized and lost over time.

Plant foliage was randomly harvested after 0, 4, and 8 irrigations with F treatments. Plant tissue samples were also collected following irrigation with deionized water and after the subsequent 2 week growth period. Foliar concentrations of F were measured after NaOH fusion (see experiment 2) using an F ion selective electrode, as discussed previously. Approximately 300 g of soil from five randomly selected pots of each treatment (20 pots in total) was collected and the soil solution extracted by centrifugation, as outlined in experiment 2.

Statistical analyses were conducted in Genstat and Minitab 16, with the relationship between number of irrigations and plant F concentrations investigated using a two-way ANOVA. Similarly, the relationship between plant species and F in irrigation water was investigated using a two-way ANOVA.

RESULTS

Experiment 1: Soil F Adsorption and Desorption. The seven soils varied substantially in their capacity to adsorb F—a Langmuir adsorption isotherm could not be fitted to the sand due to its low adsorption capacity (Figure 1 and Table 1). The

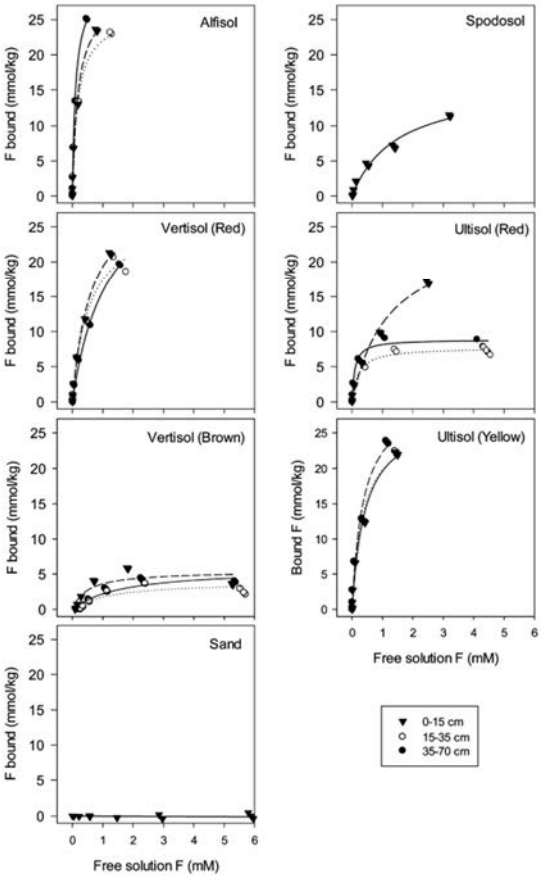

Figure 1. Adsorption isotherms of F for seven different soils (experiment 1) fitted using the Langmuir equation.

lowest binding strength was observed for the brown vertisol (K = 0.6–2.0 mmol/L) and spodosol (K = 0.7 L/mmol), suggesting that these soils weakly bind F. The highest sorption capacity (Q_{max}) was determined for the yellow ultisol (Q_{max} = 26.7–30.3 mmol/kg), alfisol (Q_{max} = 25.8–30.6 mmol/kg), and red vertisol (Q_{max} = 26.7–34.2 mmol/kg) (Figure 1 and Table 1). Interestingly, the red ultisol was the only soil to differ substantially in F sorption on comparison of different layers through the soil profile, with the surface layer (0–15 cm) having a Q_{max} value of 24.7 mmol/kg, decreasing to 8.8 mmol/

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Table 1. Langmuir Sorption Parameters Q_{max} (Maximum F Adsorption Capacity) and K (F Binding Strength) For Six Soils (All with Three Layers Excluding the Spodosol) Investigated in Experiment 1[a]

