



Defining a standard method to measure the total and bioavailable concentration of fluorine in New Zealand soils



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ABSTRACT

The concentration of fluorine (F) in New Zealand pastoral soils is increasing as a consequence of Phosphorus (P) fertiliser application, and there is concern over the long-term impact of this F on animal and soil microbiological health. Ongoing soil F monitoring to underpin comprehensive soil F management practices requires an accurate and simple test to quantify both the total and bioavailable concentration of F in soil. In this study, soils were collected from various locations across New Zealand, representing different soil orders and land uses. The total soil F concentration was measured using an ion specific electrode following extraction with four different concentrations of NaOH (4 mol L⁻¹, 8 mol L⁻¹, 12 mol L⁻¹ and 16 mol L⁻¹), or fusion with NaOH (the conventional method used to analyse total soil F). We concluded that NaOH extraction gave an acceptable level of accuracy for organic matter and volcanic parent material derived soils. Agreement was, however, less strong for recent and pallic soils. The extraction method was subsequently validated through repeat analysis of three further soils (n = 270).

To define a method for quantification of the bioavailable concentration of F in soil, samples were extracted with water, 1 mol L⁻¹ HCl, 0.01 mol L⁻¹ CaCl₂, 0.01 mol L⁻¹ KCl, and 1 mol L⁻¹ NH₄Cl. The correlation between 0.01 mol L⁻¹ CaCl₂, 0.01 mol L⁻¹ KCl, and water extracted F concentrations were significant (*p* < 0.05), and extracted the same soil F fractions. Results were normalised to the water-extractable concentration to compare recovery as a function of soil order. The recovery percentage of 0.01 mol L⁻¹ CaCl₂ was high compared with water for soils which have high Al and Fe contents. We propose that 0.01 mol L⁻¹ CaCl₂ extraction should be adopted as a standard method to assess the bioavailable F concentration of New Zealand pastoral soils.

1. Introduction

Fluorine (F) is a trace element in biological systems and has a reputation for causing harmful effects on health and the environment [1]. Fluorine is considered essential to animal life at low levels but is toxic at high levels [2,3]. Fluorine is present in all soils due to soil forming processes as well as anthropogenic inputs from glass, brick, steel, aluminium, and fertiliser industries [4]. In New Zealand, long-term and continuous application of superphosphate fertiliser to agricultural soil has had the unintended consequence of increasing total soil F concentrations [5]. A recent study [6] estimated that a further 50 years of continuous superphosphate fertiliser application at today's rates will double the present average total soil F concentration of 220 mg kg⁻¹ in New Zealand soils, and will increase the total soil F concentration to above 500 mg kg⁻¹ for 44% of New Zealand's dairy farms. A key concern for animal welfare is ingestion of soil containing F, especially

during periods of poor pasture growth or intensive grazing when animals will consume a relatively high amount of soil. Cronin et al. [4], in 2000, reported that ingestion of soil with a F concentration > 326 mg kg⁻¹ can cause chronic fluorosis in cattle. Nearly 50% of New Zealand dairy farms have a total soil F concentration above this threshold value.

1.1. Total soil F analyses

The total F concentration in soil can be determined by a number of analytical methods. These include. NaOH fusion followed by ion selective electrode (ISE); X-ray fluorescence (XRF); ion chromatography; instrumental neutron activation analysis (INAA); and atomic and molecular spectroscopy [7–10]. The accuracy of these methods in quantifying the concentration of F in analytical preparations (soil extracts or solid-phase samples) is frequently compromised by interfering elements

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in the sample. Aluminium cations form very strong complexes with fluoride ions under acidic conditions limiting sensitivity to ISE [11,12], and will also interfere with the analysis of F using XRF [13] and INAA [7]. Environmental research in New Zealand related to soil F has been hampered by the lack of a standard, reliable, and simple test for total soil F, and this has limited large-scale screening of New Zealand soils to establish accurate baseline levels for soil F.

The standard method most commonly used for the analysis of total F in soil employs NaOH fusion followed by ISE. While ISE analysis is sensitive and rapid with a reported recovery rate > 90%, its trueness is greatly dependent on careful sample preparation [8], particularly during the fusion of the soil sample with NaOH. This latter process is complex, time-consuming, and (consequently) expensive [14]. There is, therefore, considerable interest in the development of a simple and reliable alternative standard method for total soil F analysis that will help underpin more extensive environmental monitoring.

1.2. Bioavailable F analyses

While analysis of the total F concentration of soil provides a useful basis for comparison of soils, this parameter generally shows poor correlation with the environmental risk that might be posed [15]. Instead, the term bioavailable or labile F (hereinafter termed bioavailable F) is used to model the fraction of total soil F which is available to plants and microorganisms growing in the soil. Bioavailable F can be chemically defined as F that is water soluble or non-specifically adsorbed to exchange sites on soil surfaces [2]. There is growing concern that increasing total soil F concentrations in New Zealand agricultural systems may lead to an increase in the concentration of bioavailable F, and that this may negatively influence the function of soil microorganisms which underpin nutrient cycles.

