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**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

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PATRICIA MARÍA YSABEL ALBORNO JOVER

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*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 ($r>0.82$), 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.

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