A field survey of soil pH and extractable aluminium in the Ashburton Lakes Catchment, Canterbury, New Zealand

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Abstract

Soil extractable aluminium (Al) concentrations have a strong impact on the establishment, growth and persistence of pasture legumes. A survey of 21 soil profiles in the Ashburton Lakes catchment was conducted to determine the key factors driving extractable Al concentrations. The mean Al (0.02 M $CaCl_2$) concentration was 7.8 mg/kg with the highest values in the top 50 cm of the soil profile. However, there was considerable variation among sites. Landform age, rainfall and depth were all important variables for extractable Al (but R^2 was low), while landform type was not. The highest Al concentrations in the 20 cm depth zone were found at the wettest sites in the catchment where rainfall was $\geq$ 1266 mm and where pH was lowest. Farmers in this catchment could use this knowledge to determine which areas of their farms are most susceptible to elevated Al concentrations and at what depth. This would assist in determining which areas could be targeted for development and which are unsuitable.

Keywords: acidic soils, toxicity, soil profile depth, rainfall, landform type, geologic age, elevation, aspect, slope

Introduction

In the New Zealand high and hill-country soil acidity and low fertility (N, P and S) limit the growth and establishment of legumes (Haynes & Williams 1993), which provide N to the system and are a high quality feed for grazing stock. Soil extractable aluminium (Al) concentrations play an important role in the viability of pasture and forage legumes in these environments.

The few studies conducted in New Zealand examining the drivers of soil pH and Al variability focused on differences in chemistry of soils on landforms of different age and type. These studies were conducted along rainfall (climosequence) or age gradients (chronosequence). Webb *et al*. (1986) found that weathering and soil development increased with an increase in rainfall (640 to 2000 mm/year) at four sites in the McKenzie basin. Soil pH declined with an increase in rainfall as a result of the leaching of bases, and Al (1 M KCl extracted Al) concentration increased between the lowest and highest rainfall sites. Harrison *et al*. (1990) examined chronosequences of soils in the Puffer stream terrace sequence (830 mm/year) and on moraines on the Craigieburn Range (1447 mm/year) in the Waimakariri basin. Both increasing rainfall and age increased soil Al (1 M KCl extracted Al) concentrations. Dixon *et al*. (2016) examined the climate driven thresholds for chemical weathering at 28 profile sites close to the sites sampled by Webb *et al*. (1986) along the McKenzie Basin climate gradient, with mean annual rainfall ranging from 400 to 4700 mm/year. Dixon *et al*. (2016) did not report extractable Al (1 M KCl or 0.02 M $CaCl_2$), but noted threshold behaviour related to mean annual rainfall with trivalent metallic ions and other variables.

These studies all indicate potential variability of soil extractable Al related to landscape and environmental attributes yet there has been no systematic study of extractable Al variability at this scale. Moreover, to mitigate Al toxicity an understanding is needed as to which soils are most susceptible and what factors are involved other than soil pH. Therefore, the objective of this work was to determine the key factors driving variation in soil extractable Al concentrations among different landforms of similar parent material, in a landform context.

Materials and methods

Catchment description

The Ashburton Lakes catchment is located on the eastern side of New Zealand's Southern Alps, inland from Mt Somers. The catchment encompasses two inter-montane basins, Lake Heron and Lake Clearwater, and is flanked by high mountain ranges. The valley floor ranges in elevation from 500-800 m a.s.l. The study area was selected based on several criteria: i) the catchment contains valley-floor landforms commonly farmed in the high-country, ii) there is a distinct rainfall gradient and iii) the age of the land surfaces have been well defined in previous work in this area (Barrell *et al*. 2011). Landforms were classified according to their mode of origin (e.g. glacial or alluvial) and age. Soil parent materials comprised solely greywacke-derived regoliths including alluvium, till and loess. Catchment sampling was mainly from Acidic Orthic Brown soils plus two classified as Typic Orthic Brown soils (Hewitt

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2010). Landform was considered to be a proxy for subtle differences in soil characteristics engendered by differences in age, topography and soil parent material texture, not captured by soil taxa.

