

RECENT METHODOLOGY DEVELOPMENTS IN SOIL FLUORINE ANALYSIS

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Introduction

Fluorine (F) is one of several trace elements receiving much attention owing to its possible harmful effects on health and environment. There are many methods used as the standard method of analysis of total F in soil. These include: ion selective electrode (ISE); X-ray fluorescence (XRF); Ion chromatography; Instrumental Neutron Activation Analysis (INAA); and Atomic and molecular spectroscopy. The accuracy of different methods to quantify the presence of F in analytical preparations (soil extracts or solid-phase samples) is dependent on interfering elements such as the Al content of the sample; Al cations form very strong complexes with fluoride ions in acidic conditions (D'Alessandro et al., 2008). Also Al acts as an interfering element in the F-analysis by XRF (An et al., 2012) and INAA (Knight et al., 1977) where it can alter the measured intensity of F. Trace levels of F in soil and water are predominantly determined by potentiometric methods such as ISE. The analysis of F in an aqueous phase using this methodology tends to be sensitive and rapid with a reported recovery rate greater than 90%. However, the accuracy of ISE to quantify the concentration of F in soil is greatly dependent on the accuracy of sample preparation method (Campbell, 1987). NaOH fusion is used to release F ions in the ISE methodology, and this often involves high rates of handling errors. In this paper, NaOH fusion and ISE quantification is benchmarked as the conventional technique for the analysis of F in soil, and we assessed the potential for alternative techniques to be used relative to this benchmark. The total F content measured of twelve diversified soil types, each of which has a long term history (>10 years) of phosphate fertilizer application was assessed with several analytical techniques. The main objective of the current project is to validate the potential of alternative techniques to accurately and consistently quantify the concentration of F in soil.

Materials and Methodology

Bulk soil samples at 10cm depth were collected from long term fertilised pasture sites in ten different locations in New Zealand (Table 1).

Two FLRC internal soil standards (Soil A: S07052003A = $168 \pm 29 \mu\text{g F g}^{-1}$ soil; Soil B: S07052003B = $542 \pm 30 \mu\text{g F g}^{-1}$ soil) were used as the standard reference material for the total F-analysis (Bretherton et al., 2004).

Table 1: Locations and soil types of soil samples used

No.	Location	Soil Type	Land Use
1	Gordonton	Peat	Dairy
2	Otorohanga	Mairoa Ash – Allophanic	Dairy
3	Putaruru	Tirau Ash – Allophanic	Dairy
4	Reporoa	Pumice	Sheep/Beef
5	Te Anau	Brown	Sheep/Beef/Deer
6	Newstead	Ash – Horotiu	Dairy
7	Tuapaka	Pallic	Dairy/Beef
8	Manawatu	Recent	Dairy
9	Manawatu	Pallic	Dairy/Sheep
10	Te Aroha	Gley/Ash	Dairy

Methodology for NaOH alkali fusion/ion selective electrode: conventional analysis

Fuse a soil sample with concentrated NaOH (17 M) at 700°C, dissolve the fusion mass, adjust pH to 8.5. The F concentration in the filtered solutions was measured by an F-ion selective electrode after addition of an equivalent volume of total ionic strength adjustable buffer (TISAB) solution.

Total soil F measured by XRF: non-conventional technique

As stated by Anderson et al. (2013), wavelength dispersive XRF (WD-XRF) will produce sufficient spectral resolution to quantify F using the XRF analytical technique than the energy dispersive XRF (ED-XRF).

Neutron activation analysis

Neutron activation analysis is currently only carried out by a few laboratories around the world, most of which are in USA and Canada. Extensive correspondence with these laboratories established that F-analysis by INAA method is only possible if the Al concentration of a sample is less than 100 $\mu\text{g F g}^{-1}$ due to the interference of Al on F decay. Therefore, the potential of using INAA as an independent third party quantification of the F concentration in NZ soils has been discounted.

NaOH extraction methodology

The objective of this methodology is to determine the lowest concentration of NaOH required to extract F ions from the soil, with an acceptable recovery level as defined by the conventional analytical technique (fusion plus ISE). Soil samples testing in this work were separately extracted with 4, 8, 12 and 16 M NaOH at 100 °C on a water bath for 24 hours, adjusted pH to 8.5 and total F in the extract solution was analysed by ISE.

Results and Discussion

Total F Concentration in soil samples determined by alkali fusion/ISE

The ten soil samples produced F concentrations ranging from 197 to 683 $\mu\text{g F g}^{-1}$ (Figure 1) due to the wide range of soil characteristics apparent for these soils.