soil	depth (cm)	Q_{max} ± SE (mmol/kg)	K ± SE (L/mmol)	R^2
ultisol (red)	0–15	25 ± 1.5	0.8 ± 0.1	0.987
	15–35	7.7 ± 0.2	4.9 ± 0.6	0.986
	35–70	8.8 ± 0.3	11 ± 2.2	0.960
ultisol (yellow)	0–15	30 ± 2.0	2.7 ± 0.5	0.974
	15–35	27 ± 1.3	2.9 ± 0.4	0.981
	35–70	30 ± 2.0	2.7 ± 0.5	0.974
vertisol (brown)	0–15	5.4 ± 0.7	2.0 ± 0.7	0.768
	15–35	4.0 ± 0.7	0.8 ± 0.3	0.736
	35–70	5.8 ± 0.8	0.6 ± 0.2	0.854
vertisol (red)	0–15	31 ± 1.4	1.6 ± 0.2	0.992
	15–35	27 ± 1.4	1.9 ± 0.2	0.985
	35–70	34 ± 1.8	0.8 ± 0.1	0.994
alfisol	0–15	29 ± 1.0	5.5 ± 0.6	0.991
	15–35	26 ± 0.7	5.7 ± 0.5	0.990
	35–70	31 ± 1.0	9.0 ± 0.8	0.990
spodosol	0–25	16 ± 1.2	0.7 ± 0.1	0.979

[a]The values were determined by nonlinear regression, and the regression parameter R^2 is shown in the last column. The sand is excluded due to inability to fit data to the Langmuir equation with low adsorption capacity.

kg at 35–70 cm depth, whereas the binding strength increased with depth, from K = 0.8 L/mmol in the 0–15 cm layer to 11.4 L/mmol in the 35–70 cm layer.

Next, the desorption of F was investigated. As expected, the extent of F desorption increased with increasing washing steps, with ca. 20–80% of the F desorbed after seven washes (Table 2 and Figure S2 in the Supporting Information). A notable exception was the brown vertisol, which desorbed more F than was initially added in the 15–35 cm (188%) and 35–70 cm (159%) layers (Table 2), thereby indicating that this soil already contained appreciable F. In general, more F was desorbed from soil treated with a higher F concentration (6.6 mM vs 0.26 mM) (Table 2). Importantly, the desorption of F was significantly correlated (negatively) to the K value estimated by the Langmuir equation for both low (0.26 mM) and high (6.6 mM) F treatments (r = −0.54 and −0.68, respectively; P < 0.05), thereby indicating that the binding strength (K) would appear to be a useful measure for predicting the F retention capacity of the soils examined. For example, in the red ultisol, as K increased from 0.8 (0–15 cm depth) to 11.4 (35–70 cm depth), the extent of F desorption decreased from 63 to 38% (Tables 1, and 2 and Figure S2 in the Supporting Information).

Table 2. Desorption of F from Six Soils to Which F Had Initially Been Equilibrated for 7 Days using Solutions Containing F at a Concentration of either 0.26 mM (Low) or 6.6 mM (High) (Experiment 1)

		cumulative F desorbed (%)	
soil	depth (cm)	low F addition	high F addition
ultisol (red)	0–15	30.0 ± 0.3	62.9 ± 0.2
	15–35	20.0 ± 0.4	47.6 ± 0.4
	35–70	17.3 ± 0.8	38.0 ± 0.1
ultisol (yellow)	0–15	29.0 ± 0.4	53.3 ± 0.7
	15–35	25.2 ± 0.2	46.0 ± 0.5
	35–70	23.4 ± 0.0	36.1 ± 0.0
vertisol (brown)	0–15	64.3 ± 0.1	49.3 ± 0.3
	15–35	188.0 ± 8.0	99.0 ± 2.3
	35–70	159.0 ± 0.0	59.1 ± 0.0
vertisol (red)	0–15	48.6 ± 0.9	52.8 ± 0.2
	15–35	52.3 ± 0.5	55.8 ± 0.8
	35–70	77.4 ± 2.6	43.7 ± 1.1
alfisol	0–15	38.4 ± 0.9	45.4 ± 0.4
	15–35	43.5 ± 2.2	40.3 ± 1.4
	35–70	25.6 ± 0.6	27.1 ± 0.1
spodosol	0–15	79.0 ± 2.0	78.5 ± 1.6

Experiment 2: Uptake of F by Roots. The addition of F influenced plant growth to varying extents depending upon the soil type. For the sand, growth was reduced substantially, with almost complete mortality in most of the F-containing treatments. In the yellow ultisol, dry matter of lucerne and Rhodes grass decreased significantly as the F-application rate was increased from 0 to 26 mmol/kg but the dry matter of leucaena was unaffected. In the red ultisol and red vertisol, the addition of F to the rooting environment had no significant effect on the dry matter of the plants (P > 0.05).

