ENVIRONMENTAL MANAGEMENT PERSPECTIVES OF SOIL FLUORIDE IN NEW ZEALAND'S AGRICULTURAL SOILS

A thesis presented in partial fulfilment of the requirements for the degree of

Master in Environmental Management

at the Institute of Agriculture and Environment,

Massey University, Palmerston North, Manawatu, New Zealand

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2017

To the people running in my veins,
And to those who made an impact in my life, here and there

Abstract

The prolonged use of phosphate (P) fertilisers has inherited an accumulation of F in topsoils and it is considered to be building up in most of New Zealand's (NZ) agricultural soils. New Zealand research into soil F has been hampered by the lack of a reliable and simple test for soil F. The accuracy of different methods to quantify the presence of F in analytical preparations is dependent on interfering elements such as the aluminium (Al) content of the sample. The conventional methodology of NaOH fusion with an ion-specific electrode method is considered to be time consuming, expensive and very dependent on the abilities of the operating technician, thus it is not ideal for environmental monitoring.

To improve the traditional method, an alternative technique to the standard fusion protocol was developed by the Fertilizer & Lime Centre Research (FLRC), Massey University, and that found that simple extraction of soil with dilute sodium hydroxide four molar (NaOH 4M) consistently reported 80% of the total soil F across volcanic soils. The initial FLRC initial work was further examined in this research to confirm the repeatability of the NaOH extraction technique to quantify soil F in a range of NZ soil orders. Also, to assess the relative accuracy of the NaOH extraction technique across different NZ soil orders by comparing different NaOH concentrations.

The main aim was to compare different methods and NaOH concentrations to determine total soil F on a representative range of soil orders collected from 13 agricultural sites with a long-term P fertiliser application background. The variability between soils orders was assessed as a function of soil properties. Furthermore, microbiological analyses were performed to assess the impacts of total F, as determined by NaOH extraction method, on soil microbial activity. This study also provides a discussion on the environmental management implications of the emerging F issue in the NZ pastoral land.

The total soil F concentration across seven different soil orders ranged between 152 mg F kg^{-1} and 708 mg F kg^{-1}. The NaOH extraction method showed significant correlation with the alkali fusion/ISE technique ($r>0.92$). The accuracy of the F determination is very dependent on interfering elements such as Al/Fe oxy-hydroxide content, and NaOH 10M extraction method showed the lowest variation within allophane-rich soils compared to the 4M and 16M extractions. Results suggest that the NaOH 10M method can be used for wide-scale

environmental studies and monitoring programmes across a variety of New Zealand soils, particularly for Allophanic soils.

A significant correlation was found between dehydrogenase enzyme activity (DHA) and the labile or total Al and Fe content ($r>82$), whereas the microbial biomass carbon (Cmic) was positively correlated with the non-labile Al and Fe fraction in soils ($r>0.89$). These findings indicate that these microbial parameters can be used for environmental monitoring programmes. The DHA can be used to assess the effects of the labile F to microorganisms and the Cmic variable could be used as an indicator of the total F effects to livestock.

Acknowledgements

Above all, the love I share with the ones I care for is my one and only provider of all, without this source, nothing would have been possible so far in my life.

To my beloved family: Marta, Marce, Milu, Olivia, Sam and Fabi, endless thanks for your love and support, despite the distance I've always felt you close. To my grandfather, Piito Jover, who has always shown strength and perseverance and taught us how to keep things simple in life. Special mention goes to my recently passed away grandmother, Ropi Rahal, who made a huge impact on my life, and to whom I owe my passion for cook and travel.

I thank my supervisor, Dr Chris Anderson, for helping me conclude this thesis and for his support. Also, I thank my co-supervisor, Dr Paramsothy Jeyakumar, for his patience and guidance during my laboratory and data workings.

To the Ministry of Foreign Affairs and Trade (MFAT) for giving me the unique opportunity to study a higher education degree overseas by awarding me with the New Zealand Development Scholarships (NZDS). It has been one of my best experiences and New Zealand will remain in my heart forever.

To the Fertilizer & Lime Research Centre (FLRC), Massey University for supporting this project. To the international student support office (ISSO) staff at Massey University, for always disperse my worries and doubts, and giving me the support I needed every time I run to their office looking for help and advice, especially Jamie Hooper.

Also, my appreciation to Dr Mike Bretherton for his contribution to the soil description section for this study and to Matthew Taylor for his collaboration on providing very useful information on soil fluoride.

To the Institute of Agriculture and Environment staff, the soil science laboratory staff at Massey University and to the postgraduate students who offered their support during my laboratory work and helped me with sampling or clarifying some uncertainties. Each one of you helped me somehow to conclude this work: John Holland, Karen Hytten Ian Furkert, James Hanley, Glenys Wallace, Bob Toes, Quang Mai, Ross Wallace, Peter Bishop, Geretharan Thangavelautham, Grace Chibuike, Roberto Calvelo, Kamal Prassad, Aaron Stafford and Hadee Thompson-Morrison.

I am deeply grateful to Stefanía Romero and Julia Bohórquez for their input and time to read and discuss my work. Also, to Aniek Hilkens and Florentine van Noppen who made things much easier during the struggle. To my friends and the 92 Wood St family, my sincere thanks for your daily encouragement, patience, honesty and love, your hugs and smiles made all the difference. I will always carry you all in my heart. And finally, to friends in Paraguay, Dulce, Fede and Ayi for their words of alleviation, care and affection. You all contributed in relieving some of my stress out and cheered me up to get the confidence I needed to finish my studies.

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Chapter 1 Introduction

The importance of the primary sector in New Zealand is reflected in the total of this country's export revenues and gross domestic product and agriculture make up the majority of that total contribution. In order to support agricultural production, most of New Zealand's soils are fertiliser-dependent to provide the necessary nutrients for plant growth. Single superphosphate (SSP) is one of the most widespread fertilisers in New Zealand's pastoral land since it was first introduced. Phosphate (P) fertilisers carry impurities as trace elements that can accumulate in soils to toxic levels, and some of these elements are of emerging concern because very limited data is available on their fate and effects on the environment. Fluoride (F) is one of the P fertiliser-derived elements that is building up in fertilised land. Although there is sufficient data establishing the effects of F on livestock, very little is known about the implications of F on soil microorganisms of importance as major contributors to plant growth in pasture land. Some studies suggest that F might inhibit microbial activity in fertilised land. The agriculture sector benefits hugely from soil biological processes, mainly because of microorganisms participation in nutrient-fixing for pasture production.

Healthy soils enable land to sustain productivity as well as provisioning services to the environment, such as nutrient cycling and support for urbanisation, plants and other organisms (Dominati, Mackay, Green, & Patterson, 2011). Various activities such as fertilisers use can impact soil functioning and therefore, provision of ecosystem services such as productivity (Finvers, 2008). Correspondingly, assessing and monitoring soil functioning is considered one of the main aspects of environmental management for key contaminants occurring in agricultural soils such as F. Fluoride in soil matrices has been traditionally measured by the alkali fusion method, followed by determination with a fluoride ion specific electrode (ISE). The strong alkali condition in the fusion method is used to release F ions in soil samples. It was realised that requires labour-intensive preparation of samples with high accumulation of manual handling errors. In this matter, research into F concentrations in soil matrices has been hampered by a lack of a simple and reliable method to measure F relative to the traditional method (alkali fusion/ion specific electrode-ISE).

An alternative method for F analysis has been developed at Massey University in New Zealand by Jeyakumar and Anderson (2015), and obtained high F recovery levels (>80%) in a variety

of New Zealand soil orders from pastoral land. The development of a less-time consuming method that accurately measures F in a range of New Zealand agricultural soil orders is considered a milestone in environmental management strategies. Henceforth, validation of an alternative F quantification technique in a range of soil orders will assist in both monitoring programmes for soil protection and the development of soil guideline values in relation to the F issue. The present research was conducted to validate the repeatability and reproducibility of this new analytical technique to determine F in a wider range of soil orders. Therefore, results would provide sufficient evidence to suggest that the NaOH extraction followed by the ISE method is a reliable technique to accurately and consistently quantify F concentration in soils compared to the alkali fusion/ISE method.

Furthermore, the validated extraction method was used to investigate the potential effects of F on soil microorganisms. The degree of microbial activity is associated with the soil's function and hence, productivity, essentially because microorganisms participate in nutrient cycling and organic matter turnover. Consequently, the sustainability of agricultural systems can be threatened with a potential decline or rupture in specific biological processes occurring in the rhizosphere[1] and outside the rhizosphere in the bulk soil. Research results also provide insights into the environmental implications of F accumulation in agricultural soils, especially focused on land and farm management. The alternative method will also support future research on the impacts of soil F on biological receptors, assisting policy-making in developing risk-based regulations, as well as voluntary approaches, guaranteeing the food production sustainability of the country.

1.1. Objectives

Research was carried out to determine the relative accuracy of an alternative method to measure F in a varied range of agricultural soils orders and to assess the potential effects on soil biological processes. The study also revises the environmental management aspects of the implications of F accumulation in New Zealand agricultural soils. The specific objectives are to:

[1] Rhizosphere: portion of soil governed by the plant's root system in association with microorganisms (McNear Jr, 2013)

- Ensure the repeatability and reproducibility of the NAOH extraction method respect to the alkali/fusion method, tested at different concentrations in order to reliable quantify soil F in a range of soil orders.
- Assess the potential effects of total F concentrations on soil microbial activity.
- Review the environmental implications and management strategies of the emerging F issue in NZ agricultural land.

1.2. Thesis outline

The first chapter provides a general background on the thesis topic, as well as the relevance, aim and objectives of the research. The second chapter is a review of the relevant concepts related to the study and revises studies on soil F in agricultural soils, factors governing soil F retention in soils as well as the F sources and its effects on pastoral systems. In addition, it enumerates findings from similar studies on total soil F methods, F background levels in NZ soils and the effects of F on soil microbial activity.

Chapter 3 describes the methods and materials employed for the laboratory work, including a description of soil samples used for both F analysis and microbial tests, indicating data analysis and data quality control.

Chapter 4 presents the results of the study. The data obtained from the analytical work is presented in three separate sections. The first section describes properties of soils used for the F determination and microbiological analysis. The second section provides a comparison of the alkali fusion/ISE and NaOH extraction methods. The final section is dedicated to the effects of total F on soil microbial activity. This chapter also compares and discusses the results with findings from similar studies.

Chapter 5 summarises the environmental management implications of F as an emerging issue in the New Zealand agricultural context. It also summarises the most relevant outcomes of the research in accordance with the research aims, as well as giving conclusions and recommendations for further studies related to the research topic.

Chapter 2 Literature Review

2.1. Introduction

This chapter provides an overview of the sources and processes of soil F in agricultural soil in the New Zealand context, covering specific areas such as New Zealand agricultural sector and the use of P fertilisers

- Fluoride occurrence and sources in soils
- New Zealand agriculture and use of P fertilisers
- Phosphate-derived F in agricultural soils
- Factors influencing F accumulation in New Zealand agricultural soils
- Reported F effects on biological receptors, especially focused on grazing systems and potential environmental risks
- Soil F management aspects
- Fluoride measurement techniques

2.2. Fluoride occurrence and sources in soils

Fluorine is widely distributed on the earth's crust as F ions (F^-) and is one of the most reactive and electronegative of all elements so it cannot be found in its elemental form in nature. Fluorine occurs in the environment mainly as the minerals fluorapatite (Ca_5 $(PO_4)_3F$, calcium fluorophosphate), cryolite (Na_3AlF_6, sodium hexafluoroaluminate), fluorite (CaF_2, calcium fluoride) and topaz ($Al_2SiO_4(F,OH)_2$) (García & Borgnino, 2015). Inorganic and organic fluorides are naturally present in soil, water, plants and air, and it is an essential micronutrient for animals yet not for plants (Cronin, Manoharan, Hedley, & Loganathan, 2000; Hong et al., 2016). Nonetheless, at high intake dose and exposure levels, F can have harmful effects on humans, animals and plants (WHO, 2002).

Fluoride can be sourced from both natural and anthropogenic activities. The natural existence of F solutes in the environment is attributed mostly to the soil parent material. Deposits and volcanic emissions are some of the most important native F in soils. Human activities also contribute to the occurrence of F in the environment; to cite a few, fertiliser manufacturers, aluminium smelting, hydrogen fluoride (HF) alkylation in petroleum refining, glass manufacturing, cement manufacture, iron and steel manufacture and coal combustion can

increase the anthropogenic concentration of F^- in the environment (Arnesen, Abrahamsen, Sandvik, & Krogstad, 1995). The natural abundance of F in soils varies widely worldwide and the native F concentrations are dependent on atmospheric deposition, soil parent material and the cycling rate of F in the environment.

Fluorine can be expressed as both total F and labile F portions in soil samples. Labile F species are the soluble portion of total F that are readily available to plants and it is constantly undergoing chemical, physical, and biological breakdowns. The labile F portion can be extracted with water, acid and resin solutions and is generally one to three times lower than total F concentrations. Labile F appears to be more affected by industrial pollution and SP application, whereas total F is strongly influenced by prolonged and repeated P fertiliser application in grazing systems (Cronin et al., 2000). The bioavailability of soil F is dependent on the F chemical species occurring in soils and the concentration in solution. The different F species varies significantly between different soil types, because is related to the soil chemical composition (Weinstein & Davison, 2006). The most common F species occurring in soils are CaF_2 in calcareous soils and as AlF_x complexes in acidic soils (Tscherko & Kandeler, 1997).

2.2.1. Phosphate fertiliser-derived F

Phosphate rocks contain high amounts of P-bearing minerals such as limestones and mudstones. They are mined as a stock material to produce P fertilisers. Manufactured fertilisers contain F as a trace element, among others such as cadmium (Cd), arsenic (As), uranium (U), chromium (Cr), mercury (Hg), zinc (Zn), selenium (Se), lead (Pb) and vanadium (V). Most of these trace elements are contained in fertilisers mainly because there are no existent cost-effective manufacturing methods to remove them completely from final P products. Environmental risks are associated with many of these trace elements and there is the potential risk of accumulation in soils (Jiao, Chen, Chang, & Page, 2012). Table 1 shows some trace elements of environmental concern found in rock phosphates and average concentrations on the earth's crust (McLaughlin, Tiller, Naidu, & Stevens, 1996). As shown in Table 1, F concentration in phosphate rocks ranges from 1,900 mg F kg^{-1} P dw to 42,400 mg F kg^{-1} P dw, when the earth's crust average F value is only 270 mg F kg^{-1} dw (McLaughlin et al., 1996). After prolonged use of P fertilisers, potential risks of accumulation in agricultural soils are from As, Cd, Cr, F and Zn (M. McLaughlin et al., 1996). The final concentration of contaminants in P fertilisers will vary depending on the original concentration in the rock phosphate used to manufacture the

fertiliser. In addition, variation in the impurities content within fertilisers also occurs because there are no standardised protocols of approved raw materials recommended to be used to formulate fertilisers, this means that any material containing nutrients for plants can be processed to a fertiliser (Jiao et al., 2012).

Table 1. Trace elements in rock phosphate compared with average values on earth's crust

Trace element	Rock phosphate		Earth crust
	Minimum(*)	Maximum(*)	Average value(*)
U	<1	280	
Cd	1	90	0.5
F	19,000	42,400	270
Zn	<2	2,412	50
As	2	300	5

(*) mg kg^{-1} dry weight (dw)
Modified after M. McLaughlin et al. (1996)

The largest source of P in New Zealand is superphosphate (SP) fertiliser, commercially known as single superphosphate (SPP). Phosphate fertilisers, especially SSP, began to be widely used across NZ along with the popularity of its topdressing application since the manufacturers started to process imported rock phosphate in the late 1860s. In the 1940s, topdressing allowed farming extension into hill country land (Roberts, 2008). Currently, NZ continues to import various fertilisers in raw and manufactured forms from different countries, mainly phosphate rock to produce SSP. The majority of the phosphate rock (raw material) comes from Africa (Western Sahara - Morocco), Asia (Indonesia and Vietnam) and the Pacific (Christmas Island and Nauru). Other bulk and bagged manufactured products include guano, potash and urea (Duthie, 2012). Rock phosphates from which P fertilisers are produced on average contain around 3.5% of F, whereas in P fertilisers the F content ranges between 1.3% and 3%. The F concentration in the SSP fertiliser extensively used in New Zealand land is on average 1.5% (Cronin et al., 2000). Table 2 describes the average concentration of F in raw materials that New Zealand imports to produce SP.

Over the last 50 years SPP has been applied to New Zealand pasture lands, making up to around 15,000 mg F kg^{-1} being added to the agricultural soils, assuming average application rates of 400 kg SP ha^{-1} (Cronin et al., 2000; Kim, Taylor, & Drewry, 2016). In addition, most of the rock material currently processed into SP fertiliser in New Zealand comes from Western Sahara - Morocco (Bou Craa phosphate rock) and Nauru Island and Chatham Rise, which have amongst

the highest F content amongst all rock material that has been used in New Zealand (Roberts, 2008).

Table 2. Fluoride concentration of a range of phosphate rock and fertilisers that have been historically used in NZ

Material	F concentration (%)
Phosphate rocks	
Christmas Island	2.2
Bou Craa (Western Sahara - Morocco)	4.0
Nauru Island	3.0
Chatham Rise phosphorite	3.0
Fertilisers	
Single superphosphate	1.08-1.84
Triple superphosphate	1.3-2.4
Monoammonium phosphate	1.6-2.2
Diammonium phosphate	1.2-3.0

Modified after (Cronin et al., 2000), p. 299

2.2.2. Fluoride concentration in soils

Fluoride concentration in soils varies worldwide (Table 3). In respect to contaminated sites, soil F content decreases with the distance to the point source of F contamination. A study in a zinc smelter of surface soils (0-20 cm) collected from various distances (0-10 km) to the smelter in Udaipur Rajasthan reported total soil F was 189 mg F kg^{-1} at the nearest point and around 100 mg F kg^{-1} at the furthest distance (Bhat et al., 2015). Another study near an aluminium smelter in Norway found that the first 4 cm of soil surface at the nearest point to the smelter soils showed a total soil F of almost 500 mg F kg^{-1} and F levels decreased with distance to the plant, but F concentrations were also highly influenced by the wind direction (A. K. M. Arnesen et al., 1995).

On the other hand, regarding agricultural soils, the total F concentrations vary widely depending on soil parent material and P fertiliser use (P. Loganathan et al., 2003). Total F concentrations of nearly 1,000 mg F kg^{-1} were found in agricultural soils in Pennsylvania (0-10 cm, pH mean 5.5) (Gilpin & Johnson, 1980), and similar values were reported in fertilised paddy soils in China, ranging between 500 and 1000 mg F kg^{-1} (0-20 cm, pH 5.93-6.85) (Zhou & Sun, 2002). Various studies reported total soil F average concentrations across New Zealand. Gemmell

(1946) found total F ranges between 68 to 540 mg F kg^{-1} across different soil orders and that the higher concentrations were often found in clay and peat soils. A study carried out by Stewart, Manley, White, and Harrison (1974) concluded that after topdressing with SSP, on average, soils showed a total F average of 300 mg F kg^{-1}(0-7.5 cm).

Furthermore, M. McLaughlin et al. (1996) reviewed several studies and found that on average total F in farmed soils ranges between 150 to 360 mg F kg^{-1}. Another study found on average a total F concentration of 200 mg F kg^{-1} in fertilised soils and, assuming F addition of 123 kg F ha^{-1}, showed an increase of around 100 mg F kg^{-1} compared with unfertilised soils (Cronin et al., 2000). In another study, P. Loganathan et al. (2003) looked at the effect of parent material soil type and fertiliser effect on total soil F and found that fertilised volcanic soils are around two times higher in total F concentrations than unfertilised volcanic soils, 371 mg F kg^{-1} and to 180 mg F kg^{-1} respectively.

Another study analysed New Zealand pastoral soils to assess total F in relation to soil properties, and found that total soil F ranged from 212 to 617 mg F kg^{-1} (0-7.5 cm) (P. Loganathan, Gray, Hedley, & Roberts, 2006). These findings are consistent with previous findings by P. Loganathan, Hedley, Wallace, and Roberts (2001). In these studies, the highest F concentrations were found in Al and Fe oxy-hydroxides-rich soils.

Table 3. Summary of total soil F from various countries

Country – location	Land use	Total soil F	Reference
Pennsylvania, USA,	Agricultural soils	Top 10 cm of soil. 136-990 mg F kg^{-1}, related to pH, pH mean 5.5. overall, F is immobile	Gilpin and Johnson (1980)
China	Agricultural soils	Top 0-20 cm of soil 500-1,000 mg F kg^{-1} pH 5.93-6.85	Zhou and Sun (2002)
Udaipur Rajasthan	Soils collected from a zinc smelter area	Top soil (0-20) cm Ranging from 101 mg F kg^{-1} (10 km) and 189 mg F kg^{-1} (0 km) distance to the smelter.	Bhat et al. (2015)
Greece	Aluminium smelter area	Topsoil (0-5 cm) Ranging from 105 – 950 mg F kg^{-1}	Haidouti (1991)
Various countries Review	Agricultural soils	Ranging from 150-360 mg F kg^{-1}	M. McLaughlin et al. (1996)
New Zealand	A range of soil orders	68-540 mg F kg^{-1} Does not specify depth sample	Gemmell (1946)
New Zealand	Total fluorine in soils after topdressing	After topdressing with superphosphate (0-7.5 cm) 250 kg P ha^{-1} and 500 kg P ha^{-} Total F average 300 mg F kg^{-1}	Stewart et al. (1974)
New Zealand	Various pasture soils	Total F form 0-7.5 cm Range 106 – 454 mg F kg^{-1} Receiving SP over 700 kg P $ha^{-}$with 250 mg F kg^{-1}. Relationship between soil P and total F (R^2=0.55)	P. Loganathan et al. (2001)

2.3. Fluoride fate and storage in agricultural systems

Fluoride is one of the trace elements contained in P fertilisers and has been currently considered as an emerging issue in New Zealand agricultural soils because its accumulation rate in productive land is relatively rapid compared to other fertiliser-derived contaminants. As a consequence, it has been recognised as one priority contaminant emerging from agricultural development within New Zealand (McLaughlin et al., 1996). The availability of a reliable method to determine F in a range of soil types can assist soil monitoring programmes and applied research to assist land management plans and policy making.