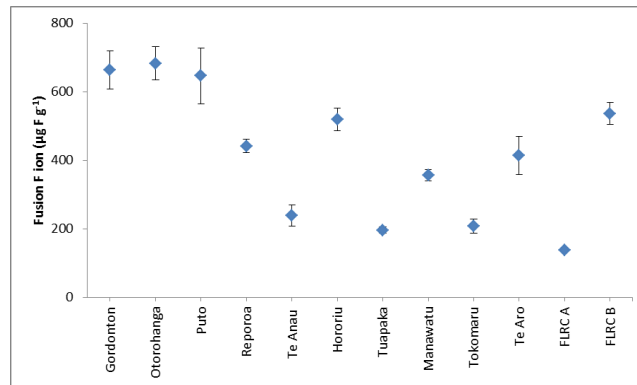


Figure 1: The total F concentrations in 12 soil samples as determined by alkali fusion/ISE.

Total F concentrations obtained for the standard reference soil samples were within the standard deviation recommend by FLRC (Bretherton et al., 2004). The soils collected from Gordonton, Otorohanga and Putaruru have longer term history of phosphate (P) fertilizer application relative to the other locations. This may have been the reason for the high F concentrations observed in these locations.

The comparison of total soil F concentration measured by alkali fusion/ISE and XRF methods

The measured F concentrations between the two methods were not in agreement for the soil samples except one (Figure 2). Seven of the samples (58%) with the XRF method measured F concentrations that have significantly lower recovery level compared to the ion selective electrode. In addition, the F concentrations of the standard reference soils were significantly lower ($sd = 29\mu\text{g F g}^{-1}$) when measured with the XRF method. However, the F concentrations obtained from the standard reference soils by the alkali fusion/ISE method were reproducible and within the sd level.

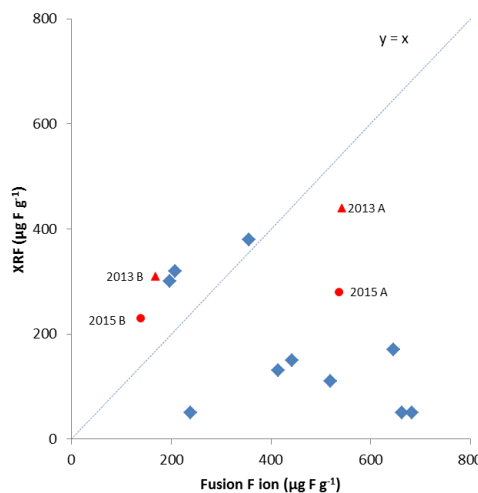


Figure 2. Comparison of the total F concentrations in soil samples as determined by XRF and AF/ISE (4 reference samples in red, 2 of which are from 2013).

Unexpectedly, there were significant variations between the XRF analysis of the same two standard reference soil samples from 2013 and 2015. In the latest XRF analysis, the total F

concentrations of reference soil samples A and B were reduced by 35% and 57%, respectively. As Pleßow (2013) stated XRF F-analysis tends to occasionally fail systematically in yielding reliable quantitative results for solid samples. We conclude that XRF for total soil F-analysis is not reliable and accurate due to poor reproducibility of results.

The comparison of total soil F concentration measured by alkali fusion/ISE and NaOH extraction methods

The total F concentration of the soil samples quantified through NaOH extraction at all four concentrations were in reasonable agreement with the fusion/ISE technique. The F concentrations of the two soil samples measured by NaOH extraction were significantly reduced relative to the fusion method. The F concentration from NaOH extraction was significantly correlated with that from fusion/ISE; the correlation coefficient (r) ranged from 0.92 to 0.95 (Figure 3). Interestingly, there were no significant differences observed between the four NaOH concentration extractions indicating that the 4M NaOH application is sufficient to obtain an F concentration with a reasonable recovery level.

