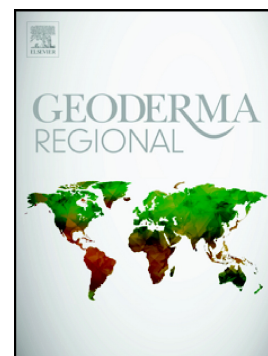


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Extractable aluminium in New Zealand Andisols and Inceptisols.

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It is critical to have a soil test that allows for the measurement of potential toxicity. A laboratory experiment was undertaken to investigate the effects of changing the concentration of salt in extract and extraction time of the standard CaCl₂ and KCl soil Al tests on the Al concentrations extracted from 13 soils from four New Zealand soil orders. Al extracted by KCl (Al_{KCl}) was 13 times higher than extracted by CaCl₂ (Al_{CaCl₂}) across all soils. The effect of changing extract salt concentration and extraction time on Al extracted differed among the four soil orders tested for the two extraction methods. Increasing the concentration of CaCl₂ in the extract increased ($P < 0.001$; $P < 0.05$) the amount of Al_{CaCl₂} (by 0.02-0.13 cmol_c/kg) for the four soil orders, while increasing extraction time resulted in a difference only in the Allophanic soils, where Al_{CaCl₂} decreased ($P < 0.01$). The interaction of the concentration of salt in the extract and extraction time for the CaCl₂ extraction did not affect ($P > 0.05$) the Al_{CaCl₂}

extracted from all soils. An increase in the concentration of KCl in the extract up to 1 M increased Al_{KCl} ($P < 0.01$) (by 0.2-0.8 cmol_c/kg) on the Allophanic, Brown and Pumice soils, with no increase ($P > 0.05$) with a further increase in concentration. Extraction time affected Al_{KCl} ($P < 0.001$) for Pallic soils, while the interaction of concentration of KCl in the extract and extraction time resulted in differences ($P < 0.001$) only for the Pallic soils. These findings suggest that the Al concentrations measured by the two extraction methods are affected by specific soil properties in the topsoil related to soil order. This means that when measuring the Al bioavailability in soils, extreme care must be taken when interpreting soil Al test results.

Keywords: soil acidification, bioavailability, standard methodology, salt concentration, extraction time, Andisols, Inceptisols

1. Introduction

Soil acidification is a global issue that affects the topsoil of an estimated 30% of the world's ice-free land area and 75% of these soils have acid subsoils (pH < 5.5; (FAO and ITPS., 2015; Von Uexküll and Mutert, 1995). Acidification increases the solubility of soil Al and promotes the formation of the phyto-toxic free ion Al^{3+} species and thus reduce productivity on acid soil (Kinraide, 1991; Kinraide, 1997; Kochian, 1995; Manoharan et al., 1996; Ryan and Delhaize, 2012). The primary site of Al toxicity is the root zone of plants, in particular the root apex, where Al can accumulate (Delhaize and Ryan, 1995). However, diagnosis of Al toxicity by visual observation of plants in the field can be difficult and only allows for retrospective management responses.

Aluminium makes up around 8% of the earth's crust and is the third most abundant

element in the earth's crust and its concentrations in soils usually range between 1.0-3.0% (Rayment and Lyons, 2011b). The bioavailability of cationic trace elements, such as Al, to plants is often determined by a combination of one or more soil factors, including total elemental concentrations, pH and soil organic matter content (e.g. McLaughlin et al., 2000). It follows that proactive and cost-effective management of possible issues arising from soil Al requires a test that can accurately integrate these factors across a variety of soils in a way that represents the soil Al fraction that can negatively affect plants between germination and harvest/grazing.

The two commonly used methods of measuring potentially toxic Al in soils involve extracting a fraction of the soil Al using dilute solutions of KCl and CaCl₂ (forthwith: Al_{KCl} and Al_{CaCl₂}, respectively). The aluminium extracted by a 1 M KCl extraction is part of an effective cation exchange capacity (ECEC) measurement that determines the amount of exchangeable cations the soil is holding at field pH, which includes the acidic cations (H⁺ and Al³⁺) (Blakemore et al., 1987). It is used in many parts of the world, including Australia, China, South America, the USA and Canada as a measure of Al toxicity and as an index for lime requirement and was previously used by commercial laboratories in New Zealand (NZ) (Abreu Jr et al., 2003; Amedee and Peech, 1976; Guo et al., 2012; MacLeod and Jackson, 1967; Marques et al., 2002; Schroder et al., 2011; Shuman, 1990; Vendrame et al., 2013; Wang et al., 2016).

The 0.02 M CaCl₂ extraction (Al_{CaCl₂}) gives an indication of plant available Al (in soil solution) and is the favoured method for distinguishing Al toxicity in New Zealand soils (Edmeades et al., 1983). This is the current commercial test used to test for soil extractable Al in New Zealand. It is based on the findings of Hoyt and Nyborg (1971;

1972), who tested ranges of concentrations, soil:extractant ratios and extraction times on a range of 40 Canadian soils and found that Al extracted using 0.02 M CaCl₂ at a 1:2 (mass:volume) ratio and 60 minute extraction time correlated best with the yield response and Al uptake of barley, turnip rape and lucerne. Subsequently, several studies have successfully linked Al_{CaCl₂} to the plant growth responses of barley, corn, white clover, sorghum, lucerne and turnip rape on a range of different topsoils and subsoils (Khalid and Silva, 1979; Shuman et al., 1990; Webber et al., 1982). Peer-reviewed literature which examines differences in the Al concentration extracted by the two extractants for both the standard tests and also by altering the methodology (concentration of salt in the extract and extraction time) is scarce for New Zealand soils. Comparisons of the two extractions by Analytical Laboratories Ltd. (Napier, NZ), an accredited (IANZ/ISO 17025 and a member of ACPAC) commercial agriculture, environmental and food testing laboratory, have found that the CaCl₂ extraction only extracts a small proportion (~5%) of the Al extracted by the more concentrated KCl extract (Venter, 2016; Venter, H.), 2017, personal communication). Manoharan (1997) suggested that Al_{KCl} comprises most of the exchangeable and soluble Al, while Al_{CaCl₂} also measures the soluble, but a much smaller proportion of the exchangeable Al.