Regarding the F risks to the environment there are no internationally agreed risk-based guidelines on soil F levels for soil protection, including soil organisms, although there are recommended values for grazing animal protection and F tolerance limits for specific plant species (Cronin et al., 2000; Taylor, 2016). Therefore, it is important to assess F risks to soil microbial activity and monitor F levels across New Zealand soils, in order to establish environmental limits for F in agricultural soils. Based on several data reviews, Cronin et al. (2000) prepared a specific cycling diagram of F in grazing systems (Figure 1). The major transfer F pathway to soils occurs via P fertiliser application, as phosphate rock is mined to produce fertilisers. The most important F storage occurs in topsoil, subsoil and grazing animal bones, depending on various factors for increasing leaching, retention or uptake by plants and grazing animals (Cronin et al., 2000; Kim et al., 2016; P. Loganathan et al., 2001).

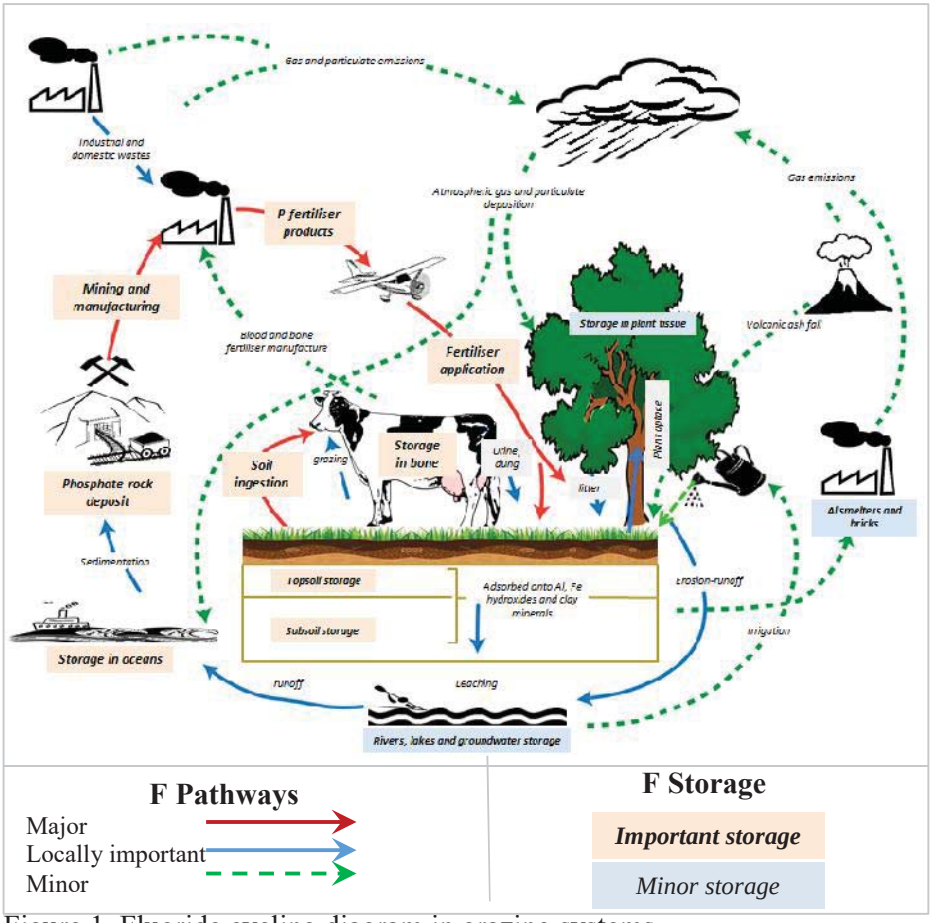

Figure 1. Fluoride cycling diagram in grazing systems
Modified after Cronin et al. (2000). p. 313

2.4. Factors influencing F accumulation in agricultural soils

Several authors have agreed that the long-term use of P fertilisers is the main source of F in agricultural soils as F is absorbed by clay minerals and oxy-hydroxides and is strongly bonded to soil particles, with only a small percentage being dissolved into the soil solution (Loganathan et al., 2003). Other point F sources but with discontinuous and irregular inputs onto land are air deposition from fertilisers manufactures, volcanic eruptions and irrigation with high F-containing water (Cronin et al., 2000; Kim et al., 2016; Loganathan et al., 2006).

2.4.1. Soil parent material and soil properties

Fluoride accumulation process in soils is influenced by soil specific characteristics, parent material and climate shaping specific soil properties. The soil properties which directly influence soil F retention and adsorption are soil pH and Al/Fe oxy-hydroxides, and indirectly, organic matter content (Cronin et al., 2000; Xiaoging & Binbin, 2014).

The chemical composition of soils is mainly determined by the parent material and the degree of degradation or leaching of rocks introduced by weathering cycles. Also, the chemical composition is influenced by addition of external chemical compounds produced by human activities. Weathering promotes decomposition of minerals and can lead to a formation of particles containing layers of oxy-hydroxide (e.g. Al and Fe) in soils surface. Other components (less ordered hydroxy species) of clay fractions such as alumina-silicates possess high capability to retain significant amounts of any species showing affinity for their large surface sites (Pickering, 1985). In addition, when F is added to the soil is adsorbed predominantly by anion exchange, F replaces the OH groups of amorphous oxy-hydroxides of Al and Fe. Also, some studies have found that addition of F ions in solution can result in Al-organic complexes leached out from acid clay soils and that percolating F solutions can induce important losses of total C Al and Fe (Pickering, 1985).

The degree of F adsorption is controlled by soil pH and is greatest in soils containing high Al content. Fluorine minimum solubility occurs at a pH range of 6.0 to 6.5, and increases at a pH below 6.0 (acidic conditions) and as well at a pH above 6.5. Fluorine is highly soluble in acidic conditions and can be associated with the presence of cationic Al-F complexes, and at a pH higher than 6.5 the increase solubility can be explained by desorption of F ions. Hence, F sorption is greatest between 5.5 and 6.5 and decreases at lower and higher pH values (Loganathan et al., 2003; Wenzel & Blum, 1992). This is also suggested by Barrow and Ellis (1986), cited by Cronin et al. (2000), who stated that at low pH values Al and F complexes form in soil solutions.

A study was carried out to investigate the co-sorption and desorption of F in agricultural soils in China and found that under acidic conditions iron (Fe) and Al (hydro) oxides are the most important factors on the F transport and mobility, and F sorption increases as well when soil pH decreases. In addition, soil amorphous Al and Fe oxy-hydroxides determine F transfer and

mobility in soil profile and subsequently, F mobility that is related to the F accumulation rate in soils (Hedley, Loganathan, & Grace, 2007).

However, the pH and sorption capacities of the soils are very weather and climate-dependent, characteristics that govern the chemical composition of soils and hence, the behaviour and mobility of trace elements in the soil profile (Taylor, 2016). Furthermore, most of NZ soils have low natural P levels and many have short-range ordered inorganic constituents which can absorb high quantities of P, causing fertiliser application rates to be very high compared to other countries worldwide (Manoharan, 1997). In addition, when there are high F concentrations in soils in the P-F coexisting system as occurs in P fertilised soils, F can suppress P sorption due to competitive effect (Zhu, Ding, Jiang, & Wang, 2007). Parfitt and McDonald (1992) cited by Veeragathipillai Manoharan (1997), reported that most NZ soils are acid (values ranging on average from 4.0 to 6.0) and contain at least one horizon with pH lower than 5.0 within the 0-60 cm depth.

Various studies have concluded that F is retained preferentially on fine soil particles, especially clay minerals, and this process is promoted at low pH conditions. Cronin et al. (2000) suggested that around 80% of F applied to agricultural soil is retained by amorphous Al and Fe oxy-hydroxides and clay minerals, and thus the labile and soluble portion of F only accounts for a small fraction of total F in soils. Fluorine occurs mainly on the top first few centimetres of soil through adsorption onto minerals and short-range ordered inorganic constituents such clay and Al amorphous oxides (Cronin et al., 2000). Furthermore, it was also found that F retention in soils follows the same pattern as P derived from fertilisers (Loganathan et al., 2001).

Some studies found a positive correlation between total F concentrations and both amorphous Al and Fe oxy-hydroxides and organic matter. This positive correlation could indicate that F in soils strongly bonds to Al polymers adsorbed to the organic matter, therefore, Al and Fe oxy-hydroxides provide adsorption sites for F in soils (P. Loganathan et al., 2006; Veeragathipillai Manoharan, 1997; J. Polomski, H Flühler, & P Blaser, 1982). Other findings suggest that a positive correlation between organic matter and F concentrations in soils could be related to the inhibition of soil microbial activity caused by the presence of F, causing a decrease in organic matter breakdown and consequently, it accumulates in the soil (Rao & Pal, 1978). The presence and abundance of Al and Fe oxy-hydroxides in soils depends on the presence of weathered minerals and leaching conditions (Fink, Inda et al. 2016). Table 4 provides a description of the

soil parent material of soil orders used for this study, in relation to the development of oxides in the soil surfaces governed by the parent material and climate conditions.

Furthermore, given soils characteristics such as presence of inorganic short-range order constituents and land use, Recent, Brown and Allophanic soils are more likely to show the highest anthropogenic F enrichment through P fertiliser use, and thus these soils are considered as "high risk" in terms of F accumulation in topsoils (Jeyakumar & Anderson, 2015; Kim et al., 2016). Additionally, these soil orders are classified as high-class[2] regarding agricultural development, and consequently, are more likely to receive repeated SSP fertilisation and are thus, more likely to present high F concentrations over time (Hedley et al., 2007).

In the following some of the soil order characteristics are described following (Hewitt, 2013). Recent soils correspond to most of New Zealand's versatile soils and cover 6% of this country's land. They are typically found in areas where erosion and sediment deposition are relatively low, with a well-developed topsoil structure, whereas Horizon B is either absent or poorly developed. They are considered fertile, deep rooting and with good water storage capacity.

Table 4. Soil Al and Fe oxy-hydroxides development in relation to soil parent material and climate conditions

Parent material	Description of soils characteristics by soil sample site
Sedimentary Parent material is primarily quartzo-feldspathic	Lincoln: is a pale coloured soil, experiencing cyclic hot summer/autumns and wet/cold winter/springs. Therefore, organic matter content returns to the soil are lower and formation of Al/Fe oxides is low. Te Anau: is a brown coloured soil, experiencing cool climatic conditions. The soil is moist throughout the year, with moderate organic matter content, and some development of Al/Fe oxides. Manawatu, Tuapaka and Tokomaru also belong to this soil group parent material.

[2] High class land (or versatile soils): corresponds to the most productive land in New Zealand and is used for food production across the country, being limited for crop growing due to farming and urban expansion (Statistics NZ, 2015).

Parent material	Description of soils characteristics by soil sample site
Organic Parent material predominantly plant material with much of the developing soil's organic cation exchange sites occupied by H^+ and Al^{3+}.	Gordonton: once drained these soils require large quantities of fertilisers (including SPP) to replace H^+ and Al^3 with nutrient cations and raise fertility during agricultural development. Very low input of mineral parent material, so low or nil in Al/Fe oxides.
Volcanic Warm and wet soil development conditions.	Otorohanga, Putaruru, Reporoa, Newstead, Te Aroha, Morrinsville, Mangakino. These soils have good annual rainfall (>1000 mm) evenly distributed throughout the year. Well-drained soils forming under a warm mild climate with a high silica parent material, therefore experiencing rapid development of allophane and Al/Fe oxides. These minerals dictate high P fertiliser application rates and indirectly, high addition of F.

Modified after (Bretherton, 2017)

Pallic soils are pale yellow coloured because of low oxidation in the subsoil profile. Soils from this order present high density and weak structure, thus rooting and drainage capacities are poor. These soils cover 12% of New Zealand's land (Hewitt, 2013).

The majority of New Zealand's land is covered by Brown soils (43%). Topsoils are normally yellow to brown colour, due to the oxides present such as Al and Fe complexes, as well as organic matter. Compared with Pallic soils, these soils have lower pH, higher drainage and are less fertile. However, microbial activity is considered to be more active than in Pallic soils. For a given parent material, a soil evolves towards a Pallic or a Brown soil depending on climate. Pallic and Brown soils are very dependent on climate (Hewitt, 2013).

Gley soils are soils with a high moisture content, typically found in wetlands, and are strongly influenced by waterlogging. Gley soils are characterised by slightly grey subsoil and generally they need to be drained for agricultural development. Gley soils only account for 3% of the total land area in the country (Hewitt, 2013).

Soils that have well-developed topsoil horizons are Pumice and Allophanic soils. Both are dominated by parent material formed from volcanic rocks, which shapes specific soil characteristics. Around 6% of New Zealand's land is made from Allophanic soils characterised

by the presence of short-range order aluminosilicates (allophane) and Al and Fe oxy-hydroxides and Al-OH complexes, which are found in volcanic areas, as weathering products. They are stable for farming and show little resistance to root growth. Also they present a high P retention capacity (Hewitt, 2013).

Pumice soils originated from volcanic eruptions in the Taupo area. These soils have a low content of clay minerals compared with Allophanic soils, with a deep rooting capacity but a lack of major nutrients. Pumice soils are mostly used for forestry and cover 7% of New Zealand (Hewitt, 2013).

2.4.2. Phosphate fertiliser use and application rate

The worldwide use of fertilisers has been extensively expanding because of the growing demand on food production (Jiao et al., 2012). The agricultural sector in New Zealand accounts for one of the biggest contributors of export revenue. In order to maintain the country's economy, the primary sector started blooming after pasture began its improvement and fertilisation became a requirement. Historically, P fertilisers have been applied to most of New Zealand's soils to increase productivity. However, P fertilisers also contain trace elements, most of which may accumulate in the environment and potentially threaten human health, animals and plants. Additionally, during these past years, some work done by Taylor et al. 2016 has suggested that the addition of phosphate fertiliser may cause an accelerated weathering due to the increase in phosphate and fluoride ligand concentration contributing to the formation of reactive Al. As a consequence, many emerging environmental issues have been associated with agricultural activities, most of which are related to the use of P fertilisers. Global awareness to protect public health, food security and land sustainability has also emerged in the past decade (He, Yang, & Stoffella, 2005; M. McLaughlin et al., 1996).

Soil is a non-renewable resource that underpins New Zealand's agriculture and other land-based activities. One of the most important economic activities in New Zealand is farming. More than half of the country's total area is used for primary production (55%), of which three quarters is in pasture land (Statistics NZ, 2008). The agriculture sector contributed around 4% of the Gross Domestic Product (GDP) in 2015, accounting for just over half of New Zealand's total exports (NZ Government, 2016). Dairy farming is the predominant activity in gross agriculture production (around 45%), followed by beef and sheep farming (NZ Government, 2016).

Regarding New Zealand's land use, classification is based on the land use capability system (LUC), which is based on soil properties and the natural soil capability to sustain certain activities (Hewitt, 2013). Agricultural land use in New Zealand accounts for around 55% of the total land area of the country (StatsNZ, 2017) (Figure 2). Of the fifteen different NZ soil orders, Recent, Allophanic, Yellow-Brown and Gley soils are generally used for agriculture development (Nathan, 2009). Of these, Recent and Allophanic soils are considered as "high-class soils" because their properties to support production are the most suitable between other New Zealand soils, covering around 5% of the country's land (Hewitt, 2013). Most of the high-class land occurs in the Canterbury and Southland region in the South Island and in the Waikato and Manawatu-Wanganui regions of the North Island (Statistics NZ, 2015).

In general, New Zealand's soils are low in nutrients, especially in P. As a consequence, farming practices rely mainly on P fertilisers to enhance the potential of soils to support and optimise pasture growth (Fertiliser Association, 2012b). Since commercial farming began in the 19th century, supplementation of nutrient deficiency began to be major a need and P fertilisers started being massive and extensively used across New Zealand. During this period, around two million tonnes of SP per annum were applied (around 180,000 tonnes of P), allowing agricultural expansion, pasture intensification and farming operation improvements (CWG, 2008).

The use of SPP accounts for almost 90% of P fertilisers applied to New Zealand soils (CWG, 2008). Compared to other P fertilisers, the widespread use of SSP was because the majority of P content (around 9% of total P) is highly water soluble and the main way of application was topdressing. In addition, the low cost of SSP and the incentive circumstances when it was first introduced also contributed to the extensive use of SPP (Quin, 2012). By the end of the year 2012, dairy farming accounted for almost 35% of total SP fertiliser use, followed by sheep and beef farming. In addition, the Canterbury, Waikato, Southland, Manawatu-Wanganui and Otago regions accounted for the highest SP fertiliser use in New Zealand (Figure 3) (Statistics NZ, 2012).

The fertiliser application rate is dependent on some pre-determined attributes, including soil type and pasture requirements. For intensive dairy farming, SP application rates range between 200 to 600 kg SP ha^{-1} y^{-1} and some pastoral farms apply more than 600 kg SP ha^{-1} y^{-1}, whereas in beef, sheep and deer farming fertiliser application rates are lower. For horticulture, the

highest fertiliser requirement is for potato crops, with application rates of SP ranging around 800 to 1,000 kg SP ha^{-1} y^{-1} (CWG, 2008). These application rates will influence the amount of F that will be added to agricultural soils.

