EFFECTS OF SOIL PROPERTIES ON BIOAVAILABILITY OF FLUORINE TO MICROORGANISMS

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Introduction

Fluorine (F) in soils is derived from many sources - volcanic activity, weathering of parent rocks, emissions from aluminium, brick, steel, glass, and fertiliser industries, and from the application of phosphorus (P) fertilisers (Cronin et al., 2000).

In New Zealand, agricultural soil F concentrations are increasing, mainly due to the continuous application of phosphorus (P) fertilisers (Loganathan et al., 2006). Increased soil F concentrations are toxic to animals (Cronin et al., 2000., Grace et al., 2003., Loganathan et al., 2006).

The effect of increased soil F concentrations on soil microbial activity may have undesirable consequences in terms of agriculture productivity. However, information on the possible effect of increased soil F concentrations on soil microorganisms is limited. Soil microorganisms play an important role in the function of the soil ecosystem by contributing to the nutrient cycles, soil formation, and symbiosis with plants (Wakelin et al., 2016). This study attempts to provide information on soil properties that influence a soils' exchangeable and total soil F concentration. This data, coupled with an ability to explain the relationship between soil F chemistry and soil microbial activity, will be important to help develop soil management practices that will minimise the negative effects of increased soil F concentrations. Preliminary understanding of the effect of soil chemistry on the bioavailability of F to microorganisms is described in this paper.

Materials and Methods

Soils were collected from seven different agriculture land use sites chosen to represent the major soil orders in New Zealand.

Table 1. Locations, land uses and soil order

Location	Land use	Soil order
Otorohanga	Dairy	Allophanic
Reporoa	Sheep/Beef	Pumice
Newstead	Dairy	Allophanic
Manawatu	Horticulture	Gley
Tokomaru	Dairy/Sheep	Pallic
Pukekawa	Horticulture	Granular
Canterbury	Horticulture	Pallic

Soil pH was measured by using a digital pH meter. The pH probe was immersed in a soil-water suspension prepared by mixing 5g of dry soil in 12.5 mL of water (solid: liquid ratio 1:2.5, Tan, 1996).

Non-crystalline Fe and Al compounds were determined by acid ammonium oxalate extraction (Blakemore et al., 1987).

Total soil F concentration in each soil was quantified following the extraction procedure described by Jeyakumar and Anderson (2015). Briefly, a finely ground subsample (0.5g) of oven dried soil was weighed into a polypropylene centrifuge tube. Ten mL of 4M NaOH was then added and the suspension was agitated in a $100^{o}C$ water bath for 24 hours. The samples were then transferred into screw-top plastic containers where the pH was adjusted to 8.5 by adding 6M HCl and the volume topped up to 100 ml with distilled water. The resultant suspension was then filtered with Whatman No.2 paper. The F concentration of the filtrate was analysed using an F-specific ion electrode after the addition of TISAB-buffer at 1:1 ratio (to avoid interference of Fe and Al).

To quantify the water and $CaCl_2$ – extractable F concentration, two 5 g soil samples were shaken with 30 ml water (Loganathan et al., 2006) and 37 ml 0.01M $CaCl_2$ (McLaughlin et al., 2001) for 2 and 16 hours respectively in an end-over-end shaker and centrifuged. The suspensions were then filtered through a WhatmanNo.42 paper. The filtrates were mixed with TISAB-buffer at a 1:1 ratio before the F concentration was measured using an F-specific ion electrode.

The fumigation-extraction (FE) method was used to measure the microbial biomass carbon (biomass C). A sub-sample equivalent to 5.0g dry soil was fumigated with ethanol-free chloroform for 24h at $25^{0}C$. For the non-fumigated sample, 5.0g dry soil from the same sample was taken. Fumigated and non-fumigated samples were extracted with 20 ml of 0.5M K_2SO_4. Carbon in the extracts was determined by digestion with dichromate and followed by titration with ferrous ammonium sulphate (Vance et al., 1987).

Regression and correlation analyses of data were performed using SPSS version 22.