The reliability and uncertainty of extractable Al measured by both the CaCl₂ and KCl extraction methods has been questioned since the methods were developed. Studies have cast doubt on the Al_{KCl} test in particular, in regards to whether it measures the fraction of soil Al that can affect plants, or if other species (potentially non-toxic forms) are also extracted (Amedee and Peech, 1976; Bache and Sharp, 1976; Lee 1988; Marques et al., 2002; Menzies, 2003; Percival et al., 1996). Previous studies have indicated that Al_{KCl} concentrations rapidly decline to negligible amounts in soils with a

pH >5.6 (forthwith, pH is reported at a soil:water ratio of 1:2.5, unless stated otherwise)(Moir and Moot, 2010; Rayment and Lyons, 2011b). Accordingly, commercial laboratories recommend testing for potential Al toxicity at pH < 5.5 (e.g. Hill Laboratories, 2014). However, others have reported high Al_{CaCl_2} concentrations (>3 mg/ kg) in soils with pHs of 5.6-5.9 (Singleton et al., 1987; Whitley et al., 2018; Whitley et al., 2016), which could be potentially toxic to sensitive legumes (Moir et al., 2016). Venter (2017b) suggested that soil type differences related to soil weathering status probably affect the amounts of Al extracted for different soil types by the two tests. There may be specific soil properties which affect the measurement of Al by these two extraction methods. This needs to be investigated further, as this soil test is the current measure that farmers have available to inform them of potential soil Al toxicity on their farms and to assist in land-use decisions. Therefore, the objectives of this research were to (1) compare the effect of different salts, their concentrations and the extraction times employed on the amount of Al extracted from a range of New Zealand soils and (2) investigate the effect of soil properties on the amount of Al extracted by each procedure.

2. Materials and methods

2.1 Soil selection and preparation

We selected 13 New Zealand soils (no treatments applied) according to a combination of prior knowledge of Al toxicity issues, pHs and soil orders from agricultural sites around NZ (Table 1). These soils incorporated both volcanic and sedimentary soils, including Allophanic (WT, WH and NB), Pumice (AR, PK, ER), Brown (MO, GM, GF and MG) and Pallic (SG, DF and LP) Soil orders of NZ (Hewitt, 2010) (Table 1). The characteristics of these soils are shown in Table 2. We also used the Ah horizon of a

Temuka Gley Soil as an internal quality control (QC) to confirm consistent values across batches of extractions. The soils were collected from the top 15 cm of the soil profile, after which they were air dried and then sieved (2 mm mesh) in preparation for analysis. The general soil characterisation was carried out by Analytical Research Laboratories Ltd (ARL) and Hill Laboratories using their in house methods (Table 2). Soil pH was measured using the 1:2.5 soil to water ratio (ASPAC 4A1), Total Carbon was analysed using no soil pre-treatment (ASPAC 6B2) and CEC and BS were determined by extraction using 1M ammonium acetate at pH 7; MP-AES analysis for cations, followed by pH change determination for H^+ (ASPAC 15A1) (Rayment and Lyons, 2011b). Total extractable Al, Fe and Mn concentrations were analysed using microwave digestion at Lincoln University using the method proposed by Kovács et al. (2000) (Table A.1, Supporting Information) and were then analysed using inductively coupled plasma–optical emission spectrometry (ICP-OES; Varian 720 ES, Varian Pty Ltd, Melbourne, Australia).

2.2 Extractable Aluminium tests

The general experimental design is summarized in Figure A.1 (Supporting Information). We examined the sensitivity of the Al_{CaCl_2} extraction on the 13 soils by measuring the extractable Al using the concentrations and extraction times in the standard test (0.02 M as $CaCl_2 \cdot 2H_2O$ and 60 minutes) (Hoyt and Nyborg, 1972), the previously used 0.01 M concentration (Hoyt and Nyborg, 1971), an additional concentration of 0.05 M and alternative extraction times of 20 and 180 minutes in all concentration-extraction time combinations; each combination was tested in duplicate. We carried the extraction out on 10 g (± 0.005 g) of soil to which 20 mL of extractant was added, following the soil:extractant ratio recommended by Hoyt and Nyborg (1972). The mixtures were

shaken on an end-over-end shaker for the specified extraction times, after which we filtered the extracts (Whatman 1; pore size 11 μm ; Sigma Aldrich, St Louis, Missouri, USA) prior to elemental analysis using ICP-OES. The extractions were carried out at ambient room temperature, which was $21\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$.

We tested the sensitivity of the Al_{KCl} extraction on the 13 soils by measuring the extractable Al using the concentrations and extraction times in the standard test (1 M KCl and 30 minutes) (Blakemore et al., 1987; Rayment and Lyons, 2011a; Sims, 1996; Van Lierop, 1990). Additional concentrations of 0.2, 0.5, 1 and 2 M KCl and alternative extraction times of 5 and 60 minutes in all concentration extraction time combinations; each combination was tested in duplicate. We carried out the extraction on 2.5 g ($\pm 0.005\text{ g}$) of soil, to which we added 25 mL of KCl extractant, using the soil:extractant ratio proposed by commercial laboratories in New Zealand (Hills Laboratories, 2016 personal communication) and previous research (Rayment and Lyons, 2011a; Sims, 1996; Van Lierop, 1990). We placed the extracts on an end-over-end shaker for the given extraction times, after which we filtered them. Blakemore et al. (1987) reported using Whatman Grade 42 filter paper and ASPAC 15G1 recommends Whatman Grade 2 for filtering the extract. In this work we decided to use Whatman Grade 1 filter paper, owing to its lower Al concentration ($<0.5\text{ }\mu\text{g/g}$ instead of $2\text{ }\mu\text{g/g}$ in the Whatman 42; no concentration given for Grade 2 paper) and consistency in pore size with the filter paper used in the CaCl_2 extraction (8 μm instead of 11 μm in the Grade 2 paper). We also used a primary reference soil (Australasian Soil and Plant Analysis Council, ASPAC Soil Check reference S49729; reference value: $0.006\text{ cmolc/kg} \pm 0.0018$) to confirm Al recovery from our samples. While, the Al_{KCl} in the reference soil was lower than in our soils, we chose this as it has been tested for Al_{KCl} using the standard method by multiple

laboratories around the world. We analysed the filtrates using ICP-OES as before and present the results as cmol_e/kg (Blakemore et al., 1987).