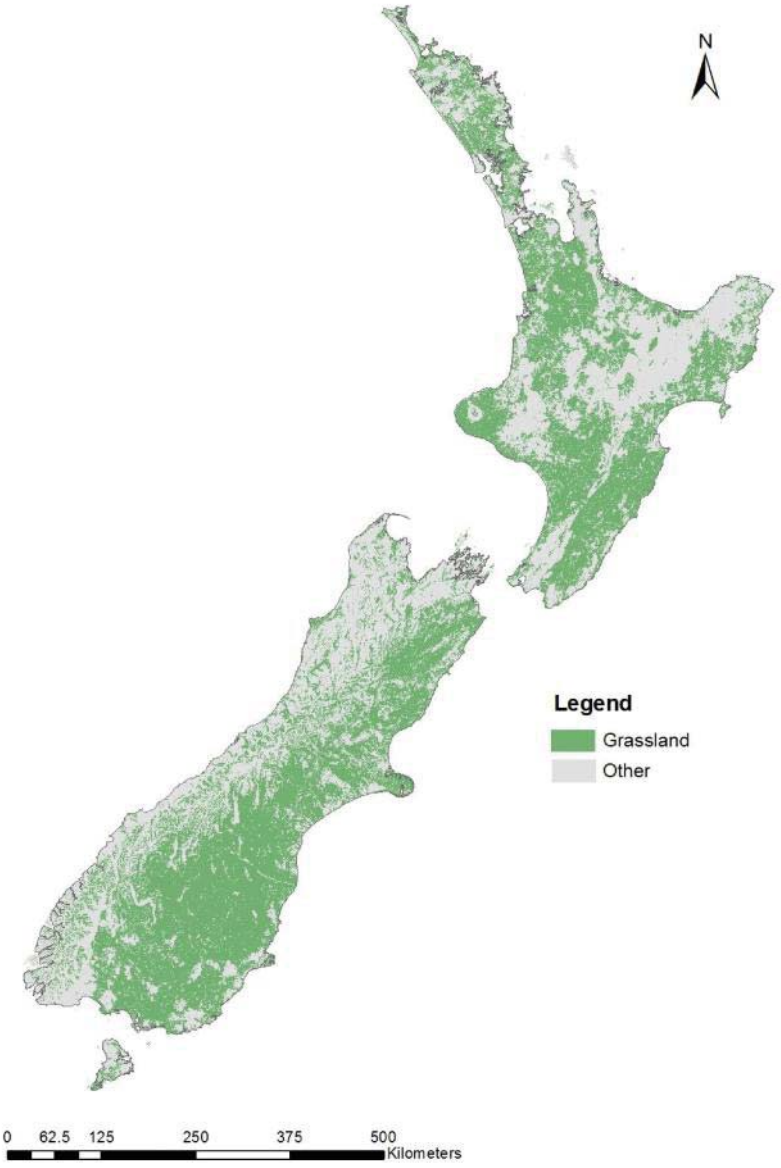

Figure 2. Grassland and horticultural land cover in NZ

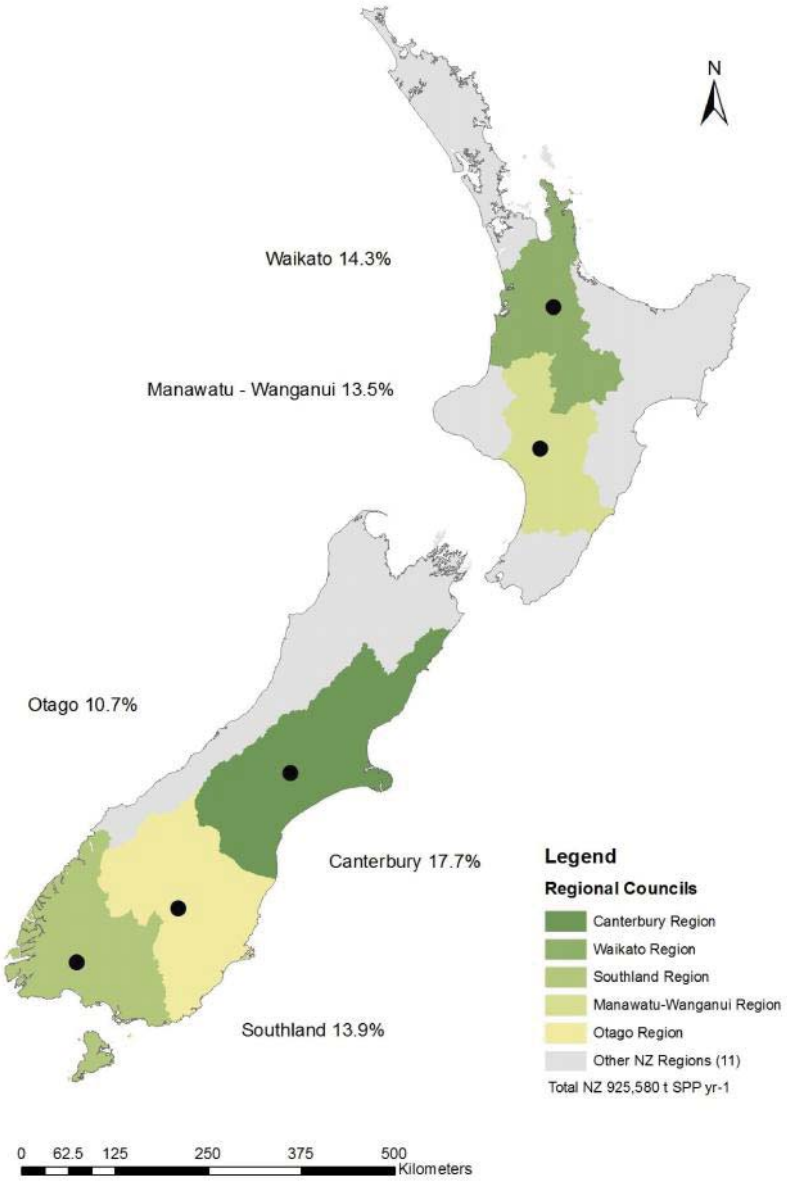

Figure 3. New Zealand regions with highest SPP use (tonnes per year, 2012)

The short-term application of SSP does not imply significant risks to soil, but repeated and prolonged SP applications to pastoral soils will accumulate fertiliser-derived contaminants to potentially harmful levels (Jiao et al., 2012). M. McLaughlin et al. (1996) assessed F soil accumulation for Australian conditions based on both background levels and P fertiliser application rates. They estimated a soil F background level of 300 mg F kg^{-1} dw, and that the time required to double soil concentration for wheat and potato crops is 100 and 25 years at an

application rate of 20 kg P ha^{-1} and 80 kg P ha^{-1} respectively. Table 5 shows the estimated balance of F in soils compared with arsenic (As) and cadmium (Cd).

Table 5. Estimated years necessary to double key soil contaminants from SP application

Element	Input[A]	Crop harvest[B]	Net rate of addition	Background soil conc[C]	Years to double soil conc. in 0-100 mm[D]	ANZECC level[E]
	(g ha^{-1})	(g ha^{-1})	(g $ha^{-1}yr^{-1}$)	(mg kg^{-1})		(mg kg^{-1})
			Wheat			
As	1.0	0.3	0.70	4.0	7,500	20.0
Cd	6.0	0.12	5.88	0.2	45	3.0
F	4,000	3.0	3,997	300	100	400.0
			Potatoes			
As	4.0	0.20	3.80	4	1,370	20.0
Cd	20.0	2.50	17.50	0.2	15	3.0
F	16,000	10.0	15,990	300.0	25	400.0

Modified after M. McLaughlin et al. (1996)

[A]Assuming 20 kg P/ha applied per wheat crop and 80 kg P/ha per potato crop and fertiliser contains (per kg P) 50 mg As, 300 mg Cd (250 mg Cd for potatoes), and 200 g F. Element inputs in irrigation water assumed to be negligible, although F may be a significant impurity in some waters.
[B]Assuming 3 t grain and 50 t potatoes harvested per crop, all stubble or haulms returned to the soil. Metal concentrations in wheat grain assumed to be (per kg) 100 µg As, 40 µgCd and 1 mg F and in potatoes (per kg fresh weight) 4 µg As, 50 µg Cd and 200 µg F. Data for element concentrations in crops taken from the AMBS (Stenhouse 1991), Tiller et al. (1976), Anon. (1984) and Wiersma et al. (1986).
[C] Assumes 'background' soil concentration equals 0.1 mg kg^{-1}, despite published analyses indicating values below this level (detection limit).
[D]Assuming soil bulk density of 1300 kg/m^3.
[E]Guideline threshold values above which investigation of the contamination should take place, from ANZECC/NHMRC (1992) and Moen (1988).

Data from Table 5 shows that for a high nutrient demand crop (around 80 kg SP ha^{-1} per potato crop containing 20 g F per kg P) F could double its concentration in the topsoil in a relatively short period of time (25 years), whereas for wheat the estimated time is 100 years. A similar trend was found for New Zealand agricultural systems. Estimations from a study carried out on long-term fertilised land showed that F could double its concentration in soils in less than 100 years, whereas other trace elements such as As could take more than 1,000 years (P. Loganathan, Hedley, & Grace, 2008).

Regarding P fertiliser use, assuming SSP application rates of 10-30 kg P ha^{-1} y^{-1}, around 0.2-0.5 kg total F ha^{-1} y^{-1} is expected to be added to pastoral soils (Cronin et al., 2000). Maximum

accumulation rates across all soils were estimated to be around 13.8 mg F kg^{-1} y^{-1}, assuming a mean intensive fertiliser application timescale of 50 years.

Several studies have found that total F concentration in agricultural soils with a long-term history of P fertiliser application is higher at the soil surface (0-15 cm) in most cases, compared with unfertilised soils. A similar situation occurs for New Zealand agricultural soils, as a study showed that soil F concentration has increased by 60% to 120% in agricultural soils with 20 years of SSP fertiliser application history, of which more than half is retained within the first 7.5 cm of soil (Cronin et al., 2000). Another study in New Zealand Pallic soils found that total F significantly increased around 70% the total F mean concentration at the surface soil (0-7.5 cm) at a SPP application rate of 60 kg P ha^{-1} y^{-1} during 10 years, accounting Winchmore and Massey Dairy N°4 sites (P. Loganathan et al., 2001).

For New Zealand soils, results from Cronin et al. (2000) research showed that some soils can retain up to 90% of F in topsoils that have been added to by P fertilisers (i.e. Brown 40%, Pallic 60% and Allophanic 90%). In addition, they estimated F accumulation rates from repeated and prolonged SP fertiliser application in surface soils (0-7.5 cm) was 7.6 mg F $kg^{-1}y^{-1}$ in Allophanic soils and 4.2 mg F $kg^{-1}y^{-1}$ in Brown soils. This was later confirmed by Kim et al. (2016), who obtained similar F accumulation rates and estimated average annual F accumulation rates (in mg F $kg^{-1}yr^{-1}$) across New Zealand pastoral soils, assuming over 50 years SSP fertilisation, in the following order: Organic (6.9) > Allophanic (5.4) > Gley (4.7) > Granular (3.9) ≥ Pumice (3.8) > Brown (3.4) > Recent (2.9) > Ultic (2.0) ≥ Podzol (1.9).

Additionally, Kim et al. (2016) proposed the only published data on F background levels for New Zealand farmed soils. They observed an average total F concentration in pastoral soils of 440 mg F kg^{-1}, with maximum values up to 900 mg F kg^{-1}. In relation to F accumulation in specific soil orders and pastoral land use, the estimated natural background and reported modern F showed that Organic and Allophanic have the greatest modern values in relation to the background levels (Table 6).

Table 6. Estimated background F levels against modern values, in relation to NZ soil orders under pastoral land use

Soil order	Estimated background F (mg F kg^{-1})	Modern soil F value (mg F kg^{-1})
Allophanic	236	505
Brown	215	387
Gley	231	465
Granular	210	403
Organic	51	394
Pumice	247	437
Recent	233	377
All orders	215	440

Modified after Kim et al. (2016)

In summary, findings by various authors suggest that F is mainly retained at the top first centimetres in soil (0-15), remaining mostly between the first 7.5 centimetres. Also, reported F concentrations in agricultural soils are in general higher than from contaminated sites.

2.5. Environmental risks of F accumulation in agricultural soils

Environmental risks from F accumulation in pastoral soils are associated with the toxicological effects of soil organisms, grazing animals and plants, and risks are related to the available forms of F in soil solution. The amount of available F will vary accordingly to the factors influencing F accumulation in fertilised soils. Other potential F impacts include F leaching to groundwater, toxicity to aquatic life and alteration of F cycling (Kim et al., 2016; Pascoe, Zodrow, & Greutert, 2014). The importance given to F is due to its capability to accumulate in New Zealand agricultural topsoils and potentially to cause fluorosis in grazing animals and to inhibit soil microbial activity (Taylor, Kratz S, Schick J, Schnug E, & Smidt G, 2014).

2.5.1. Fluorine toxic effects on plants

In general, most studies reported low concentrations of F in plant tissue, and this suggests that most plants have low F uptake (M. McLaughlin et al., 1996). Plant F uptake will depend on the same soil factors governing F sorption in soils, such as soil pH, clay content and total F concentrations, as well as plant species-specific characteristics and the F form present in soil solutions (Veeragathipillai Manoharan, 1997; M. McLaughlin et al., 1996; Taylor, 2016).

The amount of F that can be uptaken by plants is very dependent on the pH of the soil, organic matter content, soil properties and Ca and P content (P. Loganathan et al., 2003). The majority

of the total F in soils is insoluble or highly bonded to soil particles and not easily lost by leaching or volatilisation, remaining mostly fixed in the topsoil and therefore, not being available for plant uptake, especially during growth (Dey, Mondal, & Das, 2012; Groth, 1975; M. McLaughlin et al., 1996). Some studies suggested that Al-F complexes are more likely to be taken up by plants than free F^- in soil solutions (Cronin et al., 2000).

Soil acidity will determine F solubility and amount of labile F in soil solutions available to plants. In addition, the high affinity of clay and Al/Fe oxides strongly retain F and thus, very low concentrations are readily available to plants (P. Loganathan et al., 2003). The mechanism of pH affecting plant F uptake is based on the principle that AlFx formed in soils can behave as phosphorus, therefore it induces plants to uptake those complexes instead of phosphorus, and decreases in pH will control the availability of phosphorus in the soil, determining the capacity of soils to release more Al-F complexes (Veeragathipillai Manoharan, 1997). However, changes in soil pH might affect sorption processes and F speciation may change as well (Saini, Khan, Baunthiyal, & Sharma, 2012).

Given F distribution in plants, F is generally higher in roots followed by sprouts and generative organs, therefore edible parts such as leaves are low in F concentrations (M. McLaughlin et al., 1996). Although data on plant root F uptake from soils is still very limited and mechanisms involved in the process are not entirely known, a number of studies have suggested that F uptake by plants from P fertilised soils appears to be negligible. Strong adsorption to soil and low plant F uptake limits risks of F toxicity (M. McLaughlin et al., 1996).

However, some plant species are more likely to be affected at low F concentrations and the F effects in plants can manifest as necrosis on foliage and chronic chlorosis, causing a decrease in photosynthetic efficiency and therefore, a lower plant yield. Other potential effects are a reduction in flower quality and production (Cronin et al., 2000). Regarding plant characteristics, some genera are more likely to tolerate higher F levels than others without showing any toxic effects, and plants can accumulate both atmospheric and soil F concentrations (Veeragathipillai Manoharan, 1997). For instance, the *Dichapetalum. Thea, Gatrolobium, Camellia, Oxyobium, Acacia* and *Palicoure* plant species can tolerate F concentrations up to 4,000 mg F kg^{-1} dw, whereas others can show signs of toxicity with F concentrations as low as 20 mg F kg^{-1} dw. One study found that sodium fluoride (NaF) had significant impacts on seed germination and growth of *P. juliflora* (after 15 days treatment with 50 mg F l^{-1}), germination decreased to 73%,

compared to the control germination of 76%. Authors also suggest using *P. juliflora* legume species as potential bioindicators of F-contaminated areas because it was found it can accumulate F concentrations of 1,000 mg F kg^{-1} and 500 mg F kg^{-1} in roots and shoots respectively without any sign of necrosis (Saini et al., 2012).

Generally, F concentrations in pasture and herbage are relatively low compared to the F content in F-accumulators plant species. According to Cronin et al. (2000) normal F content in plants is around 2 to 20 mg F kg^{-1} in uncontaminated sites, and reported pasture F levels is around 0.7 to 16 mg F kg^{-1}. Also, according to review on other studies, little change is found in F concentration in grass and white clover under P fertiliser treatment (Cronin et al., 2000). They found that total F addition of either 39 and 78 kg F ha^{-1} over 8 years did not show significant increases in total F in pasture. In slightly acidic soils, an increasing level of soil F is not likely to cause a significant increase in pasture F concentration (Hedley et al., 2007; M. J. McLaughlin, Stevens, Keerthisinghe, Cayley, & Ridley, 2001). In other studies, the pasture herbage F concentrations were also very low compared to plants that can tolerate high F concentrations from soil and airborne. For instance, P. Loganathan et al. (2001) found herbage concentration levels below 10 mg F kg^{-1} and most below the detection limit (3 mg F kg^{-1}). They found a strong relationship between low pasture F uptake and soil properties such as Fe and Al-bearing minerals content. Also, unwashed samples were around 200 times higher in total F concentrations than in washed samples assuming the high F levels were due to contamination of pasture leaves with soil particles. A study carried out in Australia found that herbage F concentrations from fertilised plots were two times higher than unfertilised plots, around 22 mg F kg^{-1} and 11 mg F kg^{-1} respectively, applying on average 200 kg SPP ha^{-1} yr^{-1} (M. J. McLaughlin et al., 2001). Furthermore, according to Stewart et al. (1974), F residues on pasture herbage reached between 200 to 800 mg F kg^{-1} after topdressing with SPP.

Furthermore, a greenhouse study carried out in New Zealand showed detrimental effects on barley (*Hordeum vulgare* L.) root growth from the addition of P fertilisers to acid soils. The results showed that the formation of Al-F complexes was around four times higher when added F concentrations to the strong acid soils (pH 4.25) were high (160 mg F kg^{-1}) compared to low F doses (40 mg F kg^{-1}). They also found a strong correlation between Al-F complexes and root length (r=-0.83), confirming the relative toxicity of AlF_2^{1+} and AlF^{2+} species to root growth (V. Manoharan, Loganathan, Tillman, & Parfitt, 2007).

The recommended background level in plants is around <10 mg F kg^{-1} and in pasture grass is 30 mg F kg^{-1}(A.K.M. Arnesen, 1997). Other studies found toxic F levels of 100 mg F kg^{-1} for *Triticum aestivum* (Kumar, Dhaka, & Singh Arya, 2013) and 270 mg F kg^{-1} for *Spinacia oleracea* (Jha, Nayak, & Sharma, 2008).

In summary, the low F plant availability is strongly dependent on the Fe and Al oxide content, allophane and clay minerals, as well as the soil pH, which will determine Al-F formation and therefore, toxicity to pasture growth (Bhat et al., 2015; Dey et al., 2012; Jha et al., 2008; P. Loganathan et al., 2008; P. Loganathan et al., 2003; V. Manoharan et al., 2007; Saini et al., 2012; Weinstein & Davison, 2006). As a consequence, more urgent concerns are focused on the accumulation of F in agricultural soils in relation to livestock welfare and the productivity of soils and land value (Cronin et al., 2000; Kim et al., 2016).

2.5.2. Fluorine risks to grazing animals

A number of studies have assessed F risks to grazing animals by several sources, especially in New Zealand and Australian pastoral soils (Cronin et al., 2000; Hedley et al., 2007; P. Loganathan et al., 2008). For instance, a study reported significant stock losses and chronic fluorosis in grazing animals attributed to the Mt. Ruapehu volcanic eruption in 1995-1996, NZ (Shanks, 1997). On the other hand, several studies assessed the F risks from fertiliser residues to livestock in pastoral systems, especially focused in New Zealand. For instance, a study by Cronin et al. (2000) reported cattle and sheep dietary F tolerance ranging from 30 to 150 mg F kg^{-1} respectively, suggesting cattle are less tolerant to F toxic effects than sheep.
The livestock exposure to F sources are varied, pasture, water supplies, fertiliser residues and volcanic ash. For pastoral systems, soil ingestion is the most important exposure route to F. Other sources are considered negligible for the purposes of this study. Determinant factors influencing the magnitude of ingested soils are season and stocking rate (Cronin et al., 2000; Hedley et al., 2007; M. J. McLaughlin et al., 2001).

Livestock F tolerance is dependent on animal species, animal conditions such as age and gender, F forms in solution and amount consumed (Cronin et al., 2000). The effects of F toxicity can manifest weeks or months after exposure, depending on the F dose, animal conditions and farm management (Cronin et al., 2000). Cattle and other grazing animals such as sheep can accumulate F in their bones causing acute and chronic fluorosis and with continuous exposure

to large F amounts it can build-up in bones and cause death. Fluorine passive adsorption occurs in the rumen and can be affected by other feed factors such as Al salts and dietary fat. The greatest proportion of F storage is in the skeleton, specifically in the ribs and vertebrae. The non-sequestered F portion is excreted by urine. Table 7 shows the proposed threshold of total soil F concentrations to cause fluorosis to sheep and cattle, and the average soil and herbage consumption.

Table 7. Fluorosis based on F bone criteria in cattle

Livestock	Threshold total soil F (mg F kg^{-1})	Average daily soil ingestion (g F day^{-1})	Average pasture ingestion (g F kg^{-1})
Sheep	372 – 1461	75	77
Dairy cows	326 – 1085	700	143

Modified after Cronin et al. (2000)

Additionally, there is an increased likelihood of higher F intake when foraging pastures are recently dressed with SSP (Cronin et al., 2000). Therefore, months associated with high risk F ingestion from soil exposure are June, July and August, increasing the risks with long-term exposure and after topdressing with SPP (Hedley et al., 2007). A study has found that livestock F intake is higher from soil ingestion than from herbage forage (P. Loganathan et al., 2001). It was found that the average F concentration found in pasture soil is 340 mg F kg^{-1} and in pasture herbage is around 5 mg F kg^{-1}, however, soil ingestion is much lower than herbage consumption. Furthermore, soil ingestion is around six times higher during New Zealand winter for sheep, around four times higher for cows, and around two times higher for both sheep and cows at higher stocking rates during winter (P Loganathan, Bretherton, & Hedley, 2007). This is because the wetter and cool conditions during winter results in more soil particles adhere to the leaves of pasture and high stocking rates causes low pasture height, hence, increasing soil intake by livestock (Table 8).

Table 8. Average daily soil ingestion (g soil per day) by sheep and cattle in relation to NZ seasons and stocking rates

Season	7.5 ewes per ha	15 ewes per ha	2.2 cows per ha	3.3 cows per ha
Winter	110	178	1510	2430
Summer	18	30	320	775

Modified after (P. Loganathan et al., 2003)

Regarding the F chemical form, total F in soil has a positive correlation with F bioavailability within the rumen and consequently, with F absorption by grazing animals independently of the amount of extractable F in soil (Kim et al., 2016). Therefore, a high total F concentration in topsoil (0-30 cm) under pasture suggests higher risk to F intake and absorption by cattle and other livestock.

2.5.3. Fluorine risks to soil microorganisms

Microorganisms in soil play an essential and multifunctional role in the sustainability of this resource, especially in pastoral soils. Microorganisms provide soil services such as regulating nutrient fixation and thereby, supporting plant growth. However, the presence of trace elements in soils can alter biological processes and consequently affect pasture production (Tscherko & Kandeler, 1997). Several studies have suggested severe F toxic effects to wildlife and aquatic and soil organisms (Pascoe et al., 2014). However, F toxicity depends on its concentration in the environment, its chemical form and on the tolerance of organisms to the bioavailable F in the soil environment. Enzyme activity and microbial biomass are two biological indicators to assess environmental stress caused by F soil contamination (Poulsen, 2011; Saini et al., 2012; Tscherko & Kandeler, 1997). According to Martens (1995), around 200 to 1,000 mg C kg^{-1} of microbial biomass can be found in agricultural surface soils and accounts for a small proportion of the soil organic matter, around 1% to 5%. The amount of microbial biomass in soils provides an estimation of soil microbial activity, and this indicator will determine the quality and quantity of nutrient fixation in the rhizosphere, especially nitrogen (N) and phosphorus (Martens, 1995; Langer & Günther, 2001).

