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Impacts of phosphate fertiliser application on soil acidity and aluminium phytotoxicity

**A thesis presented in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy in Soil Science
at Massey University**

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Abstract

New Zealand's agricultural production systems are based largely on legume-based pastures which require a high soil phosphorus (P) status to achieve optimum production. Although application of P fertilisers undoubtedly leads to increased agricultural production and a direct economic benefit to New Zealand, concerns are growing about possible harmful side effects of long-term application of high rates of P fertilisers. These side effects can arise through contaminants contained in the fertilisers and through the direct or indirect effects of the P fertilisers on soil acidity.

The general objective of the present study was to investigate the effect of long-term application of P fertilisers on soil acidity and aluminium (Al) phytotoxicity. Particular emphasis was placed on the possible role of fluoride (F), contained in the fertilisers as a contaminant, on the chemistry and phytotoxicity of soil Al.

A field study was carried out to investigate the effects of long-term annual applications of six types of P fertilisers on soil acidity under legume-based pastures. The results from this study indicated that in a marginally acidic soil (pH(H₂O) 5.4-5.8), irrespective of the rate or form of P fertiliser used, the soil became increasingly acidic over a period of seven years. However, the rate of acidification varied with the type of P fertiliser used. By year 8, the application of North Carolina phosphate rock (NCPR) gave higher pH, exchangeable Ca and Ca saturation but significantly lowered exchangeable and soluble Al than the control plots. In contrast, diammonium phosphate (DAP) application gave significantly lower soil pH, exchangeable Ca and Ca saturation and increased soluble Al and exchange acidity. In comparison to the control plots, single superphosphate (SSP) in general had similar soil pH and exchangeable Al but increased exchangeable Ca and Ca saturation at higher rates of application. The results suggested that continuous use of certain reactive phosphate rocks such as NCPR can significantly slow down the rate of acidification of pastoral soils.

Using the same field trial, changes in soil solution composition and Al speciation were investigated. Application of DAP and high rates of SSP increased total Al concentrations in the soil solution even though SSP had no effect on soil pH. The increased Al concentration in the SSP treatments could be due to high concentrations of F (added as a contaminant in the fertilisers) complexing Al, and hence bringing more Al into the soil solution. Application of NCPR decreased total Al concentrations, presumably by increasing pH. Application of DAP increased the predicted concentrations of toxic Al species- Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^{1+}$. In contrast application of SSP decreased the toxic Al concentration, despite higher solution Al concentration compared with control treatment. The concentration of toxic Al species in NCPR-treated soil was also lower than in the control treatment.

A short-term bioassay was carried out using barley (*Hordeum vulgare* L.) to study the effects of long-term (20 years) inputs of Ca, F, and sulphate (SO_4) from P fertilisers and changes in soil pH on Al phytotoxicity. Results of this glasshouse experiment showed that the relationships between soil Al indices and barley root growth were different for soils with different P fertiliser history. The inability of total monomeric Al, and 0.02 M CaCl_2 -extractable Al to explain the variation in root growth in the combined data for fertilised and unfertilised soils indicated that the relative proportions of the phytotoxic Al were different for fertilised and unfertilised soils. These differences were due to the higher proportions of the less-toxic Al-F complexes in the fertilised soil and also due to the high concentrations of Ca in the soil solution. The ability of the activity ratio of $\text{Al}^{3+}/\text{Ca}^{2+}$ to predict Al toxicity most consistently across soils with different P fertiliser histories indicated that soil solution Ca should be taken into account together with toxic Al species in the assessment of Al phytotoxicity.

A short-term bioassay was carried out to develop a chemical test to predict the potential toxicity of Al for early root growth in widely different soil types. The results from this study showed that, in soils with similar physical properties, mineralogy and low organic matter content, short time pyrocatechol violet (PCV)-Al determination in soil solution can be used as a simple and reliable method to predict Al toxicity. However, the direct use of

short-time colorimetric procedures to predict critical Al toxicity levels for different soil types could be limited by the variations in organic Al and other factors such as ionic strength, cation and anion types and concentrations. Among the Al toxicity indices studied, as observed in the trial with similar parent materials, the activity ratio of $\text{Al}^{3+}/\text{Ca}^{2+}$ is again the best predictor of Al toxicity but now in widely different soil types.

The interactive effects of soil acidity and F were also studied using the short-term bioassay method. Increasing rates of F additions to soil significantly increased the soil solution concentrations of Al and F irrespective of the initial soil pH. However, the rate of increase was much higher at low pH than at high pH.

There was a significant interaction between soil acidity and F on root growth of barley. High rates of F addition severely reduced root growth and the effect was more pronounced in the strongly acidic soil. Speciation calculations predicted that increasing rates of F additions increased Al-F complexes in the soil solution. Results also indicated that Al-F complexes are not toxic at lower concentrations but they are toxic at high concentrations and the relative toxicity depended on the type of Al-F complexes present.

Results from this study suggest that it is unlikely that in a marginally acidic soil (pH (H_2O) 5.4-5.8) long-term F inputs via P fertilisers will have any detrimental effects on plant growth. Rather it will reduce the free Al concentration while keeping the Al-F species concentration below the toxic threshold level in the soil solution, thereby reducing the occurrence of Al phytotoxicity.

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