2.3 Statistical analysis

We \log_{10} -transformed the CaCl_2 (cmol_e/kg) and KCl (cmol_e/kg) datasets to achieve a normal distribution to satisfy the assumptions for analysis of variance (ANOVA) (Sokal and Rohlf, 2012). Using Genstat 16.0' (VSN International) we conducted ANOVA analyses for CaCl_2 and KCl separately to determine differences in the soil extractable Al concentration between the soils for concentrations and extraction times for each extractant (outputs shown in supporting information; Tables A.2 and A.3). In order to investigate the effects of the concentration of salt in the extract and extraction time on individual soil orders, we analysed the four soil orders individually using a two-way ANOVA for the CaCl_2 and KCl datasets. For the significant results, we conducted a Fisher's protected LSD 5% pairwise comparison between the means to identify differences ($\alpha = 0.05$). Differences between the standard $\text{Al}_{\text{CaCl}_2}$ and Al_{KCl} tests were tested using a one-way ANOVA, using log-transformed data as before. A P value of >0.05 was regarded as statistically non-significant for all tests. A stepwise backwards multiple regression analysis was carried out in 'Minitab 17.0' with log Al extracted as the y variable and total C, CEC, BS, pH, total Al, total Fe and total Mn concentration as the continuous predictors for the standard CaCl_2 (0.02 M and 60 minute extraction) and KCl (1 M and 30 minute extraction) tests. Terms were excluded from the model if $\alpha > 0.05$.

3. Results and Discussion

3.1 Extractable Al concentrations in NZ soils

Many of the soils have potentially phytotoxic concentrations of available Al, but the two tests do not fully agree on some soils. The results of the two tests are traditionally given in different units. Here we report them both in equivalents per mass soil (cmol/kg) to enable more direct comparison between the two extraction results. Table A.4 in the Supporting Information also includes the mean concentrations for AlCaCl_2 in mg/kg . The mean Al concentrations measured in the standard 0.02 CaCl_2 extracts exceeded the toxic threshold of 2-5 mg/kg ($0.022 - 0.06 \text{ cmol}/\text{kg}$) (Edmeades et al., 1983; Moir et al., 2016) for sensitive legume species in the Allophanic ($0.048 \pm 0.0056 \text{ cmol}/\text{kg}$, $n=6$), Brown ($0.138 \pm 0.0233 \text{ cmol}/\text{kg}$, $n=8$) and Pumice soils ($0.090 \pm 0.0088 \text{ cmol}/\text{kg}$, $n=6$), while the Pallic soils ($0.030 \pm 0.0097 \text{ cmol}/\text{kg}$, $n=6$) fell below this (mean data not shown; Figure 1 shows individual soils and is grouped by soil order). On the other hand, the Al extracted by the standard 1 M KCl test was generally around ten times greater than using the 0.02 M CaCl_2 test but only the Allophanic and Brown soils exceeded the test toxicity threshold for sensitive legume species of $1.2 \pm 0.13 \text{ cmol}/\text{kg}$ ($n=6$), and $1.6 \pm 0.27 \text{ cmol}/\text{kg}$ ($n=8$) respectively (Edmeades et al., 1983; Moir et al., 2016), and concentrations for the Pumice ($0.6 \text{ cmol}/\text{kg}$) and Pallic ($0.4 \text{ cmol}/\text{kg}$) soils were below this threshold (mean data not shown; Figure 1 groups shows individual soils and is grouped by soil order). The latter findings are broadly consistent with those of Whitley et al. (2019), whose study of New Zealand soils found that Brown soils had the highest mean Al_{KCl} and are therefore likely more susceptible to Al toxicity.

The multivariate model for the CaCl_2 extractable Al (Equation 1.) predicted 83% (R^2_{adj}) of the variation in the soils ($P < 0.0001$; Root Mean Squared Error, RMSE: $0.151 \text{ cmol}_e/\text{kg}$; other statistical information for the model coefficients is given in Table A.5).

$$\log_{10} \text{Al}_{\text{CaCl}_2} = -0.412 + 0.042 \text{ CEC} - 0.029 \text{ BS} - 3.5 \times 10^{-5} \text{ Al} + 2.4 \times 10^{-5} \text{ Fe} \text{ (Eq. 1)}$$

Where, *CEC*, *BS*, *Al* and *Fe* are the cation exchange capacity, percentage base saturation, and total extractable Al and Fe concentrations, respectively. High cation exchange capacity contributed to high extractable concentrations of $\text{Al}_{\text{CaCl}_2}$ in the soil, whereas the opposite trend was seen for base saturation. The effect of *BS* supports the earlier suggestion regarding the sensitivity of Brown soils to changing extractant concentrations and, along with *CEC*, further highlights the role of cation binding sites to regulating the amount of Al extracted using this test. The residual in the model was one of the DF soil samples, which appeared to behave differently to the other soils. With the DF soil removed the R^2_{adj} for the model would be 93%, however, it is not clear from the parameters that we measured why this soil does not appear to fit the model. Adding in soil order as a categorical variable improved the model prediction to 97% (R^2_{adj} , not shown), which suggests that a variety of general factors, such as mineralogy and texture that were not directly measured here, but may further influence the amount of exchangeable Al. The absence of *pH* from being a significant variable in this model was surprising, however, this is most probably due to the fairly narrow pH range (0.8 units) across the acidic soils considered.