Although the importance of soil microorganisms associated to legume-based systems has been largely and widely agreed, the impacts of added F from P fertiliser use on soil microbial function still remain unclear, and several authors have agreed that very few studies have examined the effects of elevated F concentrations on soil microbial activities, on most research have focused on F-contaminated sites, rather than in agricultural soils (Cronin et al., 2000; P. Loganathan et al., 2008; Wakelin, van Koten, O'Callaghan, & Brown, 2013).

Regarding F-contaminated sites, results from a study carried out near an Al smelter on the effects of atmospheric F deposits on soil microorganisms suggests that high concentrations of

soil F (highest water- extractable soil F= 124 mg F kg^{-1}) will affect the microbial biomass up to an 80% and evidence of the inhibition in microbial activity was reflected on the accumulation of organic matter in soil samples at the nearest point to the Al smelter. Furthermore, dehydrogenase enzyme activity (DHA) was significantly inversely correlated with the water extractable F in soils samples (0-10 cm), showing up to 90% inhibition of the DHA (Tscherko & Kandeler, 1997).

Similarly, findings in soils collected (0-20 cm) near an Al smelter suggest that soil F content increased with distance to the smelter, and at the nearest point (highest water- extractable F=96 mg F kg^{-1}) showed significant decreases (up to 53%) in microbial activity, and the DHA experienced a reduction of 95% compared to the control soils. Despite similar results were found within the most polluted soil samples, results suggests that there is a large variation in biological responses between the different soils studied, mostly because of the differences within soil samples (García-Gil, Kobza, Soler-Rovira, & Javoreková, 2013). In the same way, results from the research by (Langer & Günther, 2001) found that microbial biomass in soils (0-10 cm) decreased along with the distance to the P fertiliser plant and found up to a 60% decrease in DHA from soil samples to the nearest point to the plant, where the total F concentration in soil samples were on average 1,500 mg F kg^{-1}.

In contrast, a number of greenhouse experiments found that low F doses have a positive or nil influence on microbial activity and enzymatic activity. For instance, a study using different NaF soil solutions (100 to 1000 mg F l^{-1}) found no sign of microbial biomass being affected by any of the F dose treatments (Poulsen, 2011; Szostek, Ciećko, Walczak, & Swiontek-Brzezinska, 2015). On the other hand, Saini et al. (2012) found that catalase and peroxidase enzymes increased (around three folds) with increases in total F concentration (after 15 days treatment with 50 mg F l^{-1}).

In addition, a study carried out to measure changes on microbial activity in soils treated with NaF solutions found a reduction of less than 10% of the microbial biomass at the highest F doses in respect to the control treatment. However, at low F doses, microbial activity was increased by less than 20% in respect to no NaF exposure treatment (Ropelewska, Dziejowski, & Zapotoczny, 2015) (Table 9). Similarly, Szostek et al. (2015) also found that F doses ranging from 100 to 200 mg F kg^{-1} soil had positive influence in soil microbial activity.

Table 9. Effects of different F doses on microbial biomass values

F dose (mg F kg^{-1} soil)	Microbial biomass (mg C kg^{-1} soil)
0	664 ±18
500	759 ±9
1000	790 ±9
2000	727 ±0
3000	695 ±0
4000	632 ±32
5000	616 ±0

Modified after Ropelewska et al. (2015)

2.5.4. Potential F risks to land and groundwater

In general, F leaching to groundwater will be influenced by biological, chemical and physical factors governing fate of F in soils (Hedley et al., 2007). In some countries, F is a major contaminant in groundwater bodies and F-enrichment occurs naturally due to the properties of the parent rock material in aquifers and in some cases, due to large inputs from geothermal waters. However, several authors agreed that F risks to groundwater appear to be negligible or null for New Zealand soil conditions, because F is highly retained in the soils surface and hence, very little risk for F leaching into groundwater (Cronin et al., 2000; P. Loganathan et al., 2006; P. Loganathan et al., 2003). However, continued addition of F to soils from P fertilisers to agricultural soils may pose a more serious risk in the future, and more specifically, those areas with high water table in relation to soil surface and where the soil pH is below 5.5 or above 6.5 (P. Loganathan et al., 2006).

Regarding F risks to land, there are no current studies to assess the effects of F on agricultural land uses. However, there is evidence that other fertiliser-derived contaminants such as Cd can potentially cause adverse impacts on land use flexibility. For instance, land subdivision and land use change could be limited by Cd soil values above the Cd guideline values, restricting to subdivide farmed land to residential or to change it from pastoral land use to horticultural (CWG, 2008). In a similar way, F accumulation in agricultural soils may also one day limit land use flexibility.

2.6. Potential economic risks of F accumulation in agricultural soils

Despite the evident economic benefits from phosphate fertilisers use for farming, there are no current economic risk-based assessments on soil F contamination after prolonged and repeated use of P fertilisers in New Zealand. The estimations on the risks from P fertiliser-derived trace elements accumulation in agricultural soils will be related to the environmental risks for each specific key soil contaminants of concern. For instance, Cd in New Zealand agricultural soils has been assessed and agreed thresholds has been established to protect public health and the environment (CWG, 2008). Regarding soil F, short-term risks are considered to be low, but long-term effects are associated with livestock welfare and soil conservation and sustainability (Cronin et al., 2000).

Potential economic implications of F accumulation in agricultural soils are mainly related to the increasing F intake by livestock and consequently, accumulating in bones, causing chronic fluorosis. In addition, microbial activity can be negatively affected by relatively high F levels in pastoral soils, and subsequently cause a decline in the productivity of soils and land value and soil degradation. Besides, a decrease in food production could affect export revenues, either because of failings in meeting the demand or because damage in New Zealand's reputation in overseas markets due to perceived issues with food safety and the awareness of the environmental costs of the long-term SPP application (Dominati, Mackay, Green, & Patterson, 2011).

An empirical study was carried out to analyse the impact of soil contamination on farmland values using a hedonic approach for agricultural land (Schreurs, Van PasseL, Peeters, & Thewys, 2013). The model was developed by using different variables related to land productivity of a farmland and future prices of on specific parcel, taking into account factors that might affect soil functionality. Generally, land value is only measured by its capacity to produce food or to sustain a specific land use. Soil resources are important contributors of ecosystem services such as regulation and provision. The valuation of land services is very important to assist sustainable land management. Dominati et al. (2011) found that soil

regulation services[3] have more value than provision[4] of services to a land. In other words, soils are valued better because of their participation in geochemical processes such as carbon storage and role in nutrients absorption than its capacity to provide food, materials and physical support for human living and microorganisms play a pivotal role on provision of services. As a consequence, high F levels in soils could impact on soil provisioning of services as potentially cause harmful effects on soil microorganisms (Dominati et al., 2011).

The future economic risks of F in agricultural soils can be estimated by examining how soils are and might be used and aggregating the economic costs of:

- Livestock chronic fluorosis treatments, cattle losses and products and by-products not meeting international food quality standards,
- Soil productivity loss, in relation to the costs of improving nutrients in F-contaminated soils,
- Adopting new farm management strategies to minimise F risks to grazing animals,
- Potential trading losses, in relation to the public risk perception on agricultural soil contamination which may threaten New Zealand's international market reputation.

2.7. New Zealand regulatory framework on key soil contaminants

New Zealand is divided into 16 regions of local government domain (regional councils or RCs), and each regional authority is responsible for natural resource management. The Resource Management Act (RMA) 1991 and its amendments is the Act of Parliament or law containing policies related to the use of land, water and air. The purpose of the legislation is to promote the sustainable management of natural and physical resources in New Zealand and it serves as the regulatory and policy framework regarding the environmental management aspects of contaminated land and soil (Resource Management Act, 1991).

Under section 30 of the RMA, RCs are required to safeguard the life-supporting capacity of the land by regulating practices related to land use while maintaining the physical, chemical and

[3] Regulating services: some examples of soil regulation services are flood mitigation, cycling nutrients and filtering contaminants, carbon storage and greenhouse gases regulation, detoxification and the recycling of wastes and regulation of pests and diseases populations.

[4] Provisioning services: some examples are provision of food, wood and fibre, provision of raw materials and provision of support for human infrastructures and animals

biological qualities of soil (i.e. soil conservation). For that, RCs design a Regional Policy statement (RPS) that will contain all policies and methods to achieve the RMA objectives. Other RC functions are identifying and monitoring land in respect of contamination, as well as preventing or mitigating any adverse effects on land. In order to successfully meet their responsibilities, it is vital that RCs understand the impacts of contaminants to soil and biological receptors (Jo Cavanagh, 2015). The various activities to manage resources will vary from one RC to another (Resource Management Act, 1991), (Haggerty J. & Campbell H., 2008).

There are different policy regulations on soil contaminants, both for contaminated site and agricultural land use. Local governments are responsible for monitoring the effects of farming, especially those from long-term intensive land use. Land having contaminants to toxic levels is eligible to be entitled as "contaminated land" and land use flexibility can be limited (Resource Management Act, 1991), p. 34.

There is currently regulation in force to manage land contaminants, for instance, National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health (NES). However, from the agricultural perspective, from all the fertiliser–derived trace elements affecting agricultural soils, only Cd is currently being managed under a voluntary system approach. As a consequence, participation of the fertiliser industry and other stakeholders is essential in order to reduce and control Cd accumulation in soils.

Voluntary agreements have emerged from both the private sector and the government in identifying and implementing land management practices and actions to reduce the rate of Cd accumulation in agricultural soils. The Cadmium Working Group (CWG) is an example of a multidisciplinary group to investigate and assess the potential risks of Cd in New Zealand agricultural systems and to provide responses and solutions for the Cd issue. The CWG has developed the Cadmium Management Strategy (CMS), containing the Tiered Fertiliser Management System (TFMS) as a method to gradually control accumulation of Cd in New Zealand agricultural soils from P fertiliser application (Sneath, 2015).

As regards to the F in New Zealand agricultural soils, it can build up in pastoral topsoils to levels that are reasonably likely to have significant adverse effects on the environment and affect soil functions and to date there are no globally agreed F guidelines for agricultural soils or regulations to set permissible levels of F in grazing systems. However, establishing a single

threshold for soil F is difficult because soils are very complex and dynamic entities on which F behaviour is very variable, and the soil's ability to retain F changes with the soil's properties and also with the land use and management. In addition, there is large variation of reported F in various soil matrices, as well as the F speciation and variability of natural F concentration in soils (Cronin et al., 2000).

However, in respect to regulation, F has been recently recognised by both the Waikato Regional Council (WRC) and the Canterbury Regional Council (CRC) as a key soil contaminant emerged from prolonged and intensive P fertilisers use that could compromise soil conservation and land flexibility in the short-term (Kim et al., 2016; Taylor, 2016). The WRC is currently considering adopting risk-based guidelines and establishing a process to determine discharge limits for F and other key soil contaminants. Also, Environment Waikato (2011) through its Natural Resources Regional Plan (NRRP) has acknowledged F as an emerging issue that could generate soil conservation problems in the relatively near future, but the F significance is not yet entirely known.

Despite not yet being directly addressed, F in agricultural soils is indirectly being managed by the TFMS. It is a voluntary policy instrument to prevent Cd to continue building up in fertilised soils to potentially toxic levels. The TFMS policy strategy has been voluntarily adopted by the fertiliser industry in New Zealand, having implemented and adopted proposed guidelines, but assessment of its effectivity has not yet being established (Rys, 2011). Other voluntary instruments to address the F emerging issue in New Zealand agricultural soils are best farming practices for fertiliser use and application, nutrient management programmes and a fertiliser code of practice (Fertiliser Association, 2012a).

Currently, the provisional Ecological Soil Guideline Values (Eco- SGV) document was developed for F in New Zealand agricultural soils, using background soil F data published by Kim et al. (2016) (Table 10). The purpose of the Eco-SGV is to manage contaminated land and to protect soil functions. The setting of maximum soil contaminant limits pursues the protection of public health, soil organisms, plants and livestock, while accessing the maximum benefits from the application of P fertilisers (Jo Cavanagh, 2015). In addition, background values can be used as a benchmark for assessing impacts on ecosystem services associated to soil monitoring over time.

Table 10. Proposed Eco-SGV for F contamination in reference to NZ soils, added F contaminant levels and background levels

Land use	Soil	BC* (mg F kg^{-1})	ACL** (mg F kg^{-1})	Eco-SGV*** (mg F kg^{-1})
Areas of ecological significance	Volcanic soils	122 – 265	0.5	120 – 260
	Sandstone, siltstone, greywacke	204		200
Agricultural and non-food production land	Volcanic soils	122 – 265	5	130 – 270
	Sandstone, siltstone, greywacke	204		210
Residential/ Recreational	Volcanic soils	122 – 265	29	150 – 290
	Sandstone, siltstone, greywacke	204		230
Commercial/ Industrial	Volcanic soils	122 – 265	83	200 – 350
	Sandstone, siltstone, greywacke	204		290

*BC: background value **ACV: added contaminant values ***Values have been rounded and the final Eco-SGV should be based on background concentrations relevant to the site under assessment
Modified after: J. Cavanagh and Munir (2016), p 51

2.8. Determination of F in soil matrices

There are various techniques to determine F in various matrices but the main differences between methods are in the way to prepare the samples and the analytical method used to determine F. There are a range of methods to extract F from various matrices, as explained by Campbell (1987). To cite a few: diffusion, ashing, distillation, pyro-hydrolysis and fusion. Following, colorimetric methods were routinely used to determine F in extracted samples (Willard & Winter, 1933). However, since the introduction of the ISE method, total F analyses have become more reliable over time and it has also facilitated more studies to accurately assess F concentrations in aqueous-phase soil matrices.

2.8.1. Interfering elements in F analysis and TISAB function

Allophane and ferrihydrite are Al and Fe rich phases in soil and play an important role in F absorption, thus Al/Fe complexes with F can interfere with F quantification during analysis. Aluminium is the most important interfering element in F analysis, as Al forms complexes much more stable with F than corresponding Fe-F complexes (Campbell, 1987). The strong

alkali conditions of alkali fusion separate any existing Al/Fe complexes formed with F in samples (Jeyakumar & Anderson, 2015). However, under these circumstances, Al hydroxides are soluble and can enter the filtrate solution and form complexes with the F when buffering the pH solution to 5.2 for the ISE measurement. The Al and Fe oxides interactions with clays are very dependent on pH and at acidic conditions, can precipitate as positive charged oxy-hydroxides (Goldberg, 1989). Solubility of Al is minimum at neutral pH, therefore, solution pH is important in removing all interfering elements in order to avoid them entering the filtrate. For this, pH ranging between 8 and 9 after fusion is considered as optimal to precipitate Al and Fe as insoluble oxides (Jeyakumar & Anderson, 2015).

The total ionic strength adjustment buffer (TISAB) solution has three main functions in F determination, (a) to adjust pH to a constant value, (b) to minimise variation between samples and standards by providing constant ionic strength and (c) to release all F complexes that will interfere with the reading. Aluminium is the main troublesome interfering element because it forms stable compounds with fluorine (Campbell, 1987). Al and Fe oxides are extracted from soil matrices by ammonium oxalate solution, whereas for total content, the sample needs to be digested in a concentrated acid mixture of hydrochloric and nitric acids to breakdown all complexes (Blakemore, Searle, & Daly, 1987). Both the traditional and the alternative methods used in this study are followed by the ISE for F determination.

2.8.2. Fusion alkali/ISE method

Jeyakumar and Anderson (2015) reviewed 10 different analytical methods to determine total soil F, compared the matrices, sample preparation and analytical methods used in different studies. The majority of the revised studies used the ISE to measure F. For instance, the highest recovery percentage range (95% to 100%) was found in a study carried out by (McQuaker & Gurney, 1977), fusing soil samples prepared with sodium hydroxide 17 M (NaOH), filtered and subsequently buffered to pH 5.2. Formerly, colorimetric methods were routinely used to determine F in various matrices, but the fluoride ISE is the preferred procedure to measure F in aqueous solutions as it is more tolerant to interferences in the solution (Campbell, 1987). The alkali fusion/ISE is considered to be labour-intensive and complex. Since the early 1930s, the development of F determination methods has focused on improving existing techniques to establish a less time-consuming procedure (Willard & Winter, 1933; Baker, 1972; Campbell, 1987).

Baker (1972) introduced the ISE technique combined with the alkali fusion method. Fusing and ash sample with a strong alkaline solution was found to be necessary for those samples with high silicate and ash content to solubilise fluorides in the samples. Optimum results were obtained by using NaOH. Later, McQuaker and Gurney (1977) described the widely adopted NaOH alkali fusion/ISE technique and they proposed that it could be used to analyse F in soil matrices. Their modification to the conventional method included the replacement of the distillation used by Willard and Winter (1933) by filtration to eliminate interfering elements in the sample such as Al and Fe. Once F is extracted from the material of concern, measurement is done using an F-ISE probe with addition of TISAB.

2.8.3. NaOH extraction/ISE method

Although the alkali fusion/ISE method has been used in most studies (Jeyakumar & Anderson, 2015), the tedious and time-consuming process required to quantify F is a limitation for wide-scale environmental assessments and may be contributed to the lack of previous research on agricultural soil F concentrations (Kim et al., 2016; P. Loganathan et al., 2003).

A recently developed methodology by Massey University was proposed as an alternative method to determine F, the NaOH extraction followed by ISE. The method showed good correlation with the alkali fusion/ISE method (R^2=0.85–0.90) across a variety of New Zealand soil types using dilute NaOH solution (4M) (Jeyakumar & Anderson, 2015). Table 11 summarises a comparison of NaOH method in relation to the traditional method.

Table 11. Comparison of total F determination methods in soils

	Alkali fusion/ISE	NaOH extraction/ISE
Sample extraction	Extraction by fusion (700°C) using a strong alkaline solution (17 M NaOH) in Ni crucibles.	Extraction with less concentrated NaOH solution (4M) followed by water bath in centrifuge tubes
F determination	ISE (using TISAB)	ISE (using TISAB)
Advantages and limitations	Accuracy is very dependent on specific soil properties (Al/Fe oxides). Strong alkaline solution NaOH 17 M. Good reproducibility but complex sample preparation, time consuming, tedious and cumulative handling errors. Equipment might be a limitation for large-scale F analysis (e.g. Ni crucibles and furnace).	Very low variation (<15%) using soil samples high in interfering elements (Al and Fe oxides). Dilute NaOH 4M showed good recovery levels (Jeyakumar & Anderson, 2015). Good reproducibility but tested on a small sample size (10 soils). Simple equipment needed less time-consuming and less intensive labour. Relatively less costly in relation to the traditional method, potentially being used for large-size samples Less hazardous risks when handling NaOH solutions

Compiled from Jeyakumar and Anderson (2015) study and own laboratory notes.

Chapter 3 Methodology

3.1. Introduction

This research described in this thesis was conducted in two sections related to F analysis in pastoral soils. The first section is dedicated to the validation of an F determination technique recently developed in Massey University, and to assess the variability of F content across 13 New Zealand pastoral soils. The second section uses the validated methodology to assess the effects of F on the soil microbial activity of six New Zealand pastoral soils. Soil samples for total F and microbial analyses were selected from a variety of soil types across New Zealand which have a long-term history (>10 years) of P fertiliser application. This chapter provides a description of the soils used for the F analysis and the microbial analysis, as well as the laboratory methods and statistical data analysis used in the study.

3.2. Soil sample collection

For the F analysis, soil samples (0-15 cm depth) previously collected by Jeyakumar and Anderson (2015) were initially used (soils Nº 1 to 10 in Table 12) to complete the objectives of the work, additional soils samples (0-15 cm depth) were subsequently added to the soil collection, which were previously collected by FLRC staff (soils Nº 11 to 13 in Table 12). The total soil collection correspond to 13 different sites across New Zealand and were originally sampled from agricultural land use with a long-term history of P fertiliser application (>10 years).

For microbiological analyses, soils were sampled from six other pastoral sites across New Zealand. In each site, paddocks were randomly selected for sampling and subsamples were collected across the paddock through linear transects. Soils were collected from a 0-15 cm depth using a 2.5 cm diameter soil corer. In each site, approximately 2 to 3 kg of soil was collected and stored in sterilised plastic bags, labelled and kept refrigerated (5ºC) until analysis. Sampling equipment was routinely cleaned before and after sample collection to prevent any cross-contamination. Table 12 describes soil sample locations, specific land use and soil orders used for F and microbiological analyses.