Site selection

Twenty one sites were selected by stratifying the landscape according to geomorphological maps, digital elevation models (DEM) and maps of climate variables (NIWA Core funded project Climate Present and Past CAOA1501). There was replication at sample sites within a landform (five replicates). Sites differed in median annual rainfall, landform age and type, elevation, aspect and land-use (Table 1).

Soil sampling collection methods

Field soil sampling was conducted between 2014 and 2016 at the 21 sites. Soil samples were taken from a single soil pit at each site; samples were taken as 5 cm contiguous vertical increments yielding about 200 g of soil each (to 65 cm or gravels).

Laboratory methods

Soil samples were analysed for pH(H_2O) (1:2.5 soil: water ratio) (Blakemore *et al*. 1987) and extractable Al, using the 0.02 M $CaCl_2$ extraction method, and quantified using inductively coupled plasma atomic emission spectroscopy (ICP-OES: Varian 720-ES ICP-OES; Varian Inc., Victoria, Australia) analysis.

Statistical analysis

Data were analysed using a series of general linear models in Genstat version 16.0, to determine if there was a significant difference in the soil pH and extractable Al across different rainfall zones, landform age and type. For the effect of depth, a linear mixed model was constructed, because unlike the other factors, profile depth differed within a single site. Site was used as a random variable to remove the effect of site similarities, so depth could be compared across sites. Extractable Al was log transformed for analysis to achieve normal distribution and satisfy model assumptions. The Akaike information co-efficient value (AIC) was used to

Table 1 Site information for the 21 sites sampled in the Ashburton Lakes catchment including site code, landform type, geologic age, median annual rainfall (MAR), median annual temperature (MAT), elevation and land-use.

Site code*	Landform	Geologic Age	MAR (mm/year)	MAT (°C)	Elevation (m a.s.l.)	Land-use
AF1	alluvial fan	Holocene (<11.7 kyr)	1512	8.7	745	DOC
MO8	alluvial fan	Holocene (<11.7 kyr)	1529	8.4	771	Farmland
AF3	alluvial fan	Holocene (<11.7 kyr)	1169	8.8	693	Farmland
AF4	alluvial fan	Holocene (<11.7 kyr)	1449	8.5	819	Farmland
AF5	alluvial fan	Holocene (<11.7 kyr)	1207	8.7	741	Farmland
OF2	outwash surface	Latest Late Otiran (19- 14.5 kyr)	1137	9.2	624	DOC
MO1	outwash surface	Latest Late Otiran (19- 14.5 kyr)	1180	8.8	702	Farmland
MO7	outwash surface	Late Otiran (45 -14.5 kyr)	1479	8.7	752	Farmland
OF3	outwash surface	Latest Late Otiran (19- 14.5 kyr)	1282	8.6	747	DOC
OF4	outwash surface	Latest Late Otiran (19- 14.5 kyr)	1403	7.9	860	DOC
OF5	outwash surface	Latest Late Otiran (19- 14.5 kyr)	1288	8.8	689	DOC
OF1	moraine	Late Otiran (45 -14.5 kyr)	1128	9.0	657	DOC
MO2	moraine	Late Otiran (45 -14.5 kyr)	1290	8.9	703	DOC
MO3	moraine	Early Otiran or Older (360 -45 kyr)	1332	8.8	749	DOC
MO4	moraine	Latest Late Otiran (19- 14.5 kyr)	1502	8.4	811	Farmland
MO5	moraine	Latest Late Otiran (19- 14.5 kyr)	1522	8.0	929	Farmland
MO6	moraine	Latest Late Otiran (19- 14.5 kyr)	1558	8.7	734	Farmland
MO9	moraine	Late Otiran (14.5 - 45 kyr)	1500	7.6	988	Farmland
MO10	moraine	Latest Late Otiran (19- 14.5 kyr)	1260	8.4	736	DOC
MO11	moraine	Latest Late Otiran (19- 14.5 kyr)	1273	8.8	678	DOC
MO12	moraine	Latest Late Otiran (19- 14.5 kyr)	1271	8.8	696	DOC