Zołotajkin et al. (2011) found that for two forest soils at the same pH and similar CEC, the site with the higher OM and exchangeable Ca content had reduced exchangeable Al concentrations (0.1 M BaCl_2). They concluded that the reduction in Al could be related to the sorption characteristics of the organic matter. However, the comparability of that

study to this work is limited by the different concentration of the extractant and the higher OM contents, acidity and Al concentrations in their soils.

Lee (1988); Marques et al. (2002); Percival et al. (1996) have suggested that the relatively high concentration of the KCl extractant is aggressive in removing Al from the exchange sites into soil solution and may overcome more subtle factors controlling Al solubility and sample non-plant available Al from interlayer minerals. Our results partly support this assertion: the mean Al concentration extracted by the 1 M KCl were ~13 times higher ($P < 0.001$) than what was extracted by the 0.02 M CaCl₂ across the thirteen soils (Table 3). This difference is within previously reported ranges (Bertsch and Bloom, 1996; Close and Powell, 1989; Manoharan, 1997; Venter, 2017b). Venter (2017a) and Venter (2017b) analysed 200+ topsoil samples from across NZ and found a 20-25 fold difference between two extracts, and in a smaller subset of soils that the differences ranged between 16 to 21 fold between depths of 15 - 60 cm. Conversely, Manoharan et al. (1993) measured 13 times more Al in the 1 M KCl extract compared to the 0.02 M CaCl₂ in one Pacific top soil. The difference between the two extracts is likely to be driven mainly by the higher concentration of the competing cation (K⁺) in the 1 M KCl extract, which displaces more Al³⁺ from soil exchange sites (Close and Powell, 1989; Venter, 2016), despite its lower charge density.

The multivariate model for the KCl extractable Al (Equation 2.) predicts 71% (R^2_{adj}) of the variation in the soils ($P < 0.001$; RMSE: 0.199 cmol_c/kg; Table A.6).

$$\log_{10} Al_{KCl} = 3.304 - 0.01966 BS - 0.508 pH \quad (\text{Eq. 2})$$

The Al_{KCl} test appears to be more sensitive to soil acidity whereas, BS has the opposite relation to what was seen in the Al_{CaCl_2} regression model. The effect of BS and pH was similar to findings by Whitley et al. (2019), who reported that BS and pH strongly

($P < 0.001$) influenced the Al_{KCl} measured for soil samples ($n=1027$) in the top 20 cm of the soil profile from different New Zealand soil orders. In their study other variables were also significant in the top 20 cm including CEC and total N. This was different to our finding and may be a result of different soil orders included in their study (a larger number of soil orders and a larger number of samples). Including soil order as a categorical variable to the KCl model improved the model prediction (R^2_{adj} : 95% ; not shown), again highlighting the relative importance of other factors which we have not considered. The LP soil appeared to behave differently to the other soils, with residuals much lower than the other soils. This is a Pallic soil and has low CEC coupled with a high BS, which could have contributed to the lower amount of Al_{KCl} extracted from this soil. Rayment and Lyons (2011b) showed that the reliability of the Al test varies with Al concentration, particularly at concentrations < 0.5 cmol_c/kg due to analytical detection limits. This is supported by our results: the variability between analytical replicates in the standard extractions was generally higher in the soils with less Al (Figure 1 and A.2). It follows that, while the extractable Al measured in the Pallic soil is subject to some uncertainty, this is unlikely to be important for the productivity of most agriculturally significant pasture species.

3.2 $CaCl_2$ extractions

The concentration of $CaCl_2$ in the extract was a significant determinant in the amount of Al extracted from the Allophanic, Brown, Pumice soils ($P < 0.001$) and Pallic soils ($P < 0.05$), whereby increasing amounts of Al was extracted by more concentrated extractants (Table 4). The average amount of Al extracted by 0.05 M $CaCl_2$ from the Brown soils was up to three times higher than by the 0.01 M extractant, while the (lowest) difference between the two extractants was two-fold in the Pallic soils. Hoyt

and Webber (1974) found that for 33 Canadian soils, the amount of Al extracted by 0.01 M CaCl₂ was half that of the 0.02 M CaCl₂, and that the amount of Al extracted at each concentration of CaCl₂ in the extract was similar regardless of extraction time (5 minutes and 60 minutes). We propose that these effects are most likely driven by the increasing concentration of Ca²⁺ in the extracting solution and increased competition for soil cation exchange sites. While the Brown and Pallic soils have relatively low cation exchange capacities (averages of 14.6 and 14.0 cmol_c/kg, respectively) when compared to the other soils, the extent of base saturation is generally much higher in the Pallic soils (51 % on average vs 28 % in the Brown soils). We suggest that this reflects the lower amounts of Al that can be exchanged by the Ca²⁺ in the Pallic soils, while in the Brown soils the proportion of Al on exchange sites is higher and, hence, the effect of increasing Ca²⁺ concentration is greater.