Table 12. Description of soil samples used for both total F and microbiological analysis

Soil	Location	Region	Soil order	Land use(*)
Total F analysis				
1	Gordonton	Waikato	Organic	Dairy
2	Otorohanga	Waikato	Allophanic	Dairy
3	Putaruru	Waikato	Allophanic	Dairy
4	Reporoa	Waikato	Pumice	Sheep/Beef
5	Te Anau	Southland	Brown	Sheep/Beef/Deer
6	Newstead	Waikato	Allophanic	Dairy
7	Tuapaka	Manawatu	Pallic	Dairy/Beef
8	Manawatu	Manawatu	Recent sedimentary alluvial	Dairy
9	Tokomaru	Manawatu	Pallic	Dairy/Sheep
10	Te Aroha	Waikato	Gley	Dairy
11	Lincoln	Canterbury	Pallic	Dairy
12	Morrinsville	Waikato	Allophanic	Dairy
13	Mangakino	Waikato	Pumice	Dairy
Microbiological analysis				
1	Lincoln	Canterbury	Pallic	Potato -Wheat
2	Manawatu	Manawatu	Recent sedimentary alluvial	Potato
3	Massey Dairy Farm N°4	Manawatu	Pallic	Pasture - Dairy
4	Tuapaka Farm	Manawatu	Pallic	Pasture - Sheep
5	Otorohanga	Waikato	Allophanic	Horticultural
6	Pukekawa	Waikato	Granular	Horticultural

(*)Phosphate fertiliser application history (>10 years)

3.3. Soil sample preparation

Prior to the physical and chemical analyses, collected bulk soils were air-dried and sieved (<2mm), labelled and kept stored in sealed containers in a dry storage room (Soil Laboratory Massey University, Palmerston North). Prior to the F analysis, each soil sample was subsampled four times by riffle-splitting, followed by ring-grounding to obtain soil particle sizes of around 250 µm. Subsamples were then oven-dried overnight at 105ºC in containers correctly labelled and kept in a dry area until F analysis. Prior to the microbial analyses, all fresh soils were sieved (<4mm) and incubated at 80% maximum water-holding capacity (MWHC) as described by Gradwell and Birrell (1979) at 25°C for 10 days.

3.4. Laboratory methods

The soil samples were analysed for a range of variables that may assist in putting results into context. Soil physical and chemical analyses include total F concentration, pH, total and extractable Al and Fe and soil organic matter (SOM) content. The microbial analyses included microbial biomass carbon (Cmic) and dehydrogenase enzyme activity (DHA). All measurements were done in triplicate.

3.4.1. Total soil F by alkali fusion/ISE method

The method described by McQuaker and Gurney (1977) and Jeyakumar and Anderson (2015) was followed to determine total F concentration in soil. A portion of 0.25 g of prepared soil samples was analytically weighed into replicate nickel (Ni) crucibles. Small amounts of water (<2 ml) and ethanol drops were added to moisturise each soils. Sodium hydroxide 17 M (6 ml) was added to the moisture, mixed with a spatula and oven-dried overnight at 105ºC. The Ni crucibles were then placed in a furnace to fusion at 700ºC for around 3 hrs. The fused mass contained in the crucibles was then dissolved with deionized (DI) water (≃10 ml) on a hot plate (reaching temperatures of around 60ºC). Further DI water was slowly added (<20 ml) with constant stirring and scraping of the alkaline crystals using a Ni spatula. Each solution (dissolved fused mass) was then quantitatively transferred to correctly labelled 100 ml plastic containers.

Following this, the pH of the dissolved fused mass was adjusted to 8.5 by slowly adding concentrated chloric acid (HCl) while stirring with a magnetic stirrer. Approximately 3 to 4 ml of concentrated HCl was drop-wise added to adjust the pH of the solution to 8.5. The procedure was done using a pH meter (Thermo Scientific Onion ROSS sure-flow pH electrode), previously calibrated with 4 and 7 standard solutions according to the instructions of the equipment. Before and after each soil sample, the probe was carefully cleaned with DI water and dried with a soft tissue. The final solution volume was less than 100 ml. The adjusted pH soil solution was made up to 100 ml in a volumetric flask and passed through a Whatman 42 filter paper. The filtered solution was stored in 100 ml plastic containers, correctly labelled and kept refrigerated (5ºC) until F analysis with ISE.

3.4.2. Total ionic strength adjustable buffer (TISAB) solution preparation

The TISAB maximises the amount of free F ions in the solution for a more precise reading by ISE. The functions are (a) regulates the pH of the solutions and provides constant ionic strength through all the analysed samples and (b) acts as a metal ion-complexing agent. TISAB destroys the F complexes formed with the Al and Fe amorphous and crystalline oxide phases in soils (Spano et al., 2015). For the TISAB preparation 58 ml of glacial acetic was added to 300 ml of DI water; 12 g of citrate dihydrate was dissolved into the solution and pH was accurately adjusted to 5.2 with the right amounts of 6M NaOH. The final volume was made up to 1000 ml in a volumetric flask (McQuaker & Gurney, 1977).

For F determination with ISE, equal volumes of TISAB (10 ml) and a filtered soil solution (10 ml) were placed into a screw-top polypropylene container. The total F was then calculated from a calibration curve, plotting F standards against mV readings. The probe electrode stabilisation was done before use and the probe was cleaned in between samples with DI water and gently dried with soft tissues. A calibration curve was prepared from an F standard solution of 100 ppm, with ranging concentrations from 0 to 50 ppm F in solution.

3.4.3. Total soil F by NaOH extraction method

The NaOH extraction technique was followed as described by Jeyakumar and Anderson (2015). Three different NaOH concentrations were used with three replicates for each extraction. A subsample of prepared soil (0.5g) was weighed on an analytical balance into centrifuge tubes. NaOH (10 ml) was added to each tube according to the three different NaOH concentrations, 4M, 10M and 16M. Centrifuge tubes were capped slightly tight then placed in a water bath (85 to 100ºC) for 24 hrs with frequent manual shaking of each tube at least three times during this time. The solution was quantitatively transferred to 100 ml plastic containers by washing the tubes with DI water to obtain as much as soil/NaOH solution as possible while trying carefully not to exceed it using more than 10 ml DI water. Following this, the pH of the obtained solution was adjusted to 8.5 by slowly adding 3 to 4 ml of concentrated HCl while stirring with a magnetic stirrer. The adjusted pH soil solution was made up to 100 ml in a volumetric flask and passed through a Whatman 42 filter paper. The filtered solution was stored in 100 ml plastic containers, correctly labelled and kept refrigerated (5±1ºC) until F analysis with ISE.

3.4.4. Determination of soil pH (H_2O)

Soil acidity or alkalinity was measured by weighing approximately 10 g of air-dried soil into a 100 ml beaker and adding 25 ml of DI water. After stirring vigorously, the soil-water mixture was left covered overnight at room temperature (20±1ºC). The pH measurement was done with a pH meter (Thermo Scientific Onion ROSS sure-flow pH electrode) after a single stirring. Three replicates were performed for each soil (Blakemore et al., 1987).

3.4.5. Determination of Al and Fe content

The methods as described by Blakemore et al. (1987) were followed to obtained total and extractable concentrations of Al and Fe fractions in soil samples.

3.4.5.1. Acid oxalate method – extractable Fe and Al in soil

This method extracts the amorphous fraction of Fe and Al in soils and corresponds to the bioavailable portion of the oxides. Approximately 0.4 g of sieved soil sample (<2 mm) was analytically weighed into centrifuge tubes, adding 40 ml of acid oxalate reagent solution (pH=3) and shaking tubes in an end-over shaker under dark conditions for a 4 hr period. Tubes were centrifuged for 10 minutes at 10000 rpm followed by filtration with the paper Whatman Nº42. The extracted solution was stored in screw-top containers and kept refrigerated (around 4ºC) until analysis. Extractable Fe and Al content in filtered solutions was determined by the Microwave Plasma – Atomic Emission Spectroscopy technique (MP-AES 4200 - Agilent, Germany). The procedure was done in three replicates for each soil.

3.4.5.2. Digestion method - total Al and Fe in soil

This method extracts both the amorphous and crystalline Fe and Al oxy-hydroxides. Soil samples were passed through <2 mm sieve and weighed (0.4 g) into digestion tubes then 5 ml of aqua-regia (3:1 HCl (c), HNO3 (c)) was added and kept overnight at room temperature. The tubes were then transferred to the digestion block at 60ºC until reaction settled. Glass funnels were placed on top of each tube to reflux the solution at 120ºC for up to 4 hrs. The temperature was then again increased to 150ºC for final digestion until the final solution volume was around 1 ml. When the tubes were cooled down, DI water was added to make up a final volume of 25 ml. Following this, the digestion tubes were shaken on a vortex mixer and the solution was

filtered through Whatman 42 filter paper. The extracted-filtered solution was stored in screw-top containers, labelled and kept refrigerated (around 4ºC) until analysis with MP-AES. The procedure was done in three replicates for each soil.

3.4.6. Determination of soil organic matter

Ring ground soil samples were weighed in triplicate into tin metal cups (around 130 mg) with the addition of the same amount of Tungsten oxide powder. The cups were then carefully wrapped to prevent sample oxidation before analysis (Blakemore et al., 1987). The soil organic carbon (SOC) was measured by elemental analysis using an Elementar® vario max cube.. In order to compare values with soil microbial activity and other soil properties results, the SOC values were converted to SOM by using 2.0 factor (Pribyl, 2010).

3.4.7. Microbial biomass carbon

Soil microbial biomass carbon (Cmic) was quantified following the fumigation/extraction (FE) method as described by Vance, Brookes, and Jenkinson (1987). Three portions (5 g of equivalent oven dry) of incubated soil sample were weighed in centrifuge tubes, treated with 20 ml 0.5M K_2SO_4 and shaken in a rotating shaker for half an hour. The solution was then filtered using Whatman 42 filter paper and then transferred to a screw-top plastic container and kept refrigerated (~5ºC) until analysis. This portion corresponds to the “control treatment” or non-fumigated portion.

Three other portions of soil samples (5 g of equivalent oven dry) was fumigated with approximately 25 ml of ethanol-free $CHCl_3$ in a desiccator and kept dark for 24 hrs at 25°C. Following this, 20 ml of 0.5M K_2SO_4 was added and the samples were shaken and filtered as per the non-fumigated samples. Both control and microbial soil treatments were performed simultaneously to avoid differences in microbial activity between control and fumigation samples.

Following this, filtered solutions (8ml) from both control and fumigated soils were digested in a round-bottom flask with 66.7 mM $K_2Cr_2O_7$ (2 ml), HgO (70 mg) and a mixture (15 ml) of two parts H_2SO_4 (98%) and one part H_3PO_4 (88%). A few anti-bumping granules were also added to each flask to prevent splatter during distillation. The solution was boiled in open reflux

for half an hour and rinsed with 20-25 ml DI water once the flasks were cooled down. The consumed dichromate in the solution was determined by back titration, using $K_2Cr_2O_7$, ferrous ammonium sulphate (FAS) and sulphuric acid plus silver sulphate as reagents and a concentration of 25 mM 1,10-phenanthroline-ferrous sulphate complex solution as indicator. A standard curve was prepared to calculate the actual concentration of FAS.

The extractable C in soil samples was calculated assuming that 1 ml of 0.4 N $K_2Cr_2O_7$ is equivalent to 1200µg C and biomass C was calculated from biomass C=2.64Ec, where Ec is the difference between C extracted from the fumigated and non-fumigated treatments.

3.4.8. Dehydrogenase enzyme activity

Dehydrogenase activity (DHA) was used as a measurement of microbial activity in soils. The method was followed as described by Chander and Brooks (1991). A portion of incubated soil (4 g) was weighed and transferred to a screw-top plastic container. Approximately 0.1 g of $CaCO_3$ and 2 ml of triphenyl tetrazolium chloride (TTC) was added to each samples and shaken on a vortex shaker and placed them in the dark immediately for 7 days. Following this, a volume of methanol (15 ml) was added to each screw-top plastic container and mixed thoroughly using a vortex mixer. The solution was then filtered through a Whatman 42 paper filter. The amount of triphenyl formazan (TPF) in the solution was measured by using a spectrophotometer to measure by a spectrophotometer at a wavelength of 484 nm. The absorbance readings were plotted against the TPF concentration (µmol/ml) using a standard curve for calculations. For the TPF standard curve, a stock solution of 0.2 µmol ml^{-1} was prepared by dissolving 0.03 g TF in 500 ml methanol. The stock solution was diluted with methanol to produce 11 solutions with TF concentrations ranging from 0.004 to 0.10 µmol ml^{-1}. The absorbance of each solution was measured with (Burdock, Brooks, Ghaly, & Dave, 2011).

3.5. Data quality control

The methods and procedures were performed with accuracy and precision, following laboratory protocols and manuals of calibration and operation. The chemical stocks used in this study were of analytical grade. Two FLRC reference soils were also analysed as F standard materials: Soil A: S07052003A with an F concentration of 168 ± 29 mg F kg^{-1} oven-dry soil; and Soil B: S07052003B with an F concentration of 542 ± 30 mg F kg^{-1} oven-dry soil. Blank and control

samples were also included in each laboratory method to confirm the accuracy of both physical and microbial analyses. The absorbance reading for the dehydrogenase enzyme activity in the blank solution was below the detection limit (0.000).

3.6. Data analyses

All results were presented as the arithmetic mean of three replicates within standard errors. Descriptive statistics were performed to characterise data, mean values and standard deviation. Total soil F, dehydrogenase enzyme activity and microbial biomass were presented on an oven-dry soil weight (105°C) basis (mg kg^{-1} oven dry soil). The soil organic matter, soil organic carbon, Fe and Al were presented as percentage. Analysis of variance (ANOVA) was conducted using the IBM SPSS and Minitab® statistical software packages to determine whether there were significant differences in total F concentration and other soil properties and also to determine significant differences between microbial soil activity values across soil samples (differences were interpreted to be statistically significant at the 5% level). The Turkey Pairwise comparison (95% confidence level) was used to group significant similar means between soil groups. Correlation of determination test was calculated using SPSS and values were used to determine total F concentration association with soil properties. Correlation test was also performed to determine reproducibility and variation of NaOH extraction method in relation to the fusion alkali method.

Chapter 4 Results and Discussion

4.1. Introduction

In this chapter, results obtained from the laboratory and data analyses are presented and discussed with the relevant literature. A summary of the chemical and microbiological properties of soil samples investigated in this study is presented in Table 13.

4.2. Total F concentration in surface soils (0-15 cm)

The total F concentration in the thirteen soils ranged from 152±8 mg F kg^{-1} and 708±124 mg F kg^{-1} as determined by the alkali fusion/ISE method (Figure 4). The total F concentration range reported in the current work lies within the total F range of 197 - 683 mg F kg^{-1}, obtained in a similar study of a set of New Zealand soils (0-10 cm) by (Jeyakumar & Anderson, 2015). Similar results were also found by Kim et al. (2016) where the total F concentration ranged from 216 to up to 900 mg F kg^{-1}.

The highest total F concentrations were found in Organic (708 mg F kg^{-1}) and Allophanic soils (average 569 mg F kg^{-1}, n=4) collected from the Waikato region, whereas the lowest concentrations were found in Pallic soils (average 281 mg F kg^{-1}, n=3) collected from Manawatu and Canterbury regions. On average, the total soil F concentrations found in volcanic soils was 403 mg F kg^{-1} (n=7). Another study found total average F concentration in New Zealand volcanic soils to be similar - 371 mg F kg^{-1} (P. Loganathan et al., 2003). Loganathan et al. suggesting that soils formed from volcanic parent material are generally higher in total F (175 -180 mg F kg^{-1}) than soils formed from sedimentary material (43 - 13 mg F kg^{-1}), and in unfertilised New Zealand soils (P. Loganathan et al., 2003).

In comparison to the F concentration in worldwide soils, the highest total F concentration obtained in this study is similar to the maximum total F concentrations reported in agricultural soils of 990 to 1,000 mg F kg^{-1}, reported by Gilpin and Johnson (1980) and Zhou and Sun (2002). The total F ranges in this study are also relatively similar to those total F concentrations found in F-contaminated soils from industry, 105 to 950 mg F kg^{-1} (A. K. M. Arnesen et al., 1995; Bhat et al., 2015; Haidouti, 1991). However, one study carried out near an Al smelter found total F concentrations up to 2,700 mg F kg^{-1} in soil (J. Polomski, H. Flühler, & P. Blaser, 1982).

Table 13. Soil properties of the soil samples collected from different NZ agricultural sites for F analysis and microbial activity respectively

	Soil order	Location	Total F				SOM	pH	Total		Oxalate-Extractable		Cmic	DHA	Cmic/SOC ratio
			Alkali fusion/ISE	4M NaOH	10 M NaOH	16M NaOH			Fe	Al	Fe	Al			
			mg F kg^{-1}	mg F kg^{-1}	mg F kg^{-1}	mg F kg^{-1}	(%)		(%)	(%)	(%)	(%)	mg C kg^{-1}	mg TPF kg^{-1}	
	Fluoride analysis[(a)]														
1	Organic	Gordonton	708	996	830	894	45.6	5.43	0.54	2.54	0.44	2.04			
2	Allophanic	Otorohanga	688	1015	820	912	20.1	5.56	1.12	9.82	0.84	7.12			
3	Allophanic	Putaruru	613	817	821	830	16.3	5.46	0.92	6.31	0.45	4.25			
4	Pumice	Reporoa	412	673	643	628	13.8	5.56	0.73	2.08	0.42	1.43			
5	Brown	Te Anau	207	218	243	285	17.5	5.59	2.13	6.37	1.03	2.68			
6	Allophanic	Newstead	457	755	688	742	12.6	5.65	0.90	6.57	0.60	4.67			
7	Pallic	Tuapaka	152	173	208	225	5.2	5.47	0.84	4.58	0.28	0.43			
8	Recent sed. alluvial	Manawatu	298	186	224	247	4.7	5.37	1.49	4.67	0.51	0.56			
9	Pallic	Tokomaru	216	203	207	231	7.3	4.96	0.89	3.78	0.37	0.48			
10	Gley	Te Aroha	395	578	483	563	8.9	5.59	1.05	7.80	0.47	0.73			
11	Pallic	Lincoln	344	174	181	214	4.9	5.91	1.27	3.86	0.35	0.53			
12	Allophanic	Morrinsville	516	662	609	594	7.8	6.02	1.19	8.28	0.55	2.44			
13	Pumice	Mangakino	541	816	664	709	14.5	5.33	0.36	1.87	0.26	1.59			
	Soil microbial activity[(b)]														
1	Pallic	Lincoln		105			4.8	5.08	1.87	2.36	0.45	0.39	453	5.74	1.88
2	Recent	Manawatu		77			4.0	5.22	1.80	2.29	0.60	0.29	816	7.47	4.08
3	Gley	Dairy		104			7.9	6.22	1.86	2.93	0.66	0.33	195	65.56	0.49
4	Pallic	Tuapaka		97			5.7	6.25	0.77	2.07	0.62	0.36	132	42.98	0.47
5	Allophanic	Otorohanga		729			20.2	6.53	2.07	7.02	1.44	7.82	257	133.53	0.26
6	Granular	Pukekawa		368			5.4	6.28	7.01	13.20	0.78	0.78	22034	4.59	82.22

ISE=ion specific electrode, NaOH=sodium hydroxide, M=molar, SOM=soil organic matter, pH= potential of hydrogen, Fe=iron, Al=aluminium, Cmic=microbial biomass carbon, DHA=dehydrogenase enzyme activity, TPF=. triphenyl formazan, SOC=soil organic carbon. (a)13 soil sites, 7 soil orders. (b) 6 soil sites, 5 soil orders. Values are represented as the average (n=3).

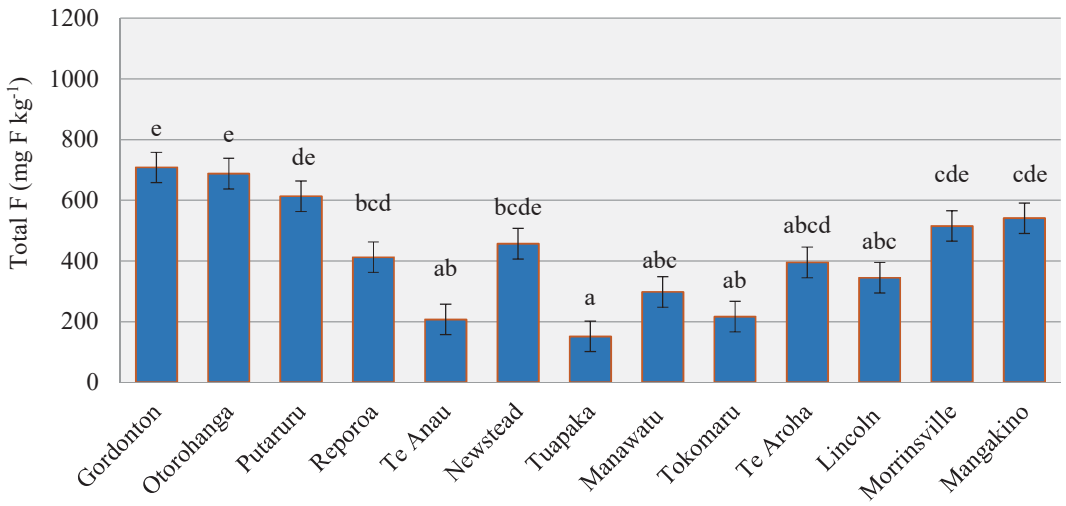

Figure 4. Total F concentrations found in 13 agricultural sites as determined by the alkali fusion/ISE method. Bars not sharing the same letter are significantly different at the 95% confidence level.

The total F concentrations found in different soil orders in this study were compared to the F background levels reported by Kim et al. (2016) and P. Loganathan et al. (2001) for NZ soils. The difference between reported background levels and the total F concentration found in this study suggests that Organic soils have the highest relative increment in total F, followed by Allophanic and Pumice soils (Table 14).