Results and Discussion

The total soil F, CaCl₂-extractable F and water-extractable F concentrations
According to Brougham et al. (2013), soils which have a total soil F content of more than 500 to 600 mg/kg have likely been polluted by industrial and agricultural activities. Cronin et al. (2000) reported that a soil F concentration of 326-1461 mg/kg will cause chronic fluorosis in sheep and cattle. Loganathan et al. in 2006 reported that soils which have total F concentrations greater than 500 mg/kg require management practices to avoid future F toxicity issues.

In this study, the total soil F, $CaCl_2$-extractable F and water-extractable F concentrations of the samples ranged from 153 to 1015, 6.85 to 1.39 and 6.35 to 1.38 mg/kg soil respectively.

Soil pH
Total soil F concentrations varied with soil pH (Figure 1). Soils with a pH range of 5.5 to 6 showed a distinct increase in total soil F concentration. Gago et al. (2002) reported that fluoride solubility increases at lower pH due to the creation of Al-F complexes which are highly soluble. Conversely, fluoride solubility increases above pH 6.5 due to an increase in negative surface charge. In this study, the relationship between soil pH and $CaCl_2$-extractable

F was significant (p<0.05, Figure 1). We selected soils with a pH range of 4.96 to 6.27. Within this range, F solubility (i.e. $CaCl_2$-extractable F) can be observed to increase markedly with a decrease in soil solution pH. However, the effect of higher pH on F mobility was unable to be tested.
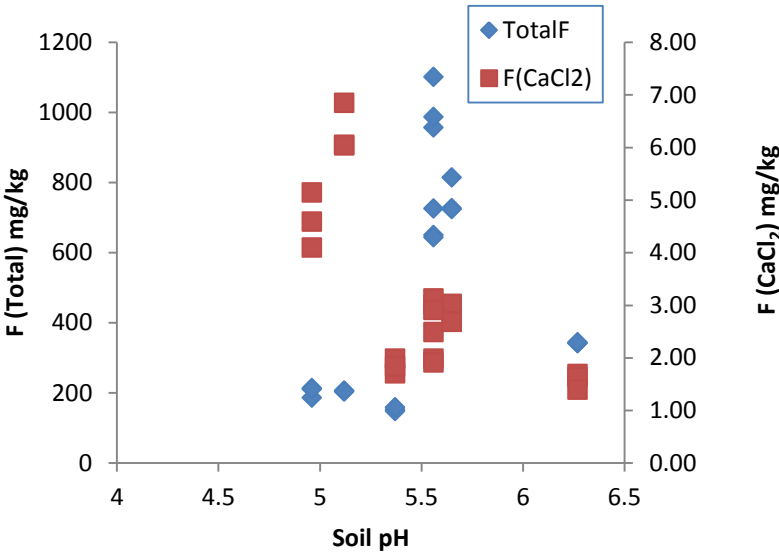

Figure 1. Relationship between soil pH, and total F and $CaCl_2$-extractable F

Acid ammonium oxalate extractable Al and Fe

Acid ammonium oxalate extracted Fe and Al represents non-crystalline forms of Fe and Al in the soil (Gago et al., 2014). Gago et al. (2012) reported that Fe (hydrous)-oxides serve as sinks for fluorine. Kaufhold et al. (2010) reported that non-crystalline materials such as allophane have high fluoride sorption capacity compared with crystalline silicates. Strong affinity between non-crystalline Fe/Al and F increases the total soil F concentration in soils which have received F from phosphate fertilisers.