Hoyt and Nyborg (1972) found that when adjusting the extraction time between 0 and 128 hours for the 0.01 M CaCl₂ extraction, the first few hours had the greatest effect on the Al concentration extracted. Subsequently, the amounts of Al extracted did not increase after 16 hours. The amount of Al extracted from the Brown, Pallic and Pumice soils by the CaCl₂ extracts was not affected by the relatively short extraction times in this work ($P > 0.05$). However, the Al_{CaCl₂} concentration decreased ($P < 0.01$) in the Allophanic soils between the 20 minute and 60 minute extraction times (Table 4). This may be due to loss of Al from the extractant through re-adsorption by cation exchange sites that bind the metal more strongly (e.g. organic matter and hydrous oxides) (Hlavay and Polyák, 2004). It is also possible that Al was lost from solution through precipitation following the slower dissolution/desorption of other constituents in these soils. Allophanic soils are well known for their ability to store P (Parfitt, 1990) and slow release of phosphate from

these high P soils may have resulted in the loss of Al from the extract solution through precipitation of highly insoluble variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) at the low pHs (Haynes, 1982). In some studies, P additions have been reported to reduce soil extractable Al concentrations without the presence of lime. Iqbal (2014) found that after 13 days in an acidic ($\text{pH}_{\text{CaCl}_2}$ 4.5) Podosol soil (Isbell, 2016), the soil extractable Al concentration declined with P applied (monopotassium phosphate; KH_2PO_4 , four levels 0, 20, 40 and 80 mg P/kg soil), particularly in the highest Al treatment (150 mg AlCl_3 / kg). A P rate of 80 mg P/kg soil (highest rate applied) was most effective at reducing soil extractable Al concentrations, suggesting a detoxification effect through the formation of insoluble Al-phosphate in the soil and the release of protons (H^+) in the process (consistent with the measured decrease in soil pH with P applied). Manoharan et al. (1996) also found a decrease in toxic Al species (Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$) in soil solution on a Pallic soil with applications of North Carolina phosphate rock (NCPR) and Single Superphosphate (SSP). In contrast, a significant decline in the 0.02 M CaCl_2 Al concentration was only found with the addition of NCPR. The authors attributed this to the formation of non-toxic Al-F complexes formed from the Fluorine derived from the fertilisers. While this suggests that the results of the standard $\text{Al}_{\text{CaCl}_2}$ test on Allophanic soils may not be comparable to other soil orders, the specific soil characteristics behind this difference remain unclear and should be explored in further work. If slow phosphorus release does have a significant influence on the amount of Al extracted using this test, then this could have important implications for predictions of Al toxicity on acid soils that have been subject to P fertilizer inputs. Further analysis of interactions of extraction time and extractant concentration on the Al extracted from the Allophanic, Brown, Pallic and Pumice soils did not find significant differences ($P > 0.05$) (Table 4).

3.3 KCl extractions

The concentration of KCl in the extract was a significant determinant in the amount of Al extracted from the Allophanic ($P < 0.001$), Brown ($P < 0.01$), Pallic ($P < 0.01$) and Pumice ($P < 0.001$) soils (Table 5). The average amount of Al extracted by 2 M KCl from the Allophanic soils was over two and a half times higher than by the 0.2 M extractant, while the (lowest) difference between the two extractants was two-fold in the Pumice soils. The Al_{KCl} concentration generally increased with an increase in the concentration of salt in the extractant and peaked at the standard test concentration (1 M KCl) which can be again attributed to the increasing competition by the K^+ cation for the soil exchange sites. A further increase in the KCl concentration in the extractant resulted in no increase ($P > 0.05$) in the Al_{KCl} extracted on Allophanic, Brown and Pumice soils, which indicates that a 1 M KCl extract has removed all exchangeable Al that can be achieved with this particular salt. In contrast, on the Pallic soils the concentration of KCl only had a significant effect when the extractable Al concentration decreased by 67% between 1 M and 2 M KCl. McElreath et al. (1992) measured a significant increase in extractable Al in two acidic Oklahoma (US) soils when KCl concentration was increased from 0.125 M to 1 M. Subsequently, Kachurina et al. (2000) found that the Al extracted by 2 M KCl was only half of that in the 1 M KCl extract in 35 soils also from Oklahoma. Both studies suggested reasons for these differences, and the absence of detailed soil data in those reports precludes further analysis of their results.

Extraction time was only important for determining Al_{KCl} concentrations in the Pallic soils (Table 5). The findings reported here generally contradict the results of Naidu (1985) and Close and Powell (1989). The former study showed that the effect of

extraction time on the Al_{KCl} concentration measured for six acidic soils from Fiji was significant between the shortest and longest extraction times of 5 seconds and 16 hrs for all but the soils with the lowest Al soil (0.3 mmol/kg), while the latter found differences between 5 minute and 16 hour extraction times between different NZ soils tested. The big difference between the longer extraction times in their study and ours is probably an important factor in explaining this discrepancy. The earlier cited study by McElreath et al. (1992) found that a range of KCl extraction times between 5 and 40 minutes did not affect the concentration of extracted Al, except in one soil where they found the lowest extracted Al concentrations at 40 minutes extraction time. They attributed this to a possible secondary reaction with clay minerals, which may also explain the result seen here in the Pallic soils.

The lack of sensitivity to extractant concentration or extraction times in the Pallic soils may be again due to the relatively low amount of exchangeable Al and high base saturation, as seen previously with the Al_{CaCl_2} results. Ultimately the differences in the concentrations were small (Figure 2) and unlikely to be meaningful biologically for plants growing in these types of soils, due to the range at which Al is toxic. However, for individual soils the differences were larger (0.3 and 0.5 cmol/kg for the SG and DF soils respectively; Figure A.3b) and have the potential to have significant impacts on the plants at those sites. While soils are variable within orders, this work could provide a general guideline for interpreting the soil tests.

3.4 Implications for testing soil Al bioavailability in New Zealand

Given that there was no difference between the Al_{CaCl_2} extracted by the standard test combination and all other concentrations of salt in the extractants and extraction time combinations for all soil orders, this implies that these soil chemical properties are

influencing the Al measured using this extraction method. This suggests that acidic soils in New Zealand with a high CEC, low BS may be at a greater risk of Al toxicity to plants; the lesser effect of total extractable Al and Fe should be explored more in further research. The standard test combination measured Al_{CaCl_2} at concentrations that exceeded the toxicity threshold for sensitive legumes on the Allophanic, Brown and Pumice soils, while the Pallic soils overall were below this threshold.