Note: The MAR and MAT were determined using NIWA annual 50th percentile climate data for each of the sites using GPS coordinates (National Institute of Water and Atmospheric Research, 2015). Aspect was derived from a DEM with 8 m resolution (LINZ, 2012). Elevation is measured in metres above sea level (m a.s.l). * For several site codes, the lettering does not correspond correctly to the landform the site was on. This was due to plotting the GPS co-ordinates of the site after sampling and the landform changing in some circumstances. In the Geologic age column the number in brackets refers to the estimated age (approximate 1000 years, kyr) of the land surface (Barrell *et al.*, 2011).

determine the fit and explanatory power of each model. A lower AIC implies a better fitting model and higher explanatory value (Akaike 1974; Sokal & Rohlf 2012). Single models and combination models of different factors were compared to determine if a single factor or a combination of factors was best for predicting pH and Al concentration. A two-sample (two-sided) t-Test was conducted on samples from the top 20 cm of the soil profile, and there was no difference in the mean log Al concentration between the two land uses (Department of Conservation (DOC) and farmed) and, as such, the effect was not considered in the linear model or decision tree analysis.

Decision trees (non-parametric test) were created in R (a software environment for statistical computing and graphics, Version 3.3.1). This technique was a tool to establish the relative importance of the predictor variables in explaining the response and the relationships between predictor (rainfall, age, landform, elevation, aspect and slope) and response variables (pH and extractable Al) in the 20 cm depth zone (top 20 cm of the soil profile and is most important for plant roots). The set of rules established in the decision tree were used to produce a catchment map using ArcPro software (version 2.0.1) of soil extractable Al for the 20 cm depth zone (Figure 2). Decision trees were also constructed for the other depth zones, but were not included in this paper (Whitley 2018). Results from deeper depth increments showed similar driving variables, but in different order of importance.

Results

Depth in the soil profile

The soil extractable Al (0.02 M $CaCl_2$) concentration ranged from 1.2-39.1 mg/kg (mean 7.8 mg/kg) and the soil pH 4.7-6.0. Depth was the strongest explanatory variable ($P<0.001$) for pH and Al concentration; however, there was considerable variation within a given depth increment among sites and the depth-function models had low R^2 values (Table 2; Figure 1).

Soils were more acidic in the top of the soil profile, with an expected value (mean) of 5.3 at 5 cm and 10 cm, increasing with depth to 5.4 at 50 cm and 5.6 at 80 cm (Figure 1a). Soil pH at any given depth varied by as much as 1.1 pH units and the variance declined with depth.

In the pooled data, the Al (0.02 M $CaCl_2$) concentration was higher in the top of the soil profile, with expected mean values of 8.4 mg/kg and 7.1 mg/kg at 5 cm and 10 cm, respectively, declining to 5.1 mg/kg at 50 cm and 3.6 mg/kg at 80 cm (Figure 1b). However, individual soil profiles varied from this pattern showing constant, increasing, decreasing or curved trends with depth. The Al (0.02 M $CaCl_2$) concentration at any given depth varied by as much as 36.5 mg/kg. Linear mixed models emphasised that the addition of other factors complicated the model (higher AIC) and did not improve the outcome from a single factor model (depth) for pH and extractable Al.

Landform age

There was a strong difference ($P<0.001$) in the soil pH and extractable Al (0.02 M $CaCl_2$) concentration measured across the different age surfaces (Table 2). The mean pH value for sites in both the Latest Late Otiran and the Early Otiran, or older, were the lowest at 5.3. These surfaces also had the highest mean extractable Al concentrations of 7.3 mg/kg and 8.6 mg/kg, respectively. There was no systematic trend of pH or extractable Al with increasing landform age (Table 2).