Methods to estimate the bioavailable fraction of total soil F include water extractable, resin-extractable, low concentration acid-extractable (1 mol L⁻¹ HCl), [4], and CaCl₂-extractable [16] laboratory procedures. Of these, water extraction has been used to model the bioavailable fluoride concentration in Al-contaminated industrial environments [17,18]. However, there is very little published literature regarding the bioavailable F concentration of soils subject to continuous applications of phosphate fertiliser.

The bioavailability of F in soil is dependent on a range of soil properties such as pH, clay mineralogy, organic matter content, and the presence of Fe and Al oxyhydroxides [19]. Linking these properties with bioavailable F in soil will help to define critical toxic F concentration levels for soil microorganisms [20], and also help guide management practices to minimise F bioavailability to microorganisms in New Zealand agricultural soils [5]. However, according to literature, there are no standard methods to determine the bioavailable fraction of F in soil [5] and this limits the usefulness of bioavailable F as a measure of environmental risk in New Zealand pastoral soils.

The current study was designed to develop and test reliable and simple methodologies to measure both total soil F and the bioavailable concentration of F in soil to underpin the ongoing sustainability of New Zealand agricultural systems.

2. Material and methods

2.1. Soil locations and sampling procedure

Soil samples were collected from operating farms which were selected to represent the dominant productive New Zealand soil orders (Table 1). Paddocks were randomly selected within each farm and samples were collected across the paddock along two linear transects to 150 mm depth using a stainless steel soil corer (2.5 cm diameter). Ten cores were collected from each transect and combined into a composite paddock sample. Soil cores were air-dried until constant weight, then passed through a 2 mm stainless steel sieve before storage at room

Table 1

Location, land use, soil order (New Zealand and US soil classification scheme) of sampled soils in randomly selected paddocks.

Location	Land use	Soil order		Analytical tests performed [#]
		US classification ^a	NZ classification	
Otorohanga	Dairy	Andosols	Allophanic	1, 3, 4
Reporoa	Sheep/Beef	Vitric andosols	Pumice	1, 3, 4
Newstead	Dairy	Andosols	Allophanic	1, 3, 4
Tokomaru	Dairy/Sheep	Luvisols	Pallic	1, 3, 4
Gordonton	Dairy	Histosols	Organic	1
Manawatu	Dairy	Fluvisols	Recent Sedimentary	1
Putaruru	Dairy	Andosols	Allophanic	1
Te Anau	Sheep/Beef/ Deer	Cambisols	Brown	1
Tuapaka	Dairy/Beef	Luvisols	Pallic	1
Te Aroha	Dairy	Gleysols	Gley	1
Kairanga ^b	Horticulture	Gleysols	Gley	2, 3, 4
Pukekawa ^b	Horticulture	Ferralsols	Granular	2, 4
Canterbury ^b	Horticulture	Luvisols	Pallic	2, 4

1 – Method development for total soil F concentration using NaOH extractions (4 mol L⁻¹, 8 mol L⁻¹, 12 mol L⁻¹ and 16 mol L⁻¹).

2 – Method verification for total soil F concentration using NaOH extractions (4 mol L⁻¹).

3 – Method development for bioavailable concentration of F in soil.

4 – Analysis of relationship between total, proposed extractable F fraction (H₂O and 0.01 mol L⁻¹ CaCl₂) and dominant soil properties.

^a IUSS Working Group WRB, 2006.

^b Pre-established research plots.

temperature. Three of the locations (Canterbury, Pukekawa, and Kairanga) each had 30 pre-established research plots. For these locations, a composite core sample was collected from each plot to generate replicate samples for repeat analysis.

2.2. Total soil F analyses

2.2.1. NaOH extractions and ISE measurement of total soil F

Triplicate subsamples of soil (0.5 g) were accurately weighed into polypropylene centrifuge tubes. Sodium hydroxide solution (10 mL of 4 mol L⁻¹, 8 mol L⁻¹, 12 mol L⁻¹ or 16 mol L⁻¹ NaOH) was then added and the suspension was maintained at 100 °C in a water bath for 24 h with frequent end-over-end agitation. These suspensions were then quantitatively transferred to screw-top plastic containers [21].

To minimise Al and Fe interferences in the ISE analysis, the pH of each suspension was adjusted to 8.5 by the slow addition of 3 to 6 mL of 6 mol L⁻¹ HCl. Each sample suspension was then made up to 100 mL with deionised water, filtered through Whatman No.2 paper, and stored in a screw-top plastic container in a refrigerator for subsequent ISE analysis.

Prior to analysis of each filtrate, an aliquot was mixed with a total ionic strength adjusting buffer (TISAB IV) at a 1:1 ratio in order to maintain a constant ionic strength in solution and to stabilise free F⁻ ions [8]. The TISAB-filtrate sample was then analysed using Orion Fluoride Ion Selective Electrode (ThermoFisher Scientific, USA).

2.2.2. NaOH fusion and ISE measurement of total soil F

This is the conventional method employed to measure total F in soil samples [22] and was used to compare the efficacy of the various NaOH extraction methods to quantify soil total F.

Triplicate subsamples of oven-dried (105 °C overnight) soil (0.25 g) were accurately weighed into nickel crucibles. The samples were then moistened with a small amount of deionised water. A few drops of ethanol (70% v/v) were added to improve water absorption in those instances where the dried soil was hydrophobic. Six milliliters of 17 mol L⁻¹ NaOH was then added to the moistened soil, mixed, and

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