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Interactive effects of soil acidity and fluoride on soil solution aluminium chemistry and barley (*Hordeum vulgare* L.) root growth

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Addition of high rates of fluoride to strongly acidic soils can reduce barley root growth due to the toxicity of aluminium–fluoride complexes formed in soil solution.

Abstract

A greenhouse study was conducted to determine if concentrations of fluoride (F), which would be added to acid soils via P fertilisers, were detrimental to barley root growth. Increasing rates of F additions to soil significantly increased the soil solution concentrations of aluminium (Al) and F irrespective of the initial adjusted soil pH, which ranged from 4.25 to 5.48. High rates of F addition severely restricted root growth; the effect was more pronounced in the strongly acidic soil. Speciation calculations demonstrated that increasing rates of F additions substantially increased the concentrations of Al–F complexes in the soil. Stepwise regression analysis showed that it was the combination of the activities of AlF_2^{1+} and AlF^{2+} complexes that primarily controlled barley root growth. The results suggested that continuous input of F to soils, and increased soil acidification, may become an F risk issue in the future.

Keywords: Aluminium toxicity; Aluminium–fluoride complexes; Barley root growth; Phosphate fertiliser; Soil acidity

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1. Introduction

There is an increasing global concern about acidification of agricultural soils and its effects on soil pollutants. Fluoride (F) is one such pollutant and it is applied to soils in phosphate fertilisers, which usually contain 1–4% F as an impurity (Loganathan et al., 2003). With increased acidification both aluminium (Al) and F become more available for plant uptake. The rhizotoxic effects of Al in acid soils are well known and it is generally believed that the main rhizotoxic Al species is Al^{3+} (Kinraide, 1997; Pavan and Bingham, 1982). Fluoride can also be phytotoxic (Weinstein and Alscher-Herman, 1982) and under acidic conditions, F and Al can exist as a number of complexes in solution such as AlF_3, AlF^{2+}, and AlF_2^{1+} (Lindsay, 1979). In the complexed form the toxicity of each of these elements would be altered.

Aluminium complexes with organic anions (Matsumoto, 2000), sulphate (Kinraide, 1997), and phosphate (Takita et al., 1999) are non-toxic to plants. However, there is a continuing uncertainty regarding the toxicity of aluminium-hydroxy species to plants. Early studies indicated $Al(OH)^{2+}$ and $Al(OH)_2^{1+}$ are toxic to plants (Alva et al., 1986; Noble et al., 1988; Wright et al., 1987). However, recent evidence suggests that that Al-hydroxy species are not toxic to plants (Kinraide, 1997).

Application of F has been shown to ameliorate Al phytotoxicity in nutrient solutions (Cameron et al., 1986; MacLean et al., 1992; Tanaka et al., 1987). This was suggested to be mainly due to a decrease in the concentrations of toxic Al (in this paper we will consider Al^{3+}, and sum of Al-hydroxy

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species as toxic species) as a result of complexation of F with Al. However, other nutrient solution studies (Kinraide, 1997; Stevens et al., 1997) have shown that Al–F complexes are not toxic at lower concentrations, but they are toxic at higher concentrations and the toxicity depends on the proportion and concentration of the different types of Al–F species in the solution. In a recent study, Gallon et al. (2004) found that Al accumulation in some aquatic plants grown in nutrient solution increased with increasing concentrations of Al–F species. However, it is unclear what would be the overall net effect of soil acidification and adding large quantities of F-containing P fertilisers on the phytotoxicity of F and Al in soils. Studies to evaluate these effects in soils are more complex than in nutrient solution, because decreasing soil pH or addition of F to soils will dissolve soil solid phase Al thereby increasing the soil solution Al concentrations. Therefore, unlike in nutrient solution studies, the total Al concentration in soil solution changes with F addition and changes in soil pH and this interactive effect will determine the proportion and concentration of the Al–F species in soil solution.

Furthermore, there is conflicting evidence on the effect of F on Al phytotoxicity in soil. Some studies have found that F application to acid soils decreased plant growth (Hani, 1978; Sikora et al., 1992), while another study reported that F application increased plant growth (Keerthisinghe et al., 1991).

The objectives of this study were to (1) investigate the interactive effects of pH and F on soil solution composition and Al speciation, and (2) determine the concentration at which the Al, F and/or Al–F complexes present in the soil solution if any are phytotoxic to barley seedlings.