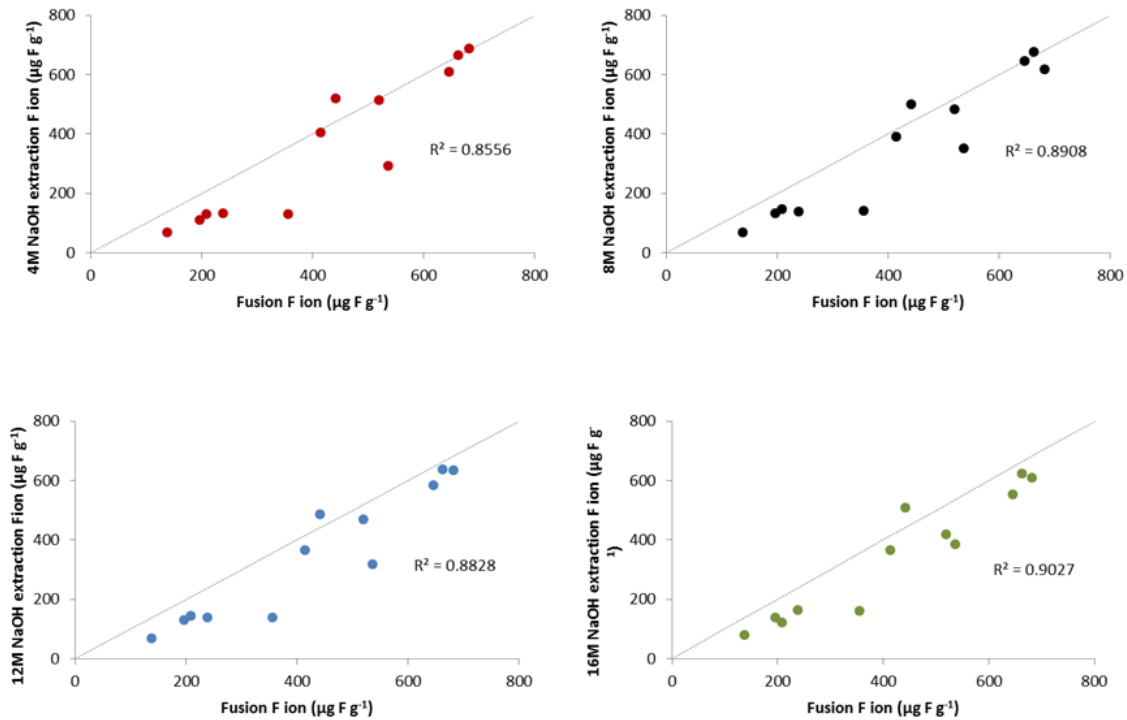


Figure 3: Comparison of the total F concentrations in twelve soil samples as determined by NaOH (4, 8, 12 and 16 M) extraction and alkali fusion/ISE methods.

Over half of the soil samples produced F concentrations which significantly ($p < 0.05$) agreed between the two methods. Agreement within 15% by the two methods is defined in this research as ‘less variable’. Soils with low variation were generally Allophanic soils in which there are high contents of Fe and Al hydroxides, and high anion exchange capacities. We assume that the ISE methods (both fusion and extraction) are highly effective with soils that are high in Fe and Al, as the methodology has been designed to resolve issues with

interferences (McQuaker & Gurney, 1977). Alternatively, extraction with NaOH may be removing only the F pool 'added' to the soil through superphosphate fertilisation. For these high F soils, this added pool is more significant due to extensive fertiliser history than for soils that have not received regular and on-going fertiliser application.

These results and soil type grouping effects indicate that the potential accuracy of a non-conventional NaOH extraction followed by ISE quantification is highly dependent on soil chemical and physical characteristics. Loganathan et al. (2006) examined a range of total F concentrations and forms of soluble F species, and their relationships to selected soil properties in New Zealand agricultural soils. They reported a significant positive correlation between P fertilizer use and F accumulation. Furthermore, the degree of correlation was significantly associated with the soil properties such as soil organic matter, pH and amorphous aluminium oxide contents. This study suggests that potentially high-risk New Zealand soils (i.e. those with high F concentration through significant fertilisation history and F retention; allophanic soils) may be semi-quantitatively assessed using a NaOH extraction. These high-risk soils are those that are of regulatory concern for their increasing F concentration. The results of the current study suggest that for some soils, especially those at high risk, NaOH extraction and ISE finish could be used for environmental management. The validity of this statement must, however, be assessed with further research, testing a greater number of soil, and including a detailed assessment of their chemical properties.

Conclusion

In this study we have compared and discussed four methods of analysis of total F in soil. The alkali fusion/ISE method is used as the conventional test for F in soil, has good reproducibility, but suffers from complex sample preparation methods and is labour intensive. The XRF method proved to be unreliable in producing repeatable concentrations for F in soil and has therefore been discounted from further investigation. INAA, considered to be a benchmark for F concentration in geological samples proved to be poorly suited for soil samples due to interference from Al in the soil matrix. Extraction of F with NaOH solution and ISE quantification of F in solution was highly correlated ($r > 0.9$) with the alkali fusion/ISE methodology. However, the accuracy was dependent on the specific soil characteristics. Extraction and the alkali fusion/ISE showed good similarity with the F concentration for high-F allophanic soils. These are the soils in NZ where increasing F concentration is of greatest concern, and are therefore the soils where total F analysis by an alternative method is in greatest demand. This study, therefore, suggests that, the opportunity for development of a 'non-conventional' extraction and ISE technique is real, and should be assessed with ongoing research.

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