Table 14. Relative total F increments of different NZ soil orders, in relation to the F background levels

Soil order	Average total F concentration [c] mg F kg^{-1}	Background F mg F kg^{-1}	Relative surface F increment mg F kg^{-1} [d]
Allophanic	795	236 [a]	559
Brown	218	215 [a]	3
Gley	578	231 [a]	347
Organic	996	51 [a]	945
Pallic	183	176 [b]	7
Pumice	745	247 [a]	498
Recent	186	233 [a]	-47

[a] (Kim et al., 2016) (0-10 cm), [b] (P. Loganathan et al., 2001) (0-7.5 cm)
[c] Total F average concentration of soil sites grouped by soil order.
[d] Relative total increase in F refers to total F obtained by the 4M NaOH extraction method.

4.2.1. Comparison of total soil F methods

Comparison of the total F concentration determined by NaOH extraction against the concentration determined by alkali fusion (Figures 5, 6 and 7) showed that the NaOH extraction method at all three concentrations are significantly correlated (r>0.92) with the conventional method (alkali fusion/ISE). In addition, no significant differences were observed between the total F concentration determined by extraction with NaOH at the three different concentrations (4M, 10M and 16 M) (r>0.93) (Appendix III). This result are consistent with results obtained by Jeyakumar and Anderson (2015), who found a strong correlation between the NaOH extraction and the alkali/fusion method (r>0.9).

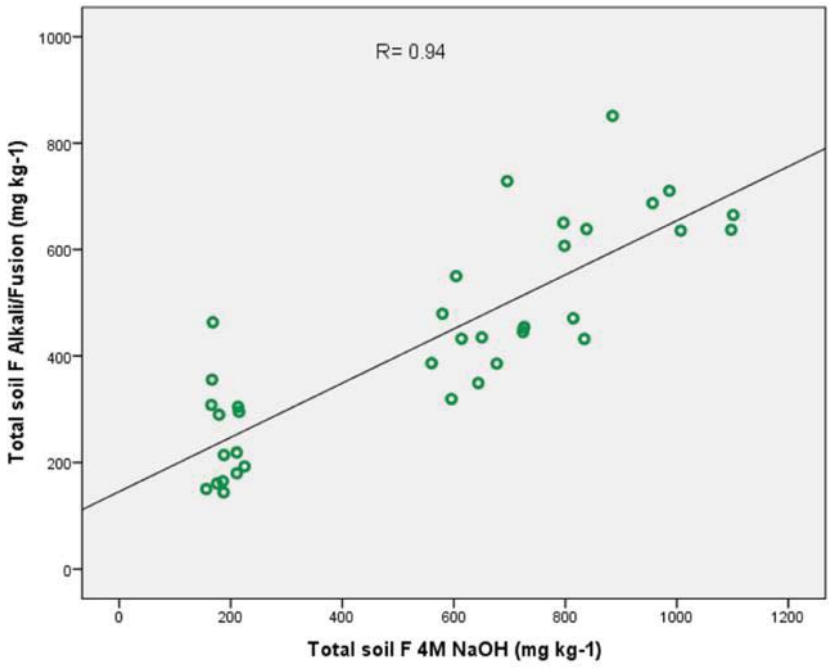

Figure 5. Scatterplot showing the comparison of the total F concentrations in 13 agricultural sites across NZ, as determined by the NaOH 4M extraction and alkali fusion/ISE methods (n=3)

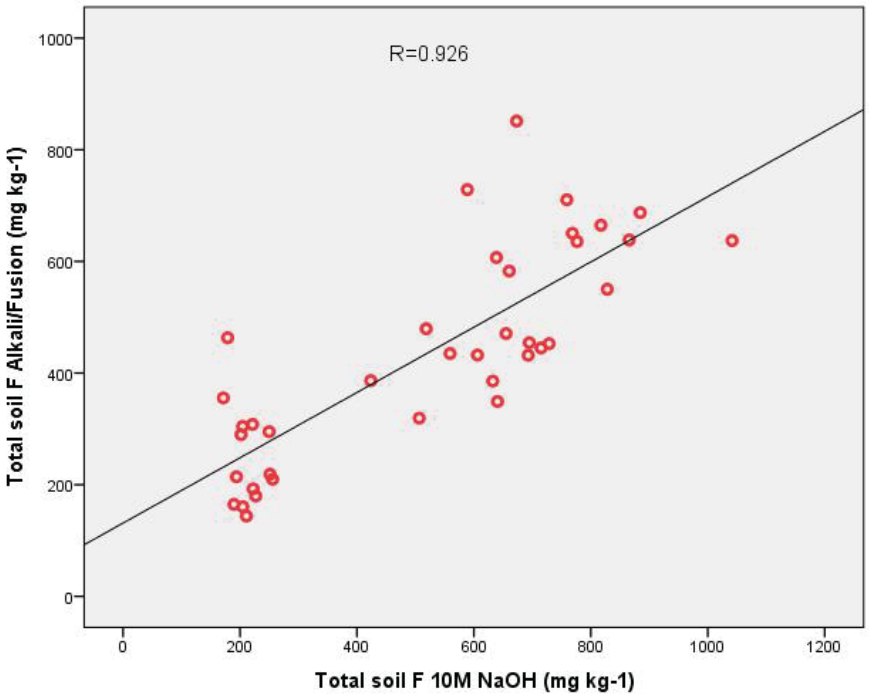

Figure 6. Scatterplot showing the comparison of the total F concentrations in 13 agricultural sites across NZ, as determined by the NaOH 10M extraction and alkali fusion/ISE methods (n=3)

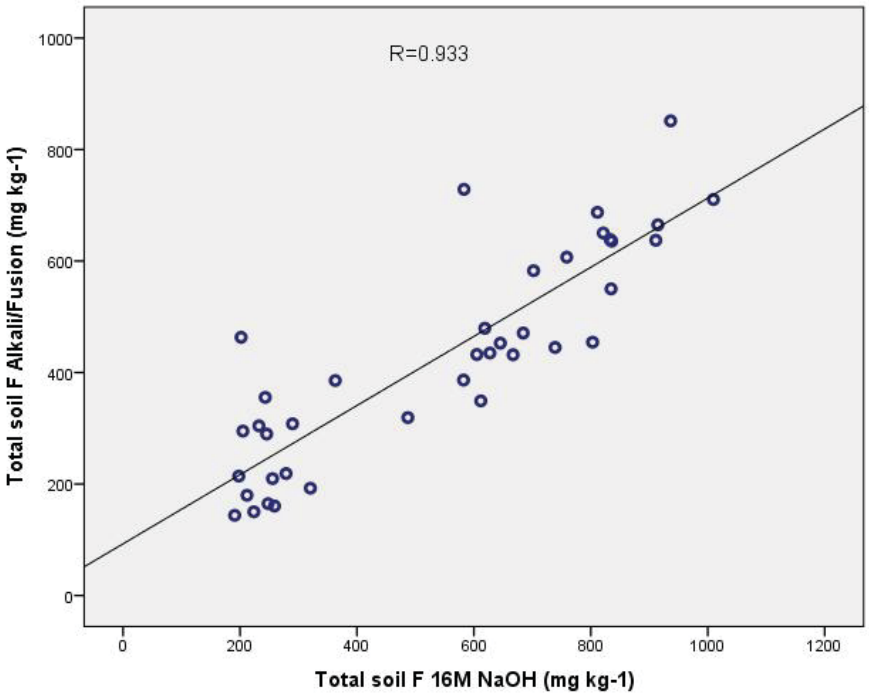

Figure 7. Scatterplot showing the comparison of the total F concentrations in 13 agricultural sites across NZ, as determined by the NaOH 16M extraction and alkali fusion/ISE methods (n=3)

The correlation tests between the traditional methodology and the NaOH extraction showed that both methods are highly correlated and over half of soil samples produced similar total F results as measured by the studied methods. Therefore, a good repeatability of soil F values is expected to be obtained using the NaOH extraction method relative to the alkali fusion/ISE. Therefore, NaOH extraction at the higher concentration followed by ISE is validated by this research as a method to reliably measure total soil F, with an acceptable F recovery level.

4.2.2. Variability of total F concentrations across soil orders as obtained by the NaOH extraction methods compared to the alkali fusion

The comparison test between the traditional method and the alternative method showed that, on average, total soil F results were significantly correlated across all soil samples. However, methods can vary within soil orders. To assess the relative accuracy of the extraction method in relation to the alkali fusion across different soils, the variability was calculated by comparing the percentage of variation between total F as measured by both the traditional and the conventional methods (Table 15), as described by Jeyakumar and Anderson (2015). Variability assessment determined the degree of variation of the methods to accurately measure F in a range of soil properties and determines the effectivity of the NaOH method in removing the F complexes with Al and Fe in soil matrices by grouping soils in relation to soil properties such as Al/Fe content. The alkali fusion was compared to the average total F determined by NaOH 4M, 10M and 16M. Agreement within 5% and 20% is defined in this study as low variability between the two methods; moderate variability ranges between 20 to 40%; and high variation exist between methods when differences are above 40%.

Comparison of the total F concentrations as obtained by the alkali fusion/ISE and the NaOH extraction method showed that on average, total F as determine by NaOH 10M was less variable (25%) across samples, and around half of the soil samples were in good agreement with the alkali fusion technique compared to the NaOH 10M and NaOH 16M extraction methods. Furthermore, Allophanic soils were less variable when measured by NaOH 10M, compared to 4M and 16M in relation to the alkali fusion.

These findings agree with the previous research results on NaOH extraction method. Jeyakumar and Anderson (2015) suggested the NaOH extraction method as an alternative method to the

alkali fusion. However, this study was performed with a higher number of samples and results also showed that NaOH is a reliable alternative method and that the NaOH 10M is considered to be the best proxy for F analysis, as it showed the lowest variability of total F concentrations across all soil orders relative to fusion. In addition, soil orders grouping effect showed that NaOH 10M is particularly good for Allophanic soils.

Table 15. Classification of soils in relation to the variability in total soil F concentrations as measured by alkali fusion/ISE and NaOH extraction

	Alkali fusion compared to NaOH 4M	Alkali fusion compared to NaOH 10M	Alkali fusion compared to NaOH 16M
Very low variability (<5%)	15- Soil B FLRC	9- Pallic Tokomaru	
Low variability (5-20%)	5-Brown Te Anau 7-Pallic Tuapaka 9-Pallic Tokomaru 14-Soil A FLRC	1 - Organic Gordonton 2-Allophanic Otorohanga 5-Brown Te Anau 12 -Allophanic Morrinsville 15- Soil B FLRC 14- Soil A FLRC	8- Recent Manawatu 9-Pallic Tokomaru 12 -Allophanic Morrinsville 14- Soil A FLRC
Moderate variability (20-40%)	3-Allophanic Putaruru 8- Recent Manawatu 12 -Allophanic Morrinsville	3-Allophanic Putaruru 7-Pallic Tuapaka 8- Recent Manawatu 10-Gley Te Aroha 13-Pumice Mangakino	1 - Organic Gordonton 2-Allophanic Otorohanga 3-Allophanic Putaruru 5-Brown Te Anau 11-Pallic Lincoln 13-Pumice Mangakino 15- Soil B FLRC
High variability (>40%)	1 - Organic Gordonton 2-Allophanic Otorohanga 4-Pumice Reporoa 6-Allophanic Newstead 10-Gley Te Aroha 11-Pallic Lincoln 13-Pumice Mangakino	11-Pallic Lincoln 6-Allophanic Newstead 4-Pumice Reporoa	4-Pumice Reporoa 6-Allophanic Newstead 7-Pallic Tuapaka 10-Gley Te Aroha

4.2.3. Relationship between total F and soil properties

The total F concentration as measured by traditional and alternative methods showed good correlation with some soil properties (Table 16). The relationship between total F and oxalate-extractable Al was significant across all F determination methods when all of the soil samples analysed in this research are considered ($r>0.59$). Figure 8a illustrates the association between total F, as determined by NaOH 4M, and the average percentage of oxalate-extractable Al. The scatterplot shows a trend that total F increases with the content of amorphous Al in soils. This suggests that most of the F^- in soils complexes with the labile fraction of soil Al ($r=0.69$) (Omueti & Jones, 1977).

These findings are in agreement with other studies. Positive correlation between total soil F and extractable Al was found in a study of the total F concentration and New Zealand soil properties ($r=0.49$) (P. Loganathan et al., 2006). Another study found that F concentrations in soil profiles were significantly correlated ($P<0.01$) to the concentration of extractable Al in soils, explained by the formation of Al-F complexes in soil in acidic conditions (Xie, Ye, & Wong, 2001). Pickering (1985) also suggested that F absorption in soils is mainly attributed to Al levels, and the degree of interaction is enhanced in acid soils. The complexion of F and Al in soil solution was also found to be significantly higher under acidic conditions, and the dominant F form in solution was AlF^{+2} ($r=0.99$). The mechanism for this association is the control of soil pH on Al and F solubility (V. Manoharan et al., 2007). Remaining variation could be explained by variations in soil parent material, soil properties and the history of P fertiliser application which determines background P concentration.

A positive correlation was found between total F concentration and the organic matter content in soils ($r>0.60$) (Figure 8b). A similar correlation ($r=0.68$) between total F and organic matter was also noted by P. Loganathan et al. (2006). Another study found a positive correlation coefficient ($r=0.31$) between the total concentration and organic matter content in soils collected in a vicinity of an Al plant (Blagojević, Jakovljević, & Radulović, 2002). The positive correlation between total F and both the labile Al portion and the SOM in soils might indicate that F is strongly bound to the amorphous Al adsorbed to the organic matter particles in soil (P. Loganathan et al., 2006).

In addition, total F was negatively correlated with total Fe (r=-0.41) (Figure 8c). A study on F adsorption in soils also found a significant negative correlation (r=-0.71) between total Fe oxides and the adsorption capacity of F^- in soils (Wang et al., 2002). Also, P. Loganathan et al. (2006) found a significant negative relationship between total F and total Fe (r=-0.58).

Table 16. Correlation coefficients (r) between total soil F and soil properties

Total F determination method	Soil pH	Total Fe (%)	Total Al (%)	Extractable Fe (%)	Extractable Al (%)	SOM (%)
Alkali fusion/ISE	0.181	-.412**	0.171	0.046	.590**	.612**
NaOH 4M /ISE	0.132	-.483**	0.228	0.217	.683**	.680**
NaOH 10M /ISE	0.107	-.514**	0.165	0.046	.655**	.607**
NaOH 16M /ISE	0.055	-.484**	0.172	0.111	.687**	.657**

*. Correlation is significant at the 0.05 level
**. Correlation is significant at the 0.01 level

When looking at the correlation between soil properties (Table 17), a positive correlation between labile Al and SOM is apparent (r=0.34). This relationship might be indicating that total soil F is strongly associated with the amount of organic matter in soils, as well as with the amorphous or labile portion of Al in soils. Another interesting correlation was found between total Al and soil pH (r=0.39), reflecting the significant effects of acidic conditions on Al-F complexes formation (soil samples pH ranged between 4.96 and 6.02) (V. Manoharan et al., 2007).

Table 17. Correlation coefficients (r) between soil properties

	SOM (%)	Soil pH	Total Al (%)	Amorphous Al (%)	Total Fe (%)
SOM (%)					
Soil pH	-.118				
Total Al (%)	-.159	.399*			
Amorphous Al (%)	.346*	.188	.606**		
Total Fe (%)	-.275	.287	.465**	.047	
Amorphous Fe (%)	.203	.223	.609**	.595**	.716**

*. Correlation is significant at the 0.05 level
**. Correlation is significant at the 0.01 level

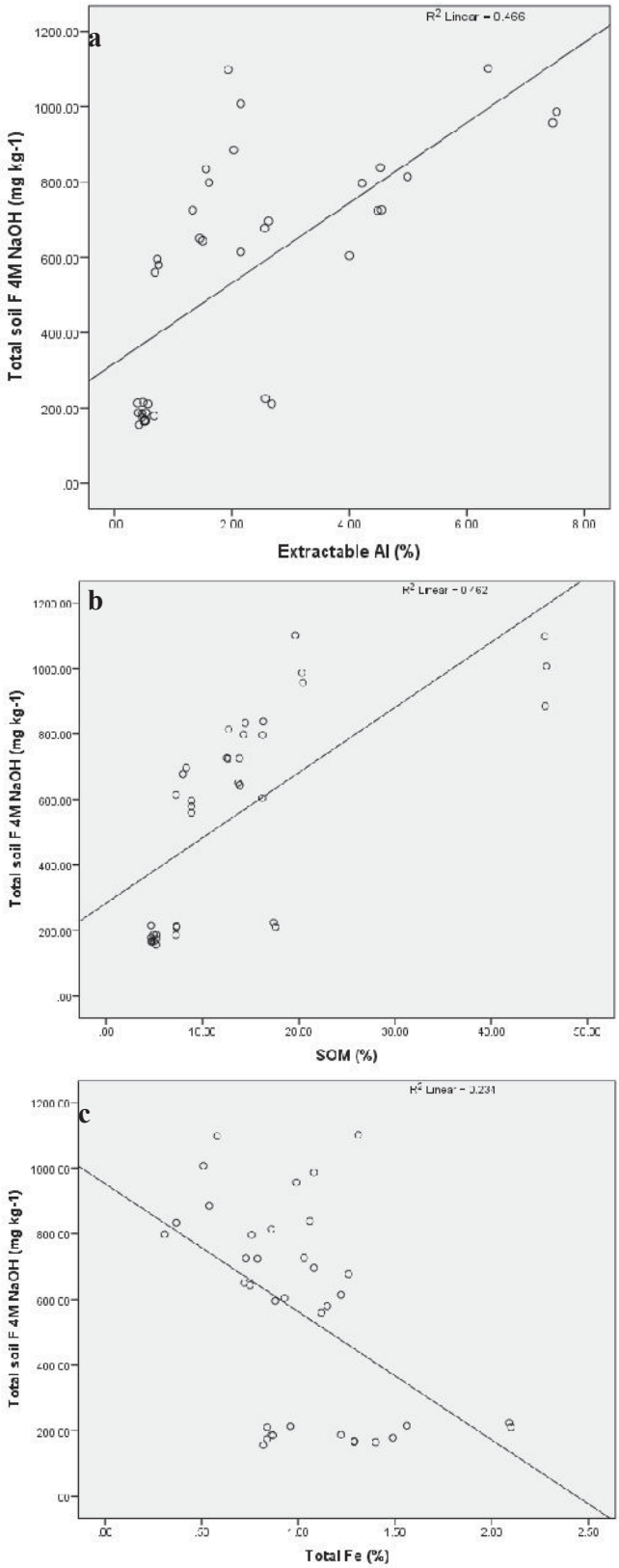

Figure 8. Relationship between total F concentrations as measured by NaOH 4M and soil properties (a) extractable Al, (b), SOM, (c) total Fe, in 6 different NZ agricultural sites (n=3)

4.3. The effects of F on soil microbial activity

Soil microbial activity was measured in this work through quantifying Cmic and DHA. The chemical and biological properties of the soils used for these analyses were previously presented in Table 13. Although the NaOH 10M showed less variability to repeatedly report total soil F concentration in relation to alkali fusion when measuring different soil orders, compared to the 16M and 4M, the 4M NaOH extraction was used to quantify the total F concentration of the soils used in the microbiological part of the current study because the laboratory safety advantages of using a more dilute extractant. In addition, soil analysed for microbial activity varied well across soil orders, therefore, the NaOH method was considered as a good proxy for total soil analysis on the levels tested on this research.

4.3.1. Microbial biomass carbon and dehydrogenase enzyme activity

The average Cmic values for the soils of this study ranged between 133 mg C kg^{-1} and 22,034 mg C kg^{-1}. The highest value was found in Granular soil (Pukekawa site), which was significantly different to the other soil samples (Figure 9). The Cmic values found in all soils except the granular soil are consistent with Martens (1995) and Tscherko and Kandeler (1997) who reported Cmic values in agricultural soils ranging around 200 and 1,000 mg C kg^{-1}. The concentration of DHA ranged from around 5 to 133 mg TPF kg^{-1} (Figure 10). The highest DHA was found in the Organic soil (Otorohanga site) which was significantly different to the other soils. These results agree with a previous study (Tscherko & Kandeler, 1997) which reported DHA ranging from 12 to 234 mg TPF kg^{-1} for agricultural soils and with García-Gil et al. (2013), who found values ranging from 5.1 to 431.7 mg kg^{-1}.