The standard test combination measured Al_{KCl} at concentrations that exceeded the toxicity threshold for sensitive legumes on the Allophanic and Brown, while the Pumice and Pallic soils overall were below this threshold. More generally, the Al_{KCl} results support the results from the Al_{CaCl_2} extraction and indicate that plants grown on acidic soils with low BS may be more likely to experience deleterious dissolved Al concentrations; however, this should be tested systematically with plant growth trials to provide more robust evidence in support of this theory.

While soils are variable within orders, this work can provide a general guideline for interpreting these two Al soil tests (Figures A.3a and b). For the standard Al_{CaCl_2} extraction, the overall mean Al soil order concentration overestimated the amount of Al on one of the Allophanic soils (NB soil), while the concentrations were underestimated on one of the Pallic soils (DF soils; Figure 1; Figure A.2). In contrast, for the standard Al_{KCl} extraction, the overall mean Al soil order concentration overestimated the amount of Al for one of the Allophanic soils and one of the Brown soils, WH and MG soils respectively (Figure 1; Figure A.2). The two tests did not agree on whether the extractable Al indicated potentially harmful effects on plants for certain soils.

Generally, the threshold value for the 0.02 M extraction was exceeded in the Pumice soils,

while the Al_{KCl} concentrations fell below their respective threshold. On an individual soil level, there were many soils in which the tests disagreed in terms of Al concentrations that could be toxic to plants between the two standard tests. For the WH, DF, ER, PK and AR soils the $CaCl_2$ test indicates potentially harmful levels of extractable Al, while the KCl extraction does not (Figure 1). In contrast for the NB soil the Al_{KCl} concentrations exceeded the threshold for that test, while the Al extracted by $CaCl_2$ was below its threshold. It is also important to consider that the concentration at which dissolved Al in soils begins to have harmful effects on a given plant may be affected by other soil-specific factors (e.g. soil moisture) that cannot be directly represented by a laboratory extraction and that one single threshold value for all soils is unlikely to be equally representative of 'toxicity' in every soil. We believe that fully cost-effective proactive management of Al toxicity requires soil type-specific thresholds where the concentrations extracted from the different soils are related to plant growth. This is the next step for this research.

4. Conclusions

This laboratory investigation has identified that changes in the concentration of extractant and extraction time of the $CaCl_2$ and KCl extraction methods affected the soil Al concentrations in the extracts. The effect of the concentration of the salt in the extract and extraction time on the Al concentrations extracted, differed among the four soil orders tested in this experiment. Results indicated that soil order specific chemical properties are influencing soil Al extraction in the laboratory. This is an important finding, as it shows that for farmers who have acidic soils in New Zealand, that the CEC, BS, total Al and total Fe are influencing the Al_{CaCl_2} extracted from the sample that they send away to the laboratory and whether the concentrations are high enough to be

toxic to plants.

For the Al_{KCl} extraction, soils with a low BS and high CEC are most likely to have higher Al_{KCl} extracted from acidic soils. There was no difference in Al_{KCl} extracted by the standard test combination and all other concentrations of salt in the extractant and extraction time for the Allophanic, Brown and Pumice soils, however, for the Pallic soils, differences were measured. The reason for the differing results among soil orders for this extraction remains unclear.

Differences in soil response and the Al concentration measured were found even with small changes in the concentration of the salt in the extract and extraction time for the two extraction methods, which implies that the effects of the extraction conditions (concentration of salt in the extract and extraction time) affect the soils differently and may not measure the Al at equilibrium for all soils. Moreover, some soils such as Allophanic soils, may have properties which influence the amount of Al extracted, such as P retention. If slow phosphorus release does have a significant influence on the amount of Al extracted using this test, then this could have important implications for predictions of Al toxicity on acid soils that have been subject to P fertilizer inputs. This means that when measuring the Al bioavailability in soils, extreme care must be taken when interpreting soil Al test results. This is an area that requires more research.

While soils were variable within soil orders, this work could provide a general guideline for interpreting the two Al soil tests on these soil orders. However, additional studies are required with a larger number of soils for each New Zealand soil order. It is critical that the next study assesses the relationship between these different test combinations using plant growth as a bio-indicator for a range of New Zealand soils.

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Table 1. The designated soil code, location of the property the soils were collected from, soil order, pH and Al_{CaCl_2} concentrations of soils used in this laboratory investigation.

Soil code	Site of soil collection	Soil order NZSC	Soil order USDA
WT	Waitomo, Waikato	Allophanic	Andisol
ER	Reporoa, Waikato	Pumice	Andisol
AR	Aratiatia Station, Taupo	Pumice	Andisol
PK	Panekiri Station, Gisborne	Pumice	Andisol
NB	Te Kuiti, Waikato	Allophanic	Andisol
SG	Palmerston North, Manawatu	Pallic	Inceptisol
DF	Palmerston North, Manawatu	Pallic	Inceptisol
WH	Whanganui, Manawatu-Whanganui	Allophanic	Andisol
MO	Molesworth Station, Marlborough.	Brown	Inceptisol
GM	Glenmore Station, Tekaipo	Brown	Inceptisol
LP	Lindis Peak Station, Tarras	Pallic	Inceptisol
GF	Glenroyle Station, Hawea	Brown	Inceptisol
MG	Mount Grand Station, Hawea	Brown	Inceptisol

Note: ^aSites are listed by their geographic location from north to south. The soil order in United States Department of Agriculture classification (USDA) defined in Schoeneberger et al. (2012). The soil order in the and New Zealand Soil Classification (NZSC) defined in Hewitt (2010).

Table 2. Soil chemical characteristics of 13 New Zealand soils used in this experiment. The soil codes are given in Table 1.