For this experiment, increases in soil solution F concentrations followed trends expected from the Q_{max} and K values obtained in the laboratory-based study (i.e., experiment 1). For example, when F was added at a rate of 26 mmol/kg, soil solution concentrations of F were highest in the sand (96 mM), followed by the red ultisol with 4.5 mM, the yellow ultisol with 1.0 mM, and the red vertisol with 0.58 mM (see Figures 1 and 2 and Table 1). For the red ultisol, the addition of F increased the pH of soil solution by ca. 3 pH units, with the increase in the other soils being ca. 1 pH unit (Figure S3, Supporting Information). Interestingly, the pH in the solutions of soils growing Rhodes grass was higher than those for lucerne and leucaena in red ultisol, yellow ultisol and red vertisol in every F treatment (excluding red ultisol 26 mmol F/kg; Figure S2, Supporting Information)—this requires further investigation.

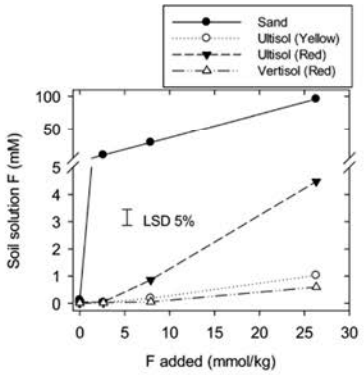

Figure 2. Soil solution F concentration (averaged across all three plant species) for four soils treated with increasing concentrations of F (0, 2.6, 7.9, or 26 mmol F/kg, experiment 2). The vertical bar represents the least significant difference (LSD, 5%) to allow comparison either between soils at a single rate of F or between F rates for the same soil.

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Given the increase in soil solution F concentrations (see above), it was also not surprising that the addition of F to soils increased the foliar concentrations of F (Figure 3). A significant

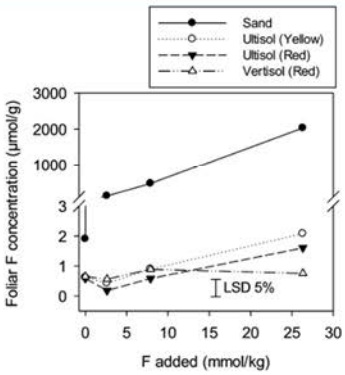

Figure 3. Concentration of F in plant foliar material (averaged across all three species) grown on four soils treated with increasing concentrations of F (0, 2.6, 7.9, or 26 mmol F/kg, experiment 2). The vertical bar represents the least significant difference (LSD, 5%) to allow comparison either between soils at constant F or between F concentrations for the same soil.

interaction ($P < 0.001$) was found between the soil type and the rate of F addition, indicating that while the addition of F to the soil significantly influenced the concentration of F in plant material, the pattern of this response varied for each soil (Figure 3). Indeed, the increase in foliar F was greatest in sand (increasing from an average of 1.9 to 2000 μmol F/g) and least for the red vertisol (increasing from an average of 0.63 to 0.74 μmol F/g) (Figure 3). The uptake of F was influenced not only by soil type but also by plant species. For the yellow ultisol, red ultisol, and sand (but not the red vertisol), analyses of individual plant species identified a significant interaction between the rate of F addition and plant species ($P < 0.001$) (Figure 4). For example, in the sand, yellow ultisol and red ultisol treated with 26 mmol of F/kg, lucerne accumulated significantly more F in the foliage than did Rhodes grass or leucaena.

To determine the factors regulating the uptake of F from the soil solution, the foliar concentrations were first related to total concentrations of F in the soil solution. When the foliar concentrations of F were examined across the different soils, data for the sand had to be excluded from linear regressions, as these high F concentrations had statistically high leverage. Across the remaining three soils, the foliar F concentration was not related to the total concentration of F in the soil solution for either Rhodes grass ($R^2 = 0.079$) or leucaena ($R^2 < 0.001$), although a weak relationship was found for lucerne ($R^2 = 0.539$) (Figure 5). These differences between species are perhaps not surprising, given that lucerne was the only species in which tissue F concentrations increased substantially (excluding the sand treatments) (Figure 4). Unsurprisingly, when the foliar F concentrations were examined for each soil individually, the relationship was also generally poor (other than for the sand) (Figure S4, Supporting Information). Given the lack of relationship with the total soluble F concentrations, thermodynamic modeling was also conducted using PhreeqcI v3.1.2 (Minteq database) to determine if the F concentration in the foliage was related to the speciation of F in the soil solution.