Landform type

There was a small difference ($P<0.001$) in the mean soil pH among the different landforms (Table 2). The mean pH was highest on alluvial fans at 5.5, and slightly lower at 5.4 on the outwash surfaces and moraines. There was no difference in mean extractable Al (0.02 M $CaCl_2$) concentration among landforms.

Rainfall

Soil pH showed a linear trend ($P<0.05$) of increasing with increasing rainfall, but the relationship had low explanatory power ($R^2=0.02$, Table 2). At any given rainfall pH varied by as much as 0.7 units. The Al (0.02 M $CaCl_2$) concentration showed a trend ($R^2 = 0.03$, $P<0.01$) of decreasing Al concentration with increasing rainfall (Table 2). At a given rainfall the Al concentration varied by as much as 30.4 mg/kg. The high variance in soil pH and extractable Al at a given rainfall implies there are other factors involved.

Patterns of pH and extractable Al in the Ashburton Lakes Catchment

Decision trees identified that rainfall was the most important factor for soil pH in the 20 cm depth zone, followed by elevation and aspect. There was a large area in the south of the catchment with rainfall <1174 mm/year, where soils had a mean pH of 5.6. The most acidic soils were identified as a band through the centre of the catchment from east to west, and an area surrounding Lake Heron, where rainfall was ≥1174 mm/year and are positioned on the valley floor (<699.1 m a.s.l).

Rainfall was the most important factor determining soil Al (0.02 M $CaCl_2$) concentration in the top 20 cm, followed by aspect (Figure 2). The higher concentrations in the catchment were found at rainfall ≥1266 mm/year and seem to mirror the areas that were identified as most acidic. The lowest Al concentrations, with a mean Al of 3.8 mg/kg are in areas with <1266 mm/year rainfall and south facing sites.