Soil Analysis	Soil code												
	WT	ER	AR	PK	NB	SG	DF	WH	MO	GM	LP	GF	MG
pH(1:2.5 soil:H ₂ O)	5.2	5.2	5.2	5.1	4.9	5.7	5.4	5.5	5.2	5.0	5.6	5.3	5.2
*AlCaCl ₂ (mg/kg)	5.0	2.4	4.8	7.4	10.0	1.3	4.7	6.1	13.1	6.6	0.9	7.1	2.6
Olsen P (µg/mL)	7	114	37	16	32	4	22	6	13	18	13	12	12
P retention (%)	99	39	46	57	74	24	18	95	59	42	21	38	25
Sulphate sulphur (µg/g)	17	98	6	7	29	<4	11	34	9	15	11	5	5
Ext.org sulphur (µg/g)	20	7	8	7	14	5	11	14	11	10	5	5	6
Organic matter (% w/w)	22.2	15.3	8.5	11.5	16.4	6.1	9.7	16.8	8.5	10.6	4.7	7.1	6.2
Total P (mg P/kg)	1982	1916	1069	1014	2070	378	515	1046	1130	1469	761	985	914
Total N (% w/w)	1.02	0.67	0.43	0.57	0.55	0.30	0.39	0.84	0.38	0.53	0.24	0.31	0.31
Total C (% w/w)	12.89	8.9	4.93	6.70	9.50	3.30	5.60	9.7	4.91	6.18	2.74	4.14	3.60
Carbon/Nitrogen	12.6	13.3	11.5	11.8	10	11	14	11.5	12.9	11.7	11.4	13.4	11.6
CEC (cmol _c /kg)	21	32	11	15	35	12	17	23	14	17	13	13	15
Ca (QTU)	3	13	5	4	9	3	5	3	<1	5	8	3	5
Mg (QTU)	16	21	13	8	29	27	45	14	7	14	20	11	21
K (QTU)	6	16	10	6	19	10	10	8	7	7	7	7	9
Na (QTU)	6	2	8	6	8	7	22	5	1	2	5	4	2
Base saturation (%)	26.9	61.0	37.4	35.9	38.0	52.0	47.0	21	12.9	34.1	53.6	24.6	42.0

Note: Soil codes are listed by their geographic location from north to south. * 0.02 M CaCl₂ extractable. QTU stands for quick test unit, indicating plant available Ca, Mg, K and Na.

Table 3. Mean Al concentrations (cmol_c/kg) [†] extracted by 0.02 M CaCl₂ and 1 M KCl across all soils.

		Mean extractable Al (cmol _c /kg)
extractants		
	CaCl ₂	0.06 _b
	KCl	0.78 _a
	SEM (upper/lower)	(0.26,0.19)
	Grand mean	0.2
P value	extractant	***

[†]Data are back-transformed. *** Significant at $P < 0.001$ level, ** significant at $P < 0.01$ level, * significant at $P < 0.05$ level, ns- no significant difference.

Table 4. Mean Al_{CaCl_2} concentrations (cmolc/kg)[†] extracted by $CaCl_2$ for individual soil orders, Allophanic, Brown, Pallic and Pumice soils with increasing extractant concentration and extraction time.

	Soil Order	Mean Al_{CaCl_2} (cmolc/kg)			
		Allophanic	Brown	Pallic	Pumice
	Grand mean	0.05	0.12	0.03	0.09
Concentration (M) (mean of the three extraction times, $n = 6$)	0.01	0.03 _c	0.07 _c	0.02 _b	0.06 _c
	0.02	0.04 _b	0.12 _b	0.03 _{ab}	0.09 _b
	0.05	0.11 _a	0.20 _a	0.04 _a	0.13 _a
	SEM (upper/lower)	(0.053, 0.047)	(0.125, 0.110)	(0.031, 0.020)	(0.093, 0.081)
	<i>P</i> value concentration	***	***	*	***
Extraction time (min) (mean of the three extract concentrations, $n = 6$)	20	0.06 _a	0.12	0.03	0.09
	60	0.05 _b	0.11	0.02	0.09
	180	0.04 _c	0.11	0.02	0.08
	SEM [@] (upper/lower)	(0.053, 0.047)	(0.125, 0.110)	(0.031, 0.020)	(0.093, 0.081)
	<i>P</i> value extraction time	*	ns	ns	ns
	<i>P</i> value concentration x extraction time	ns	ns	ns	ns

Note: [†]Data are back-transformed. *** Significant at $P < 0.001$ level, ** significant at $P < 0.01$ level, * significant at $P < 0.05$ level, ns- no significant difference. Numbers with letter subscripts in common are not different ($\alpha = 0.05$) based on the Fisher's protected LSD. The upper and lower SEM are reported for each soil in relation to the grand mean and back-transformed. [@] The SEM (upper and lower) are the same for extract concentration and extraction time.

Table 5. Mean Al_{KCl} concentrations (cmol/kg) [†] extracted by KCl for individual soil orders, Allophanic, Brown, Pallic and Pumice soils with increasing extractant concentration and extraction time.

Soil Order	Mean Al_{KCl} (cmol/kg)			
	Allophanic	Brown	Pallic	Pumice
Grand mean	0.8	1.3	0.2	0.4
Concentration (M) (mean of the three extraction times, $n = 6$)				
0.2	0.4 _c	0.8 _b	0.2 _{ab}	0.3 _b
0.5	0.7 _b	1.0 _{ab}	0.3 _a	0.3 _b
1.0	1.1 _a	1.6 _a	0.3 _a	0.5 _a
2.0	1.1 _a	1.6 _a	0.1 _b	0.6 _a
SEM (upper/lower)	(0.85, 0.74)	(1.48, 1.07)	(0.25, 0.16)	(0.44, 0.36)
<i>P</i> value concentration	***	**	*	***
Extraction time (min) (mean of the four extract concentrations, $n = 8$)				
5	0.8	1.0	0.1 _b	0.4
30	0.8	1.3	0.3 _a	0.4
60	0.8	1.3	0.3 _a	0.4
SEM [@] (upper/lower)	(0.83, 0.76)	(1.45, 1.10)	(0.25, 0.16)	(0.44, 0.36)
<i>P</i> value extraction time	ns	ns	***	ns
<i>P</i> value concentration x extraction time	ns	ns	***	ns

Note: [†]Data are back-transformed. *** Significant at $P < 0.001$ level, ** significant at $P < 0.01$ level, * significant at $P < 0.05$ level, ns- no significant difference. Numbers with letter subscripts in common are not different ($\alpha = 0.05$) based on the Fisher's protected LSD. The upper and lower SEM are reported for each soil in relation to the grand mean and back-transformed. [@]The SEM (upper and lower) are similar for extract concentration and extraction time.