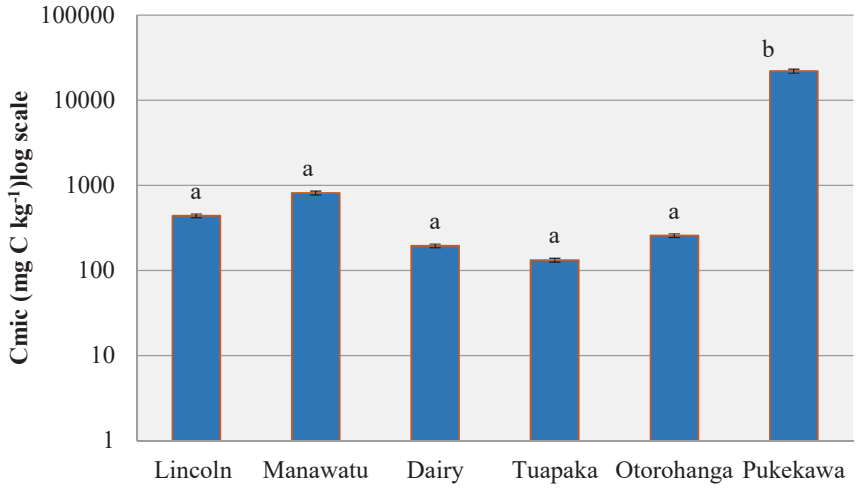

Figure 9. Average Cmic values obtained in the 6 soil samples collected from different NZ locations

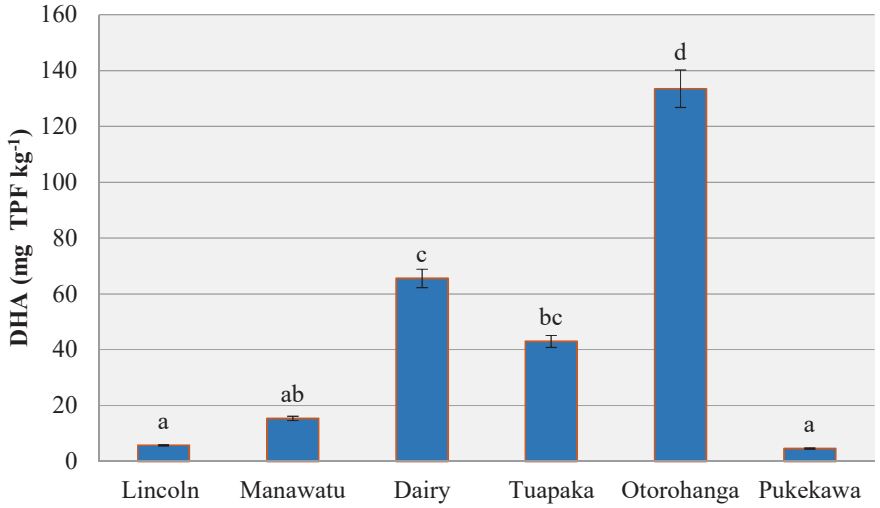

Figure 10. Average DHA values obtained in the 6 soil samples collected from different NZ locations

4.3.2. Relationship between total F and soil microbial activity

Correlation analysis showed a very weak association (r=0.186) between total F and Cmic in soil samples. One study on the toxic effects of F to soil microorganisms found a significant negative correlation between soil F and microbial biomass (r=-0.8), and microbial activity decreased substantially when total F concentrations were >100 mg F kg^{-1} (Tscherko & Kandeler, 1997).Other authors have found a positive influence of F on microbial activity. One

experiment found that microbial biomass increased at total F doses ranging from 500 to 3000 mg F kg^{-1} (Ropelewska et al., 2015). Another study found a positive influence of F on Cmic activity, with total F concentrations ranging between 100 – 200 mg F kg^{-1} (Szostek et al., 2015). Furthermore, another study did not find any correlation between microbial biomass and F concentrations between 100 and 1,000 mg F kg^{-1}. The variability of published results suggests the further assessment of the reliability of the Cmic parameter to measure F effects in the short term. (Poulsen, 2011).

Correlation between soil total F concentration and DHA (r=0.71) showed that those soils with high total F and high DHA have high organic matter, and apparently F influenced positively the dehydrogenase activity (Figure 12). Other authors have also found a positive influence of low total F concentrations (100–200 mg F kg^{-1}) on enzymatic activities, under controlled conditions achieved through dosage with F solutes (Langer & Günther, 2001; Ropelewska et al., 2015; Szostek et al., 2015).

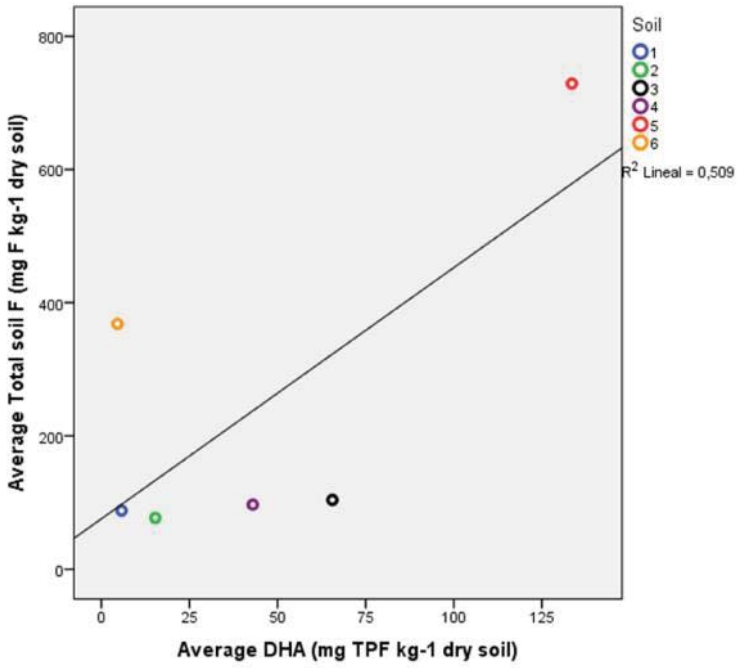

Figure 11. Scatterplot showing the relationship between dehydrogenase enzyme activity and total F measured in 6 different NZ agricultural sites (n=3)

Correlation analysis between microbial parameters and soil properties (Table 18) showed that soil pH, SOM and the Al/Fe oxide content influences microbial activity. The Cmic was strongly correlated with the total Al and Fe content in soil (r=0.89 and r=0.95 respectively). The DHA was positively correlated to the amorphous Al and Fe (r=0.84 and r=0.82 respectively), to the SOM (r=0.91) and to soil pH (r=0.60).

Table 18. Correlation coefficients (r) between microbial activity and soil properties

	Soil pH	SOM (%)	Total Fe (%)	Total Al (%)	Oxalate - extractable Fe (%)	Oxalate - extractable Al (%)
Cmic	0.247	-0.216	.958**	.896**	0.022	-0.149
DHA	.601**	.919**	-0.303	0.007	.825**	.847**

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

Results showed in Table 18 suggests that, to some extent, microbial activity can be used as a parameter to indicate F toxicity in the environment. The Cmic vales showed positive correlation with the non-labile or total Al and Fe content in soils, which suggests that this microbiological parameter might be affected by the total F concentration in soils. On the other hand, DHA is correlated with the amorphous portion of Al and Fe in soils (oxalate-extractable Fe and Al), and this suggests that DHA is affected by fraction of soil F that is adsorbed to soil surfaces, or soluble complexes of F with Al and Fe in soil solution.

The bioavailability of F in soils is associated with the F concentration in soil solution and the chemical F species present. As explained in literature, soil pH is the main factor controlling F solubility, and under acidic conditions, free F^- complexes with Al and Fe, predominantly forming soluble complexes with Al such as AlF_x, and the chemical properties of the complexes which are formed will determine the level of toxicity to organisms in the environment (Weinstein & Davison, 2006). In contrast, F toxicity to livestock is dependent on the rate of soil that is ingested during grazing, and the extent to which this soil contains a high F concentration (Hedley et al., 2007; M. J. McLaughlin et al., 2001). Therefore, for animal health, total soil F, as opposed to bioavailable soil F is the environmental parameter of concern. Plants are more sensitive to the toxicity of the soluble AlFx complexes in soils which will define (in part) the bioavailable fraction of F in soil solution (Arnesen, 1997).

The current research indicates that Cmic could be used as an indicator of the total F effects for grazing animals in soils because it relates to the total amount of soluble and non-soluble content. On the other hand, DHA could be used a sensitive indicator of the F effects to soil microorganisms, as it is correlated with the labile F fraction in soil solutions.

4.4. Environmental management implications of F accumulation in New Zealand agricultural soils

This section integrates data from the literature and findings from the current study in order to identify environmental management options for the environmental issue of F in New Zealand agricultural soils. This section is subdivided in four parts:

- General scheme of environmental management of F in agricultural systems
- Overview of the F issue in New Zealand pastoral land
- Recommended environmental management approach to address the F issue
- Environmental policy challenges.

In order to provide a framework for environmental management, Figure 13 was developed to address soil protection in relation to F in agricultural systems.

Selecting the unit and purpose of management.

To manage an environmental issue, the first step is to establish a management area as a minimum unit to implement strategies and achieve the desired goals. Regarding F-fertiliser derived contaminant, agricultural land is the main focus and more specifically, the high risk areas (i.e. elevated total soil F concentrations in soil) as a smaller scale unit. Following this, the soil value intended to protect is soil functions, essentially to ensure the sustainability, productivity and versatility of soils. According to the Resource Management Act (1991), soil conservation involves maintaining the physical, chemical and biological qualities of soil to ensure its life-supporting capacity and land use flexibility.

Regarding F accumulation in soils, it was not until recently that it became an issue in New Zealand agricultural soils. Awareness arose because of the reported F toxicity to livestock and the chronic fluorosis risks to cattle and sheep, and also because the F effects to microorganisms in pastoral soils are not entirely known. As a consequence, more research was carried out in order to assess F risks to the environment and to assist policy-making in managing soil F.

Research and monitoring:

Undertaking science-based research will enable the closing of knowledge gaps and assist in effective decision-making. One of functions of Regional Councils is to control the use of the land for the purpose of soil conservation and to identify and monitor contaminated land. Regional plans should consider the likely effects and risks of any activity potentially affecting soil function and conservation. Data from monitoring allows RCs to set a baseline of the current environmental conditions to establish quality standards, and also data can be used to track changes of a management unit and assist modelling for key soil contaminants. Normalisation of data to New Zealand soil conditions and factors influencing F accumulation in soils is also an essential component to research, as well as investigating the cumulative effects of F in soils.

In terms of F analysis, the lack of wide-scale research on soil F for environmental risk assessment has been agreed to be related to the very time-consuming and tedious nature of the traditional method to measure F in soil matrices (Jeyakumar & Anderson, 2015; Kim et al., 2016; P. Loganathan et al., 2003). As a consequence, the need for a reliable and cost-effective alternative method to quantify is considered as a national priority. Therefore, the purpose of this study was to validate and confirm the reliability of a recently developed NaOH extraction method followed by ISE to quantify F in a range of soil orders in relation to the fusion alkali method. The validation of an alternative method is a contribution within the soil protection management framework in relation to carrying out research to determine F background levels and monitoring programmes. A nationally agreed alternative method to quantify F will assist RCs and district councils in standardised F monitoring results and reports across New Zealand.

Development of risk-based guideline and target values:

The development of risk-based guideline values requires science-based research. The purpose of setting F soil limits is to regulate F inputs from fertilisation and control F pathways in agricultural systems in order to minimise risks to the environment and maximise benefits from P fertiliser use. The target values will be based on the desired goals of maintaining soil functions in the short, medium and long term. This step is linked back again to the research, monitoring and reporting of the F concentrations within the management units. Setting target values should allow agricultural development without compromising public and environmental health. It will also determine the level of protection in respect to land use.

Policy and management tools:

The instruments to manage the F issue in agricultural soils can be of regulatory or non-regulatory nature. For example, regulatory approaches applied to the F issue in agriculture soils are an obligatory compliance and are focused on regulating activities that might threaten public health and the environment. For instance, the adoption of F limits or thresholds values, laws to protect land and regulation on activities discharging contaminants to soils by limiting resource consents. On the other hand, non-regulatory tools are voluntary approaches to manage contaminants and are generally based on public awareness, education, incentives, regulated by market standards and collaborative work. Typically, regulatory approaches are focused on point sources of contamination and voluntary instruments are focused on non-point sources of contamination. None of the tools alone can ensure the effective management and control of soil contamination; however, the implementation of both approaches will result in a more integrative and multidisciplinary policy framework in order to accomplish the desired goals. The participation of advocacy groups, stakeholders and communities will ensure the compliance and enforcement of policy and management tools.

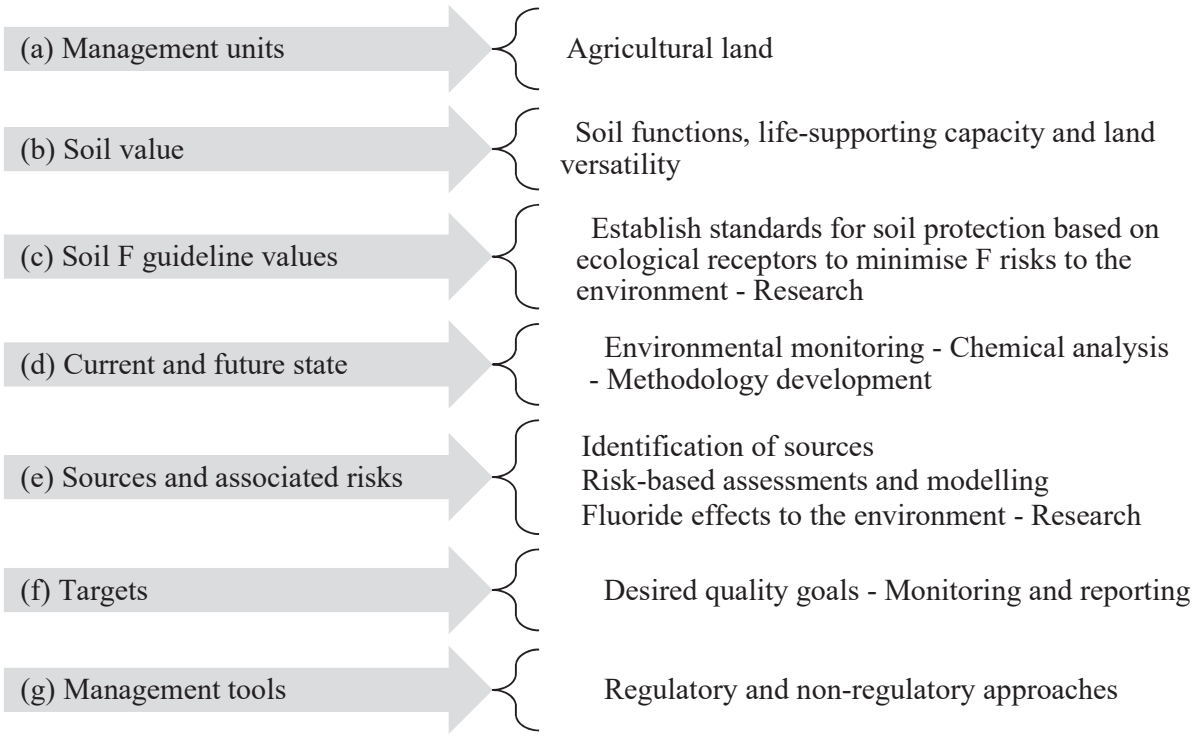

Figure 12. Environmental management scheme focused on soil F in agricultural soils
Modified after Ministry for the Environment (2013)

Regarding the presence of F in New Zealand agricultural soils, Figure 14 describes the emerging issue as a cycle. The figure illustrates the factors influencing a cause effect sequence on the mechanisms of F accumulation and the likely risks in the long term due to the historical and ongoing use of P fertilisers. It also relates to the soil properties and other factors influencing F loads to soil. First, the P fertiliser use in New Zealand started with agricultural expansion in the late 1880s (Roberts, n.d.). Most New Zealand soils are naturally acid and the availability of P in soils is regulated by pH; in acidic conditions P is not readily available to plants, thus P fertiliser addition is needed to raise the soil's pH and to compensate nutrients for pasture growth (Fertiliser Association, 2012b). Liming is a common agricultural practice in New Zealand and is one way to control pH, stimulate microbial activity and minimise the toxicity of metallic ions to plants (e.g. Al). Furthermore, the amount of F added is directly correlated to the past and current amount of P fertiliser applied to land (Cronin et al., 2000), and the identified largest fertiliser users are dairy, beef and sheep farmers (Statistics NZ, 2012).

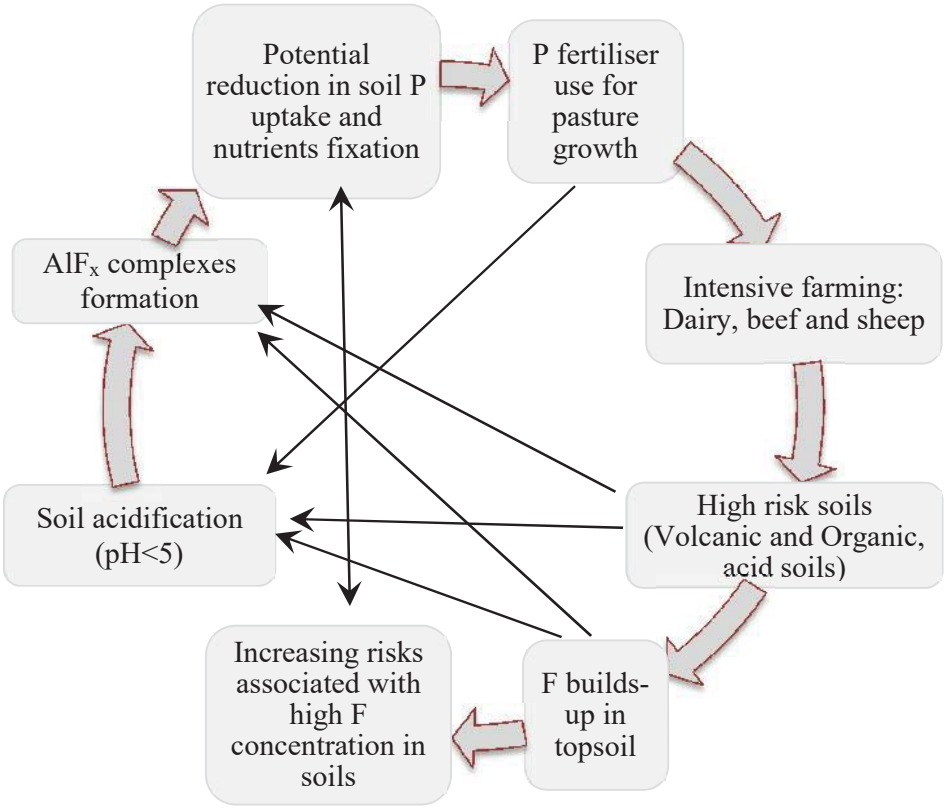

Figure 13. Overview of the F issue cycle in NZ pastoral land

Another factor influencing the cause-effect cycle is that New Zealand soils are very prone to F accumulation in the top centimetres of the soil because of the soil properties (P. Loganathan et al., 2006). The pH controls the F sorption, which is greatest in acidic conditions and F presents a high affinity to the Al and Fe oxide content in soils and complexes with Al the highest at low pH conditions (Manoharan et al., 2007). As the findings of this study show, Volcanic and Organic soils have the greatest total F concentrations in soils (0-15 cm), and F retention was positively correlated with the amorphous Al fraction (oxalate-extractable) in soil samples ($r>0.59$). Soils high in Al and Fe oxide content are considered by other authors as "high risk" soils (Jeyakumar & Anderson, 2015). Consequently, these soils have the highest risks for chronic fluorosis to livestock and inhibitions to microorganisms. However, based on the results of this work, there does not appear to be any evidence that F influences negatively the soil microbial activity at the levels tested in this research.

In addition, New Zealand soils are very likely to have acidification and the formation of soluble AlF_x complexes, which increases in acidic conditions and is found to cause detrimental effects on the root growth of some plant species (Manoharan et al., 2007). The toxicity is caused by a reduction in phosphate fixation because AlFx complexes can act as phosphate analogues or mimic phosphate and reduce P uptake by plant roots, affecting pasture yields (Kim et al., 2016; Veeragathipillai Manoharan, 1997). Therefore, the addition of P fertilisers to soils and liming is needed and the cause-effect circle repeats.

In order to address the F issue, Figure 15 illustrates a scheme as a response to manage the most urgent areas within agricultural land. First, there was a need to identify New Zealand regions areas with prolonged P fertiliser history application and where the high risk soils occur. Based on the findings of this study, the highest total F concentrations were found in Allophanic and Organic soils collected from agricultural land use in the Waikato region. It is likely that in these sites the risks associated with F still remain unknown in relation to both farmers' awareness and lack of risk-based assessments. Therefore, in most cases no actions are yet being taken to manage the F issue, especially in relation to livestock risks. Consequently, these sites are recommended to be allocated as priority areas for further assessment and monitoring regarding high F levels, especially quantifying non-labile F forms as indicators of F risks to livestock risks and labile F fractions to assess the F effects to microorganisms in soils. Also, there is a need to adopt voluntary strategies to minimise F risks to grazing animals, as recommended by

P Loganathan et al. (2007), such as low stocking rates during winter seasons, maintaining high pasture levels by using controlled grazing systems and avoiding grazing after fertilisation.

Other management options to minimise F accumulation in soils are the implementation or reinforcement of the TFMS as a strategy of the Cd management plan as an important indirect tool to control F loads from P fertiliser use. In addition, there is the need for the adoption of nutrient management strategies, undertaking periodical soil tests which will allow effective P fertiliser use, assisted by agriculture precision tools such as the OVERSEER® software. Furthermore, there is a need to prioritise alternative options to P fertilisation, such as farm dairy effluent (FDE) land irrigation, implementing crop rotation and effective irrigation systems.