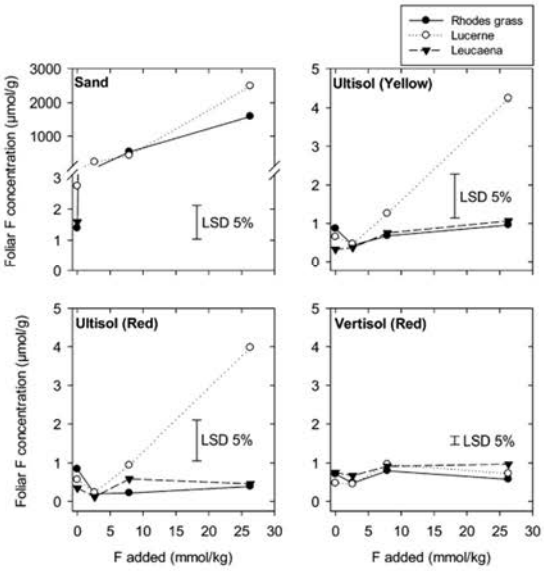

Figure 4. Foliar F concentrations of Rhodes grass, lucerne, and leucaena grown on four soils (a sand, a yellow ultisol, a red ultisol, and a red vertisol) treated with 0, 2.6, 7.9, or 26 mmol F/kg (experiment 2). Due to greatly reduced growth, leucaena plants in the 2.6, 7.9, and 26 mmol F/kg treatments could not be analyzed in the sand due to insufficient dry plant material. The vertical bar represents the least significant difference (LSD, 5%) to allow comparison either between plant species at constant F or between F concentrations for the same species.

As expected, the speciation of F varied substantially between soils, with F present predominantly as the free F^- ion in both the Red Ultisol and the Sand but as Al−F complexes in the yellow ultisol (data not presented). Although various relationships were observed using this thermodynamic modeling, no consistent relationship was found across all four soils and three plant species (data not presented).

Experiment 3: Foliar Retention of F. Overhead irrigation of F-containing groundwater was found to influence the foliar F concentration (Figure 6a). The accumulation of F in the foliage resulting from soil uptake was negligible, given that the concentration of F within the soil solution of the oxisol averaged across all four treatments was <0.003 mM (cf. experiment 2; see Figure 2 for example).

A significant interaction was found between increasing irrigations of F-containing water and plant species ($P < 0.001$), indicating that not only does the cumulative application of F in irrigation water increase foliar F concentrations but also the pattern of response differs between plant species (Figure 6a). Lucerne was found to retain the highest concentration of F in the foliar material; after four irrigations (second harvest) with 0.26 mM irrigation water, the concentration of F in lucerne foliar tissues increased from 0.37 to 1.7 μmol F/g, and following eight irrigations (third harvest) the plant material increased further to 2.3 μmol F/g: a ca. 6-fold increase ($P < 0.05$, Figure 6a). Conversely, increases in tissue concentrations were more modest for the other two plant species, increasing from 0.53 to 0.79 μmol of F/g for Rhodes grass and 0.37 to 1.1 μmol of F/g for leucaena after eight irrigations at ca. 0.26 mM (Figure 6a). The concentration of F within the irrigation water

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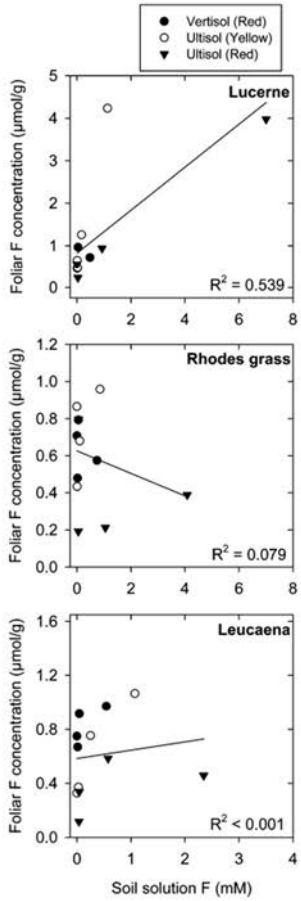