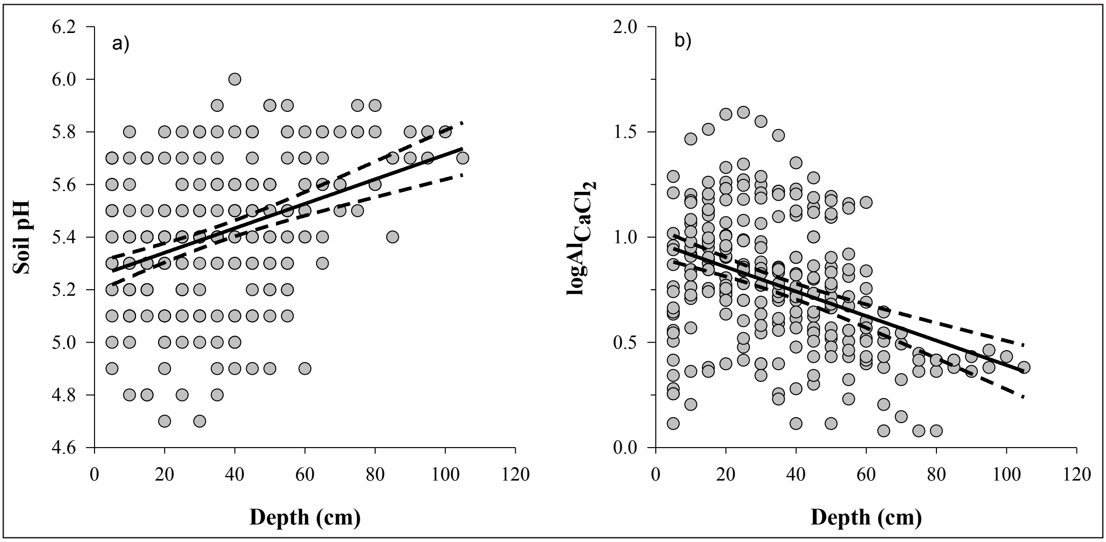


Figure 1 Soil pH a) and log soil Al (0.02 M $CaCl_2$) b) against soil depth for the 21 sites from the Ashburton Lakes catchment, Canterbury, New Zealand. Forms of the regressions (solid black lines) are: a) pH=5.25(±0.029) + 0.0047(±0.0007)x (R^2=0.15) and b) log soil Al=0.98(±0.036)-0.0058(±0.0009)x (R^2=0.15). Values reported in brackets are standard errors of the parameters. Dashed lines represent the 95% confidence intervals.

Table 2 Mean soil pH and extractable Al (0.02 M $CaCl_2$, mg/kg) across different landforms and aged surfaces in the Ashburton Lakes Catchment and the significance (P values) of landform, age of the surface, rainfall and depth for predicting soil pH and Al (0.02 M $CaCl_2$) from the 21 sites sampled in this catchment.

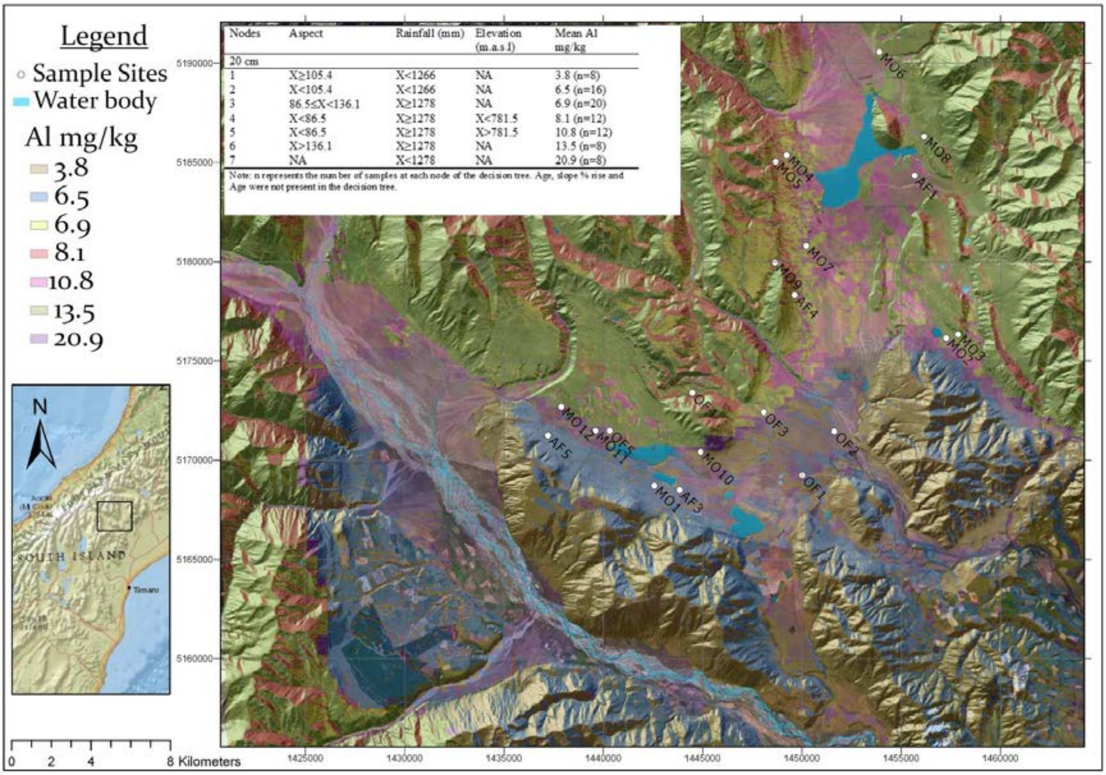
	Expected values (mean)				
Landform	**pH**	**SEM**	**LogAl**	**SEM**	**Al (mg/kg)**
alluvial fan	5.5	0.03	0.74	0.04	5.5
outwash surface	5.4	0.03	0.76	0.04	5.8
moraine	5.4	0.02	0.79	0.03	6.2
P value (Landform)	<0.001		0.612		
Age of surface	**pH**	**SEM**	**LogAl**	**SEM**	**Al (mg/kg)**
Holocene	5.5	0.03	0.74	0.04	5.5
Latest Late Otiran	5.3	0.02	0.86	0.03	7.3
Late Otiran	5.6	0.02	0.56	0.04	3.7
Early Otiran or older	5.3	0.04	0.94	0.05	8.6
P value (Age)	<0.001	-	<0.001	-	-
P value (Rainfall)	<0.05	-	<0.01	-	-
P value (depth)	<0.001	-	<0.001	-	-