Figure Captions (Figures were uploaded as separate files).

Figure 1. Mean (a) Al_{CaCl_2} (cmol_c/kg) and (b) Al_{KCl} concentrations (cmol_c/kg) for the standard tests presented for each of the 13 soils and grouped by soil order. Values are means \pm 1 SEM ($n=2$). The scale on the $CaCl_2$ y-axis is 10x less than on the KCl. Soil acronyms are described in Table 1. The threshold for Al toxicity for sensitive legume species for the 0.02 M $CaCl_2$ test at 0.033 cmol_c/kg and 1 M KCl at 1.0 cmol_c/kg (Edmeades et al., 1983; Moir et al., 2016).

Figure 2. Back-transformed mean Al_{KCl} concentrations (cmol_c/kg) across four extractant concentrations (M) of KCl in the extractant of 0.2 (●), 0.5 (▽), 1 (■) or 2 M (◇) and three extraction times of 5, 30 or 60 minutes on the Pallic soils. Values are means \pm 1 SEM (*upper and lower bounds*), calculated from grand mean are for the interaction of concentration (M) and extraction time. Soil acronyms are described in Table 1.

Highlights

- On average, the Al extracted by KCl was 13 times higher than extracted by CaCl₂ across the soils considered
- The effect of changing extract salt concentration and extraction time on Al extracted differed among four soil orders
- Findings suggest that the Al concentrations measured by the two extraction methods are affected by specific soil properties
- When measuring the Al bioavailability in soils, extreme care must be taken when interpreting soil Al test results

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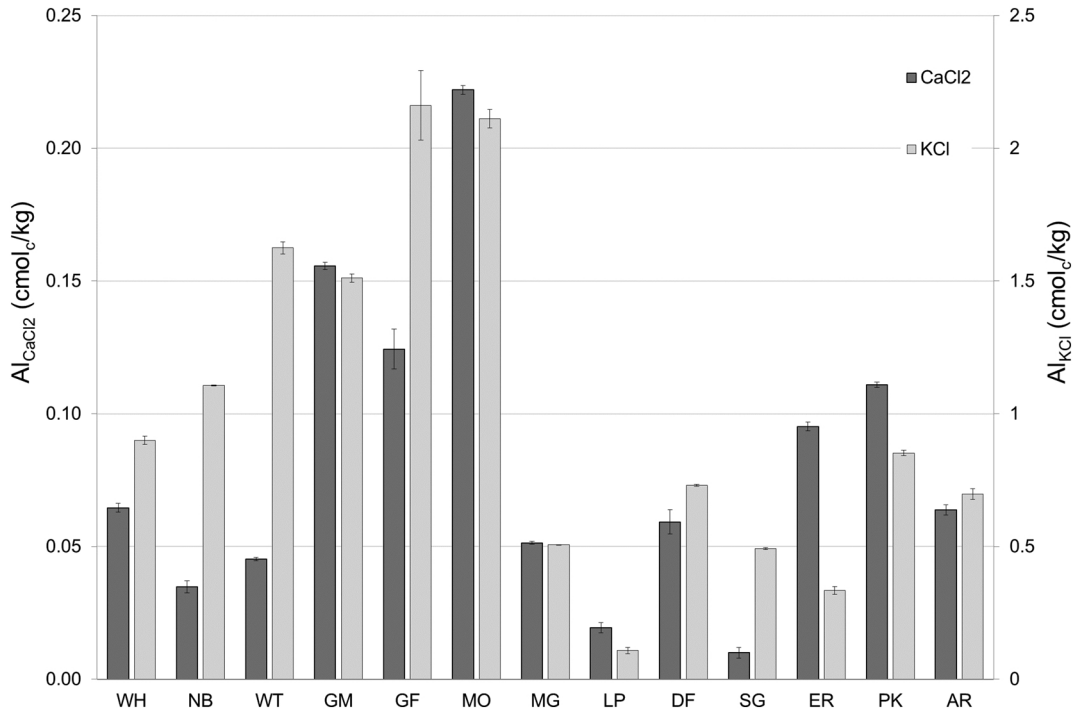


Figure 1

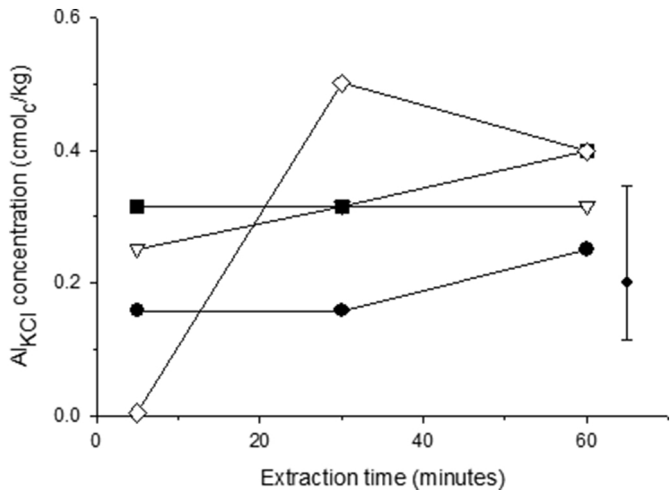


Figure 2