Figure 5. Relationship between the concentration of F in the foliar tissues of three plant species (lucerne, Rhodes grass, and leucaena) with the total concentration of F in the soil solution (experiment 2). Data are presented for three soils, but the data for the sand were excluded because these values had statistically high leverage. Note that the scales are not constant.

also had a significant effect on foliar F concentrations, with a significant increase in tissue F concentrations when the F concentration of the water was raised from 0 to ca. 0.16 and 0.26 mM (Figure 6b).

After eight irrigations with F-containing groundwater, deionized water was applied to simulate rainfall and to investigate the potential leaching of F from the foliage. Relative to tissue concentrations after eight irrigations with water containing ca. 0.26 mM, tissue concentrations decreased significantly (from 2.4 to 1.5 μmol of F/g) for lucerne but there were no significant differences for the two other plant species (Figure 6a). For groundwaters containing lower concentrations of F, the effect of rainfall on tissue F concentrations was not clear (Figure 6b). Allowing the plants to grow undisturbed (i.e., no overhead irrigation) for a further 2 weeks after the simulated rainfall generally had no significant effect on tissue concentrations (Figure 6, $P > 0.05$).

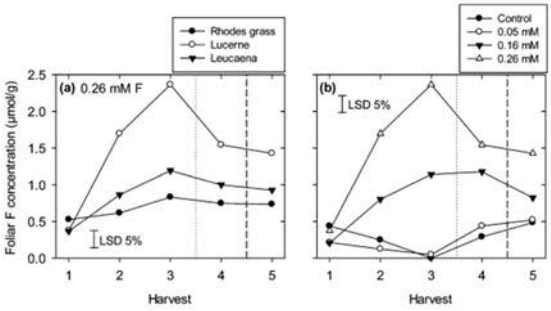

Figure 6. Concentrations of F in plant foliage following four irrigations (harvest 2) or eight irrigations (harvest 3) with artificial groundwater containing F (experiment 3). Plants were then irrigated with deionized water (harvest 4) and grown for a further 2 weeks without overhead irrigation (harvest 5). (a) Concentrations of F in foliage of Rhodes grass, lucerne, and leucaena irrigated with water containing F at a concentration of 0.26 mM. (b) Concentrations of F in the foliage of lucerne irrigated with water containing F at a concentration of 0, 0.053, 0.16, or 0.26 mM. The vertical bar represents the least significant difference (LSD, 5%) to allow comparison between harvests for a single treatment or between treatments for a single harvest.

■ DISCUSSION

Both the direct addition of F to soils and the foliar retention of F-containing irrigation water resulted in increases in the foliar F concentration. However, under the current experimental conditions, these increases in foliar F concentrations through either pathway were modest and concentrations generally remained lower than the MTL of 1.8 μmol/g (35 mg/kg) for cattle (excluding plants grown on sand). For example, even when F was added at a rate of 26 mmol/kg (this soil concentration would be reached after irrigation with water containing 0.26 mM at a rate of 5 ML/(ha year) for 25 years), most plant tissue concentrations were <1 μmol/g (with the highest values being for lucerne, 4.2 μmol/g; Figure 4) and hence were generally was less than the MTL of mature beef cattle (2.6 μmol/g), sheep (3.2 μmol/g), chickens (10 μmol/g), and swine (7.9 μmol/g).[4] Furthermore, with addition of F at a rate of 7.9 mmol/kg (i.e., reached after 8 years of irrigation at 5 ML/(ha year) with 0.26 mM) plant foliar tissues did not increase above 1.3 μmol F/g in any treatment, this being less than the MTL for young beef calves and heifers, 1.8 μmol F/g.[4] Therefore, for short- to medium-term irrigation projects (for example, irrigation to establish forestry or grazing systems), the addition of realistic rates of F-containing groundwater is unlikely to increase the soil F concentrations in soils (excluding highly sandy soils) to levels above which plant uptake of F from the soil may affect grazing animals.