2. Materials and methods

2.1. Soil sample collection and incubation

A bulk soil sample from 4 to 10 cm depth was collected from an unfertilised pasture site at Ballantrae (near Woodville), New Zealand. This site had not received P fertiliser for over 20 years. The soil at the site is classified as a Typic Dystrochrept in the US soil Taxonomy classification system. Subsamples (3 kg) of the moist soils were incubated with different amounts of HCl for 2 weeks to obtain five pH levels (4.25, 4.61, 4.96, 5.24, and 5.48) (hereafter called ‘initial pH’). After 2 weeks, four rates of F (0, 40, 80, 160 mg F kg^{-1} soil) were added in the form of NaF solution, and the samples were again incubated at field capacity moisture content at 25 °C for 30 days. Samples were mixed thoroughly at frequent intervals. Fluoride loading rates were approximately equivalent to the application of 300 kg single superphosphate (SSP) (F = 1.5%, P = 9%) ha^{-1} y^{-1} for 10–40 years resulting in the addition of 40–160 mg F kg^{-1} of the surface soil (assuming a soil depth of 0–7.5 cm and a soil bulk density of 1500 kg m^{3}). Treatments were arranged according to a completely randomised factorial design.

2.2. Plant growth and soil analysis

Incubated soil samples were placed in 250-mL intact plastic cups. Seeds of barley were pre-germinated for three days and planted in the incubated soils at the rate of four seedlings per cup. Each treatment had three replicates. The plants were grown for three days in a glasshouse maintained at 16 ± 2 °C minimum (night) and 28 ± 3 °C maximum (day) temperature. At the end of the growth period the seedlings were removed from the soil and the lengths of the longest root of each plant were measured. About 200 g moist soil samples were removed from the cup and soil solutions separated by centrifugation as described by Manoharan et al. (1996a). The soil solutions were analysed for pH, electrical conductivity (EC), Na, K, Ca, Mg, Cl, NO_3, SO_4 and F, as described by Manoharan et al. (1996a). The ionic strength of the soil solution was calculated from the EC using the following equation (Lindsay, 1979):

$$\text{Ionic strength (mol/L)} = 0.013\text{EC (dS/m)}$$

Labile (mainly inorganic) monomeric (Al(inorg)) and non-labile (mainly organic) monomeric Al in soil solutions were determined according to the methods outlined by Driscoll (1984). Organic-monomeric Al was separated by passing an aliquot of soil solution through a column of strongly acidic cation-exchange resin (Amberlite IR-120). This procedure assumes that inorganic forms of Al complexes are decomplexed, and Al^{3+} is retained on the cation-exchange column while strongly bound Al-organic complexes pass through the column. The difference in concentration between the total monomeric Al (in solution before passing through the cation-exchange column) and organic-monomeric Al (in solution after passing through the column) is assumed to be the Al(inorg) concentration (Driscoll, 1984; Gallon et al., 2004). The cation-exchange column was prepared using a glass tube 60 mm long and 3 mm in diameter. The ion-exchange medium was prepared by mixing the Na form of the resin with a small amount of the H form of the resin and adjusting the proportions until the resin-solution pH was close to the pH of the solutions being analysed. This adjustment minimised the changes in the pH of the samples when processed through the exchange column. A peristaltic pump was used to maintain a constant flow rate of solutions when they were passed through the cation-exchange column. The Al in the soil solution before and after it passed through the column was measured by the pyrocatecol violet (PCV) method (Dougan and Wilson, 1974). A 4-min reaction time was used for the determination of Al(inorg) (Seip et al., 1984).

Aluminium speciation was estimated using an MINEQL^{+} computer equilibrium program (Schecher and McAvoy, 1991), assuming that all dissolved species are in equilibrium. In this study, the sum of the concentrations of the Al^{3+}, Al-hydroxy species, Al–sulphate complexes and Al–fluoride complexes is considered as the Al(inorg) as reported by Driscoll (1984). Activity coefficients were calculated using the Davies equation $\log \gamma_i = -0.509 Z_i^2 (u^{1/2}/(1+u^{1/2})) - 0.3u$, where $\log \gamma_i$ is the activity coefficient, Z_i is the valency of the ion concerned and u is the ionic strength (Stumm and Morgan, 1981). Statistical Analysis System (SAS) programs were used for all statistical analyses.

3. Results and discussion

3.1. Effects of soil pH and F additions on soil solution pH and Al concentration

Soil solution pH increased slightly or remained constant with increasing rates of F addition for all soil pH treatments (Fig. 1). The increase of pH was significant ($P \leq 0.05$) at the highest initial pH of 5.48 for the addition of 160 mg F kg^{-1}. Addition of F to soils has also been shown by other workers to increase the soil and solution pH (Moore and Ritchie, 1988; Perrott et al., 1976). This is primarily due to the reaction of F with Al oxides and Al-bearing clay minerals which involves release of OH^- to the solution (Omueti and Jones, 1977; Perrott et al., 1976). The significant increase in solution pH with F additions at the highest initial pH but not at the lower initial pHs is primarily because at lower pHs, the released OH^- groups would have been neutralized by a greater number of Al^{3+} and H^+ associated with these strongly acidic soils.

The Al(inorg) in soil solution significantly ($P \leq 0.05$) increased with increasing rates of F addition and decreasing