In this study, a significant linear (p<0.05) relationship between acid ammonium oxalate extractable Fe, Al and total F concentration was observed (Figure. 2).
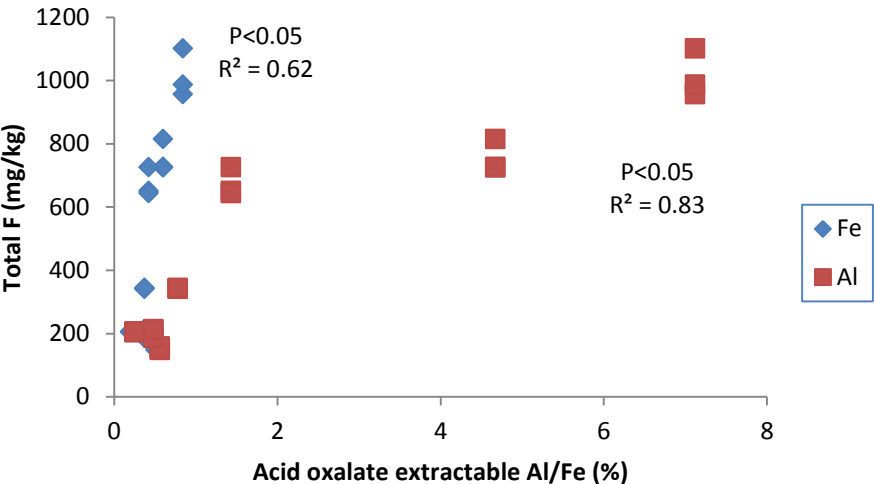

Figure 2. Relationship between total soil F and acid ammonium oxalate extractable Al and Fe

Microbial biomass C

Quantification of soil microbial biomass is a vital measurement for ecological tests, as soil microbes play an important role in nutrient cycling, organic matter dynamics and decomposition processes which are important in maintaining soil quality (García-Gil et al., 2013).

In this study, the microbial biomass C was measured for the Manawatu, Pukekawa, and Canterbury soils. The Pukekawa soil had high microbial biomass C (Figure 3).
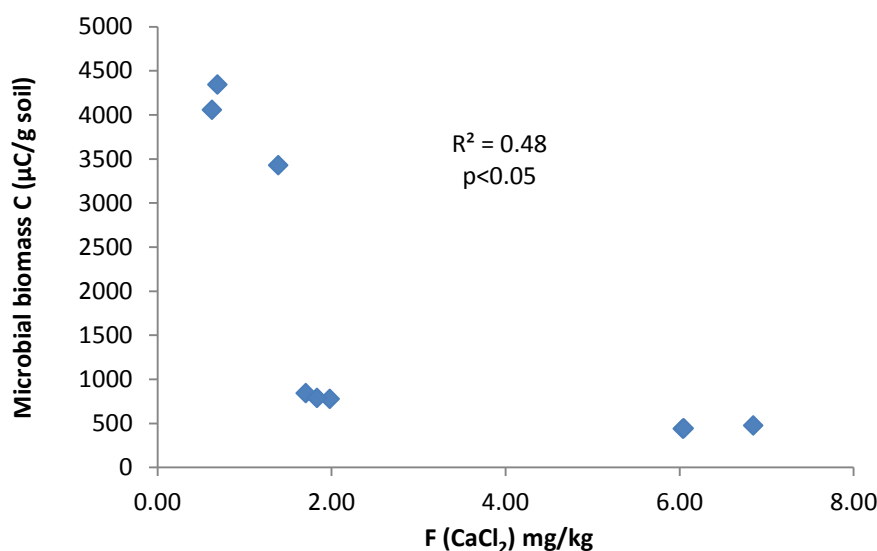

Figure 3. Relationship between microbial biomass C and CaCl2 – extractable F

The correlation between total soil F and microbial biomass C was not significant ($p > 0.05$). However, $CaCl_2$-extractable F was significantly ($p < 0.05$) correlated ($r = -0.69$) with microbial biomass C. Gao et al. (2012) reported that exchangeable and water-soluble fluoride fractions are more bioavailable to microorganisms compared with other fluoride fractions.

Conclusions

$CaCl_2$-extractable and water-extractable F concentrations were two orders of magnitude lower than the total soil F concentration and soil pH is a key factor that affects fluorine retention and mobility in agriculture soils. The concentration of acid ammonium oxalate extractable Fe and Al in soil appears to have a strong influence on soil total F concentrations. With respect to the impact of soil F on microbiology, there is no evidence to say that total soils F concentration can be used as an indicator of soil quality. However, there is a relationship between soluble fluorine and microbial biomass C. The relationship is currently being further investigated as a function of land use and soil orders.

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