These conclusions need to be considered carefully before extrapolating to other situations. For example, the present study examined the irrigation of F-containing water in short- to medium-term systems, but long-term irrigation with water containing high concentrations of F would result in the addition of F at levels higher than those considered here. Also, it is apparent that both the soil type and the plant species influences the retention and uptake of F, with the present study only examining seven soils and three plant species. Finally, irrigation of water with F concentrations lower or higher than this value would also alter the volume of water that could be safely irrigated.

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Variation in the Concentration of F in the Soil Solution Depending upon the Soil Type. The extent to which F was available in the soil solution varied substantially depending upon the soil (Figure 1). In the laboratory (experiment 1), the relationship between F adsorbed and F remaining free in the soil solution could be estimated using the Langmuir equation, with Q_{max} providing an estimate of maximum adsorption capacity and K providing an estimate of the binding strength (Figure 1 and Table 1). Similarly, in the greenhouse (experiment 2), the concentrations of soluble F in the soil solutions were related to the Langmuir parameters determined in experiment 1, with total soil solution F present in the 26 mmol of F/kg treatment in the order (decreasing) sand > red ultisol > yellow ultisol = red vertisol (Figure 2). Thus, adsorption isotherms are likely to be useful for (i) identification of soils which are likely to be unsuitable for irrigation with F-containing waters (such as the sand in the current study) and (ii) estimation of the volume of irrigation water which could be applied before the concentration of F in the soil solution exceeds a given threshold (for example, the concentration of F permitted in drainage water). However, within the range of relevance to the MTLs, the relationship between the concentration of F in the foliage and the concentration of F in the soil solution was comparatively poor (see next section). It is known that adsorption (and therefore the amount of F remaining in solution) is determined by a number of factors, among them pH, ionic strength, presence of poorly crystalline Fe and Al hydrous oxides, and clay mineralogy,[13,14,17,30−32] and these factors have differed between the soils used in this study (Tables S1 and S2, Supporting Information). However, there were no clear relationships between these soil factors and the F uptake in this study, likely due to the limited number of soils used.

It was also decided to investigate the desorption of F, given that it is this desorption (i.e., movement back into the soil solution) which will result in a buffering of the F concentration in the soil solution. The desorption of F from all soils was significantly correlated (negatively) to the estimated K, indicating that desorption capacity of soils can be estimated from the Langmuir adsorption parameters. The desorption of F was in the range of ca. 20−40% for soils with high K values, increasing to 60−80% for soils with low K values (Tables 1 and 2). As expected, the proportion of F that desorbed increased as the rate of F addition increased (Table 2), most likely due to the fact that high affinity binding sites for F become saturated, resulting in F being less strongly bound as the rate of F addition increases. It was also noted that the desorption of F decreased when adsorption equilibrium time increased (data not presented) due to the occurrence of slower reactions such as CaF_2 (fluorite) precipitation and diffusion into pores.[9,11] This indicates that desorption rates observed in the present study would likely be reduced further following an increase in equilibration time, as would occur in the field.

Uptake of F from the Soil Solution and Its Accumulation in the Foliage. The accumulation of F in the foliage varied substantially depending upon both the plant species and the soil type (Figures 3 and 4). Under the present experimental conditions, lucerne was the only plant species which accumulated F in the foliage to concentrations >1.3 μmol F/g (excluding sand), although the reason as to why lucerne accumulates more F than other species is not known. Interestingly, Hansen et al.[33] also found lucerne concentrated high F in foliar material, with 5.3 μmol of F/g observed when soils were loaded with ca. 84 mmol of F/kg. Similarly, tissue concentrations of up to 3.4 μmol of F/g were found in lucerne grown in acid soil amended with flue gas desulfurization gypsum.[34] More study is required in this regard, but it is possible that Rhodes grass and leucaena are F excluders, and hence the concentration of F within their tissues was not closely related to F availability within the soil. It is also possible that water use efficiency is lower for lucerne than for other species, resulting in greater F uptake; alternatively, translocation of F complexes in the xylem differs between plant species and it has been suggested that Ca limits translocation from roots to shoots either by membrane effects or by precipitation on the root surface.[30,34,35]

The accumulation of F in the foliage varied substantially depending upon the soil type (Figure 3). This was expected, given the differences observed in the adsorption capacities of these soils (Figure 1) and the resultant variations in soil solution F concentrations (Figure 2). However, despite being the immediately "plant available" fraction, soluble F in the soil solution was not generally related to the concentration of F in the foliage (Figure 5). Similarly, there was no consistent relationship between F uptake and F speciation in the soil solution, with F uptake closely related to F^- activity in some soils but to the activity of Al−F complexes in other soils (data not presented).