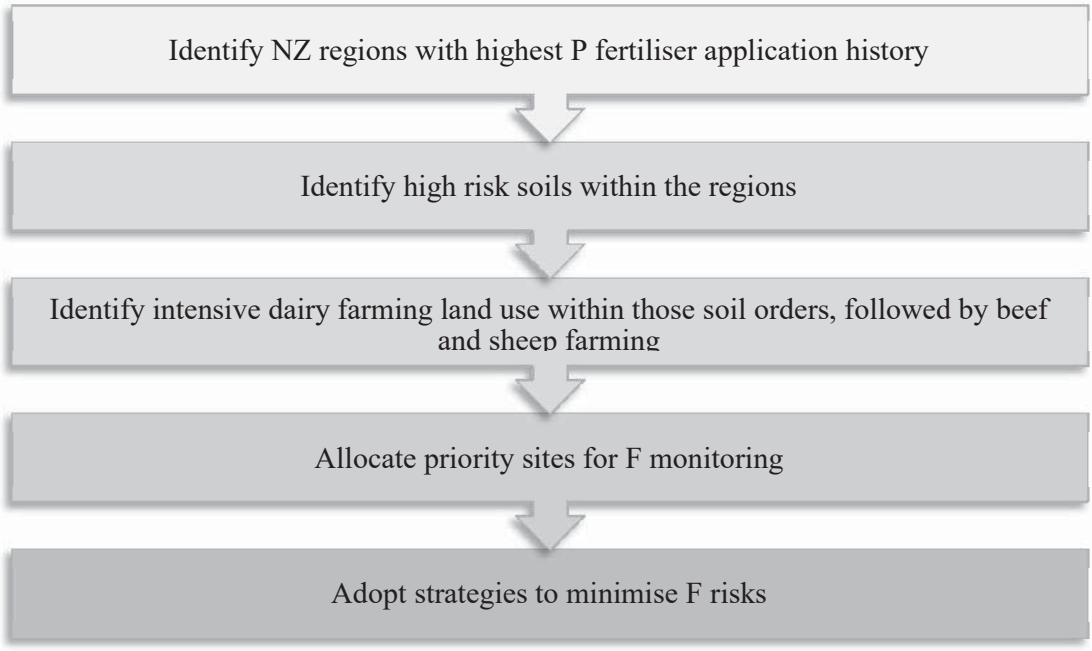

Figure 14. Specific actions to address F issue in most urgent NZ agricultural sites

The challenges for policy-making to address the F issue in New Zealand pastoral soils are related to a number of factors. First, there is a need to acknowledge F as a key P fertiliser-derived soil contaminant and it is very likely to accumulate in most of agricultural soils across New Zealand. The F issue requires further science-based research to close knowledge gaps regarding cumulative F effects as some environmental risks still remain unclear. The management approach has to be integrated to existent policies and regulation and the development of specific measures to control F in high risk sites is a priority. Also needed is the

implementation of soil protection and conservation programmes, raising awareness of the potential F risks, while encouraging farmers and stakeholders to participate in decision-making.

Chapter 5 Conclusions and Recommendations

The outcomes of this study are summarised in the following sections.

5.1. Summary of main findings

This study compared the reproducibility of the NaOH method relative to the alkali fusion/ISE method to measure F and was conducted on seven New Zealand soil orders collected from 13 agricultural sites across different regions. Results indicate that the alternative method at the three different concentrations (4M, 10M and 16M) were highly correlated to the traditional method ($r>0.92$). Additionally, the total F concentrations, as obtained by the NaOH method at 4M, 10M and 16M were not significantly different between methods (Appendix III). This suggests that NaOH 4M is sufficient to extract F from soil matrices.

However, the accuracy of the determination method is very dependent on soil properties. The pairwise test across the different soil orders in relation to total F concentrations, as determined by traditional and conventional methods, indicated that the NaOH 10M method consistently reported the lowest variability in comparison with the alkali fusion method, particularly amongst Allophanic soil samples. This suggests that NAOH 10M extraction method is more accurate to analyse F in soils containing high Al/Fe oxides compared to the NaOH 4M and the NaOH 16M methods.

The ability of the NaOH 10M method to effectively quantify total F in soils containing high Al/Fe oxide content suggests that it can be used as a reliable alternative technique to monitor F-contaminated soils of most concern across New Zealand. Other advantages of the alternative method are related to a less time-consuming procedure needed to extract F from soil samples during the water bath. Also hazardous chemical risks are less, due to the relatively low concentration used to extract total F from soils (NaOH 10M) compared to the NaOH 17M required for the alkali fusion.

Relationship study between total F concentration and soil properties showed a high correlation between F and Al and Fe amorphous and crystalline oxide content, pH and organic matter. These are factors that will determine the extent to which F is accumulated in agricultural soils, as well as the P fertiliser rate applied to land.

The results obtained for microbial biomass carbon and dehydrogenase enzyme activity were consistent with reported values in agricultural soils by similar studies. However, a correlation between total soil F and microbial activity in soils was not clear. Nevertheless, findings from microbial activity relationship with soil properties showed that DHA is good indicator of the labile portion of F in soils (adsorbed to the available Al and Fe content in soils), whereas the Cmic parameter indicates the effects of total F in soils (adsorbed by the non-labile Al and Fe content in soils). Therefore, this may implicate that DHA can be used as an indicator of the effects of extractable F to microorganisms and plants. On the other hand, the Cmic parameter could be used as an indicator of the total F effects to livestock. This is because the toxic effects of F to cattle depend on the concentration of total F ingested with soil. However, it was suggested not to be reliable for short-term F effect studies (Poulsen, 2011).

The most important 'established' environmental risk related to F accumulation in pastoral soils is chronic fluorosis to cattle. The impact of F on soil microbiology which might affect productivity is as yet unknown. Long-term there is also potential for soil F to affect land use versatility. The environmental management implication of these risks is the need to establish a policy framework or action scheme to manage the F issue. Findings from this study suggest that higher risks of F accumulation in agricultural soils are in New Zealand sites following these criteria: high risks soils (Al/Fe oxide-rich content) with intensive farming development, along with long-term P fertiliser history use and under ongoing application. Furthermore, no agreed F threshold values yet exist. However, F accumulation in agricultural soils due to P fertiliser application has been recognised in some New Zealand regions as an emerging issue that needs to be managed in the near future.

5.2. Recommendations

Based on the main findings from this study, the NaOH 10M extraction is recommended as a technique to monitor F in New Zealand agricultural soils. The advantages of the technique are associated with a less time-consuming procedure, fewer risks while handling more diluted NaOH solutions, and therefore a less expensive method compared to the traditional method.

As regards the total F concentrations found in the 13 different agricultural sites, five sites were greater than the recommended F value for the protection of grazing animals (>500 mg F kg^{-1}). Therefore, management actions are suggested to be taken in these sites.

As part of the recommended action scheme to manage F in pastoral land, environmental monitoring of F across New Zealand high risk soils areas is needed. Findings from this research are to consider DHA as a microbial parameter for environmental monitoring of the labile F effects to soil microorganisms and the use of Cmic as an indicator of the effects of total F to assess risks to grazing animals.

5.3. Further research

Prioritise areas of research to close knowledge gaps: assessment of the effects of total soil F on soil microbial activity with further research, including F labile forms.

Assess the effects of AlF_x toxicity on seed germination and root growth of New Zealand's economically important cultivars (such as ryegrass and white clover) to assist future management options for farmers who own land on high risk. Results may suggest the best tolerable crops.

Implement F monitoring programmes on those areas of most urgent concern and establish surveillance of F level in groundwater and freshwater ways, especially when land use changes and soil pH can be compromised.

Assess the contribution of other F sources to agricultural soils (volcanic ash deposition and irrigation water).

Appendix List

Appendix I Descriptive statistics total F concentrations as determined by alkali fusion/ISE and NaOH/ISE extraction methods - Soils used for F analysis

Total soil F alkali fusion/ISE (mg F kg^{-1})

Soil N	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	3	708	124	72	400	1016	636	851
2	3	688	23	13	631	744	665	710
3	3	613	55	32	477	749	550	650
4	3	412	55	32	275	550	349	453
5	3	207	13	8	174	240	193	219
6	3	457	13	8	424	489	445	471
7	3	152	8	5	131	173	144	161
8	3	298	9	5	274	321	290	308
9	3	216	77	44	26	406	165	304
10	3	395	80	46	195	595	319	479
11	3	344	125	72	34	655	214	463
12	3	516	186	107	53	978	386	729
13	3	541	95	55	305	776	432	607
Total	39	427	190	30	365	488	144	851

Total soil F 4M NaOH (mg kg^{-1})

Soil N	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	3	996	107	62	731	1262	885	1098
2	3	1015	76	44	825	1204	957	1101
3	3	746	125	72	436	1056	604	838
4	3	673	45	26	561	786	644	725
5	2	218	10	7	129	307	211	225
6	3	755	51	30	627	883	724	814
7	3	173	16	9	134	212	156	187
8	3	186	26	15	123	250	165	215
9	3	203	15	9	166	241	186	213
10	3	578	18	10	534	623	560	596
11	3	174	12	7	144	204	166	188
12	3	662	43	25	556	769	614	696
13	2	816	25	18	590	1043	798	834
Total	37	556	317	52	450	661	156	1101

Total soil F 10M NaOH (mg kg^{-1})

Soil N	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	3	830	190	110	358	1303	673	1042
2	3	820	63	36	664	976	759	885
3	3	821	49	28	699	942	768	866
4	3	643	85	49	432	853	559	729
5	3	243	18	10	198	288	222	256
6	3	688	30	18	613	764	655	715
7	2	208	4	3	169	247	205	211
8	3	224	24	14	164	284	202	250
9	3	207	19	11	160	254	190	227
10	3	483	52	30	355	611	424	519
11	3	181	11	7	153	210	172	194
12	3	609	22	13	555	663	589	632
13	3	664	27	16	596	732	639	693
Total	38	517	259	42	432	603	172	1042

Total soil F 16M NaOH/ISE (mg F kg^{-1})

Soil N	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	3	894	52	30	764	1025	836	937
2	3	912	99	57	665	1158	811	1010
3	3	830	7	4	811	848	821	835
4	3	628	17	10	587	670	612	645
5	3	285	33	19	203	366	256	320
6	3	742	59	34	594	890	684	803
7	3	225	34	20	140	309	191	259
8	3	247	42	24	141	352	205	290
9	3	231	18	10	186	276	212	248
10	3	563	68	39	394	731	487	619
11	3	214	25	14	152	276	198	243
12	3	517	134	77	185	849	363	605
13	3	709	46	27	594	824	667	759
Total	39	538	268	43	451	625	191	1010

Appendix II ANOVA test - Soils used for F analysis

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Total soil F Alkali/Fusion (mg kg-1)	Between Groups	1189842.732	12	99153.561	13.706	.000
	Within Groups	188094.575	26	7234.407		
	Total	1377937.307	38			
Total soil F 4M NaOH (mg kg-1)	Between Groups	3542790.014	12	295232.501	85.808	.000
	Within Groups	82574.753	24	3440.615		
	Total	3625364.767	36			
Total soil F 10M NaOH (mg kg-1)	Between Groups	2375534.969	12	197961.247	44.281	.000
	Within Groups	111763.065	25	4470.523		
	Total	2487298.034	37			
Total soil F 16M NaOH (mg kg-1)	Between Groups	2635134.772	12	219594.564	61.913	.000
	Within Groups	92217.776	26	3546.838		
	Total	2727352.547	38			

Appendix III Correlation between F determination methods - Soils used for F analysis

		Total soil F Alkali/Fusion (mg kg-1)	Total soil F 4M NaOH (mg kg-1)	Total soil F 10M NaOH (mg kg-1)	Total soil F 16M NaOH (mg kg-1)
Total soil F Alkali/Fusion (mg kg-1)	Correlación de Pearson	1	,940**	,926**	,933**
	Sig. (bilateral)		,000	,000	,000
	N	13	13	13	13
Total soil F 4M NaOH (mg kg-1)	Correlación de Pearson	,940**	1	,986**	,993**
	Sig. (bilateral)	,000		,000	,000
	N	13	13	13	13
Total soil F 10M NaOH (mg kg-1)	Correlación de Pearson	,926**	,986**	1	,993**
	Sig. (bilateral)	,000	,000		,000
	N	13	13	13	13
Total soil F 16M NaOH (mg kg-1)	Correlación de Pearson	,933**	,993**	,993**	1
	Sig. (bilateral)	,000	,000	,000	
	N	13	13	13	13

**. La correlación es significativa en el nivel 0,01 (bilateral).

Appendix IV Tukey pairwise test - Soils used for F analysis

Total soil F Alkali/Fusion (mg kg^{-1})

Tukey HSD[a]

		Subset for alpha = 0.05				
Soil	N	1	2	3	4	5
7	3	151.5300				
5	3	206.9900	206.9900			
9	3	216.2900	216.2900			
8	3	297.5700	297.5700	297.5700		
11	3	344.2933	344.2933	344.2933		
10	3	394.9733	394.9733	394.9733	394.9733	
4	3		412.2767	412.2767	412.2767	
6	3		456.7567	456.7567	456.7567	456.7567
12	3			515.5333	515.5333	515.5333
13	3			540.5033	540.5033	540.5033
3	3				613.0367	613.0367
2	3					687.5633
1	3					708.0433
Sig.		0.066	0.054	0.067	0.140	0.052

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Total soil F 4M NaOH (mg kg^{-1})

Tukey HSD[a,b]

		Subset for alpha = 0.05				
Soil	N	1	2	3	4	5
7	3	172.9467				
11	3	173.9933				
8	3	186.2933				
9	3	203.2833				
5	2	217.7700				
10	3		578.4800			
12	3		662.2233	662.2233		
4	3		673.1533	673.1533		
3	3		746.3733	746.3733		
6	3		754.8900	754.8900		
13	2			816.1750	816.1750	
1	3				996.4700	996.4700
2	3					1014.7600
Sig.		0.999	0.064	0.156	0.054	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.786.

Total soil F 10M NaOH (mg kg^{-1})

Tukey HSD[a,b]

Soil	N	Subset for alpha = 0.05			
		1	2	3	4
11	3	181.4333			
9	3	206.9833			
7	2	207.8150			
8	3	224.2900			
5	3	243.1167			
10	3		482.8700		
12	3		609.0533	609.0533	
4	3		642.7033	642.7033	642.7033
13	3		663.9100	663.9100	663.9100
6	3			688.2800	688.2800
2	3				820.2033
3	3				820.7033
1	3				830.3400
Sig.		0.994	0.114	0.960	0.089

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.889.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Total soil F 16M NaOH (mg kg^{-1})

Tukey HSD[a]

Soil	N	Subset for alpha = 0.05					
		1	2	3	4	5	6
11	3	214.2633					
7	3	224.5167					
9	3	230.7133					
8	3	246.7367					
5	3	284.8633					
12	3		516.9900				
10	3		562.6667	562.6667			
4	3		628.1100	628.1100	628.1100		
13	3			709.2500	709.2500	709.2500	
6	3				742.0800	742.0800	742.0800
3	3					829.5867	829.5867
1	3						894.4333
2	3						911.8333
Sig.		0.955	0.545	0.178	0.508	0.429	0.068

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Appendix V Relationship between total F and soil properties – Soils used for F analysis

Total F determination method		Soil pH	SOC (%)	Total Fe (%)	Total Al (%)	Extractable (%)
Alkali fusion/ISE	Pearson Correlation	0.181	.612**	-.412**	0.171	0.046
	Sig. (2-tailed)	0.269	0.000	0.009	0.298	0.781
	N	39	39	39	39	39
4M NaOH/ISE	Pearson Correlation	0.132	.680**	-.483**	0.228	0.217
	Sig. (2-tailed)	0.438	0.000	0.002	0.176	0.196
	N	37	37	37	37	37
10M NaOH/ISE	Pearson Correlation	0.107	.607**	-.514**	0.165	0.046
	Sig. (2-tailed)	0.523	0.000	0.001	0.323	0.786
	N	38	38	38	38	38
16M NaOH/ISE	Pearson Correlation	0.055	.657**	-.484**	0.172	0.111
	Sig. (2-tailed)	0.741	0.000	0.002	0.295	0.500
	N	39	39	39	39	39

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Appendix VI Descriptive statistics and ANOVA test - Soils used for microbial analysis

Descriptive Statistics

	N	Minimum	Maximum	Mean	Std. Deviation
Total soil F 4M NaOH (mg kg-1 dry soil)	17	73.51	868.06	236.6665	258.45450
Soil pH	18	4.83	6.74	5.9283	.59618
SOM (%)	18	3.96	21.22	7.9611	5.79601
Total Fe (%)	18	.25	7.69	2.5450	2.13573
Total Al (%)	18	1.26	13.76	4.9500	4.21678
Extractable Fe (%)	18	.40	1.53	.7528	.34421
Extractable Al (%)	18	.24	8.14	1.6622	2.84100
Cmic (mg kg-1 dry soil)	18	93.75	23741.41	3979.6883	8327.23120
Formazan (mg kg-1 dry soil)	18	4.19	160.36	44.6220	47.40934
Valid N (listwise)	17				

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Total soil F 4M NaOH (mg kg-1 dry soil)	Between Groups	1015465.077	5	203093.015	41.903	.000
	Within Groups	53314.562	11	4846.778		
	Total	1068779.639	16			
Cmic (mg kg-1 dry soil)	Between Groups	1174417302.000	5	234883460.400	639.146	.000
	Within Groups	4409947.827	12	367495.652		
	Total	1178827250.000	17			
Formazan (mg kg-1 dry soil)	Between Groups	36952.884	5	7390.577	70.550	.000
	Within Groups	1257.083	12	104.757		
	Total	38209.966	17			

Appendix VII Tukey pairwise test - Soils used for microbial analysis

Total soil F (mg kg^{-1} dry soil)

Tukey HSD[a,b]

Soil	N	Subset for alpha = 0.05		
		1	2	3
2	3	76.8333		
1	3	88.4833		
4	3	97.0933		
3	3	104.2800		
6	2		368.0000	
5	3			729.0867
Sig.		.997	1.000	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 2.769.
b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Cmic (mg kg^{-1} dry soil)

Tukey HSD[a]

Soil	N	Subset for alpha = 0.05	
		1	2
4	3	132.8100	
3	3	195.3067	
5	3	257.8033	
1	3	441.3933	
2	3	816.3800	
6	3		22034.4367
Sig.		.737	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.000.

DHA (mg kg^{-1} dry soil)

Tukey HSD[a]

Soil	N	Subset for alpha = 0.05			
		1	2	3	4
6	3	4.5950			
1	3	5.7412			
2	3	15.3294	15.3294		
4	3		42.9798	42.9798	
3	3			65.5558	
5	3				133.5308
Sig.		.788	.054	.146	1.000

Means for groups in homogeneous subsets are displayed.
a. Uses Harmonic Mean Sample Size = 3.000.

Appendix VIII Correlation test between total F and other soil properties - Soils used for microbial analysis

Correlations

		Total soil F (mg kg-1 dry soil)	Cmic (mg kg-1 dry soil)	DHA (mg kg-1 dry soil)	Soil pH	SOM (%)	Total Fe (%)	Total Al (%)	Extractable Fe (%)	Extractable Al (%)
Total soil F (mg kg-1 dry soil)	Pearson Correlation	1	.186	.765**	.562*	.873**	.295	.614**	.896**	.920**
	Sig. (2-tailed)		.474	.000	.019	.000	.251	.009	.000	.000
	N	17	17	17	17	17	17	17	17	17
Cmic (mg kg-1 dry soil)	Pearson Correlation	.186	1	-.401	.247	-.216	.958**	.896**	.022	-.149
	Sig. (2-tailed)	.474		.099	.322	.388	.000	.000	.932	.556
	N	17	18	18	18	18	18	18	18	18
DHA (mg kg-1 dry soil)	Pearson Correlation	.765**	-.401	1	.601**	.919**	-.303	.007	.825**	.847**
	Sig. (2-tailed)	.000	.099		.008	.000	.222	.977	.000	.000
	N	17	18	18	18	18	18	18	18	18
Soil pH	Pearson Correlation	.562*	.247	.601**	1	.590**	.238	.480*	.651**	.483*
	Sig. (2-tailed)	.019	.322	.008		.010	.341	.044	.003	.042
	N	17	18	18	18	18	18	18	18	18
SOM (%)	Pearson Correlation	.873**	-.216	.919**	.590**	1	-.113	.216	.919**	.969**
	Sig. (2-tailed)	.000	.388	.000	.010		.655	.390	.000	.000
	N	17	18	18	18	18	18	18	18	18
Total Fe (%)	Pearson Correlation	.295	.958**	-.303	.238	-.113	1	.923**	.137	-.044
	Sig. (2-tailed)	.251	.000	.222	.341	.655		.000	.587	.861
	N	17	18	18	18	18	18	18	18	18
Total Al (%)	Pearson Correlation	.614**	.896**	.007	.480*	.216	.923**	1	.439	.284
	Sig. (2-tailed)	.009	.000	.977	.044	.390	.000		.068	.254
	N	17	18	18	18	18	18	18	18	18
Extractable Fe (%)	Pearson Correlation	.896**	.022	.825**	.651**	.919**	.137	.439	1	.932**
	Sig. (2-tailed)	.000	.932	.000	.003	.000	.587	.068		.000
	N	17	18	18	18	18	18	18	18	18
Extractable Al (%)	Pearson Correlation	.920**	-.149	.847**	.483*	.969**	-.044	.284	.932**	1
	Sig. (2-tailed)	.000	.556	.000	.042	.000	.861	.254	.000	
	N	17	18	18	18	18	18	18	18	18

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

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