Foliar Retention of F from Overhead Irrigation. The overhead irrigation of water containing F at a concentration of 0 or 0.053 mM had no observable impact on the foliar concentrations of F (Figure 6). However, for water containing F at a concentration of either 0.16 or 0.26 mM, overhead irrigation resulted in significant increases in the foliar F concentration (Figure 6). This finding is in agreement with the study of Wallender and Keller,[25] who found that foliar concentrations of F in bush beans increased with increasing concentrations of F in the irrigation water. In the present study, lucerne was the only species to concentrate F in foliar material above the MTL (1.8 μmol/g) following eight consecutive irrigations with water containing 0.26 mM (Figure 6)—further investigation is needed in this regard. For example, it is known that cuticular thickness, cuticular composition, and stomatal density influence the uptake/absorption of foliar applied elements.[36]

The finding that overhead irrigation with good-quality water reduced foliar F concentrations (at least somewhat) is similar to the observation of Maclean et al.,[37] who, in a study of lucerne and tall fescue grass (*Festuca arundinacea*) exposed to atmospheric F, also found that rainfall (or washing with detergent) reduced the foliar concentration of F. Several mechanisms may result in a decrease in tissue F concentrations, including growth dilution, leaf death, translocation, or volatilization, with the last mechanism considered a major contributor of F removal from plants.[38] Therefore, to investigate this possibility, plants were grown without overhead irrigation for another 2 weeks following the irrigation with deionized water. During this time, foliar F further reduced slightly for plants in the 0.16 and 0.26 mM treatments (although this decrease was significant only in lucerne irrigated with 0.16 mM F) (Figure 6). It is known that HF is volatile, and hence if F is on the leaf surface or within foliar material, it is possible that volatilization will occur. However, in the present study, allowing the plants to grow undisturbed (i.e., without overhead irrigation) generally had no significant effect on tissue concentrations of F (Figure 6), possibly because plants were

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only grown for 2 weeks before harvest, thereby potentially limiting volatilization.

The present study has examined the accumulation of F within soils and plants on irrigatation with F-containing groundwater. Generally, under the current experimental conditions, F did not accumulate in plant foliage to levels likely to be deleterious to grazing fauna, even when used at rates equivalent to irrigation for 25 years (assuming irrigation at a rate of 5 ML/(ha year) with water containing F at a concentration of 0.26 mM). First, when the F was added to the soil, the extent to which the soluble F concentration increased varied significantly between soils. Given that the extent to which F accumulated in the foliage did not appear to be related to the total concentration of F in the soil solution, it would be difficult to accurately predict the amount of F which could be added to the soil before the MTL would be exceeded. In addition, the extent to which F accumulated in the plant foliage varied depending upon the species (being greatest in lucerne). Second, when water was overhead-irrigated, foliar F concentrations increased in all three species due to foliar contact with F-containing water. However, lucerne was again the only species which accumulated foliar F above MTL for young beef cattle. The data presented here regarding the behavior of F in soils and plants will assist in the rigorous regulation of the maximum volume of F-containing water per soil type and crop species to ensure maximum productivity while simultaneously minimizing potential environmental harm.

■ ASSOCIATED CONTENT

Supporting Information

Detailed description of the chemical properties of the soils used in the experiments (Table S1), soil mineralogy (Table S2), changes in soil solution pH following addition of F in experiment 1 (Figure S1), cumulative desorption of F from the soils (Figure S2), changes in soil solution pH following addition of F in experiment 2 (Figure S3), and the effect of soil solution F concentrations of foliar F concentrations (Figure S4). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.5b01001.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS USED

ANOVA, analysis of variance; K, Langmuir binding strength for F; MTL, maximum tolerable level; Q_{max}, Langmuir maximum sorption capacity for F

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