Values in the table are from general linear models that determined the significance of landform type, age of the surface and rainfall for soil pH and Al concentrations in this catchment. All Al concentrations are 0.02 M $CaCl_2$ extractable. The Al is the back-transformed Al concentration from the log output. For depth, the P values are from a General Linear Mixed Model (with site as a random variable) that determined the significance of depth for soil pH and Al concentrations in this catchment.

Discussion

Depth was the strongest explanatory variable for pH and Al (0.02 M $CaCl_2$). In the pooled data set soil pH increased with depth in the soil profile and Al declined (Figures 1a and 1b). Harrison *et al.* (1990) reported similar trends - an increase in soil pH with depth in the soil profile for a sequence of terrace soils and a decline in extractable Al (1 M KCl extracted Al) for terrace and moraine soils, particularly below 40-50 cm. Eger & Hewitt (2008) also found that the soil pH increased with depth in the soil profile for eight hillslope sites in the Canterbury high-country. However, the pooled data set trend masks strong inter-profile variability in depth trends of Al (0.02 M $CaCl_2$). The factors determining the depth variability remain unknown.

Extractable Al (0.02 M $CaCl_2$) was measured at concentrations that would be toxic to legumes, ranging



Nodes	Aspect	Rainfall (mm)	Elevation (m.a.s.l)	Mean Al mg/kg
20 cm				
1	X≥105.4	X<1266	NA	3.8 (n=8)
2	X<105.4	X<1266	NA	6.5 (n=16)
3	86.5≤X<136.1	X≥1278	NA	6.9 (n=20)
4	X<86.5	X≥1278	X<781.5	8.1 (n=12)
5	X<86.5	X≥1278	X>781.5	10.8 (n=12)
6	X>136.1	X≥1278	NA	13.5 (n=8)
7	NA	X<1278	NA	20.9 (n=8)

Note: n represents the number of samples at each node of the decision tree. Age, slope % rise and Age were not present in the decision tree.

Figure 2 A map of mean extractable Al (0.02 M $CaCl_2$) concentration for 0-20 cm depth in the Ashburton Lakes catchment, constructed using rules from the decision tree analysis. The table contains a list of rules associated with each node of the decision tree for soil Al for the 20 cm depth zone. To view this map in colour visit the hyperlink to the online version.

from 1.2 mg/kg to 39.1 mg/kg (mean 7.8 mg/kg). Despite the overall trend of decreasing Al concentration with depth, even at a depth of 80 cm the mean Al concentration was 3.6 mg/kg and likely to be 'toxic' for lucerne and other sensitive legumes, as the threshold for toxicity is species specific (Moir *et al*. 2016). These results highlight that surface soil samples (< 20 cm) are inadequate for an assessment of potential Al toxicity and that soil sampling should go to a depth of 80 cm, if possible, to be able to advise the farmer on legume selection.

The general linear models, which used the whole data set, showed no strong landscape patterns of pH and extractable Al, perhaps because those patterns were overwhelmed by strong depth variability.

There were some differences in Al (0.02 M $CaCl_2$) and pH with landform age, but it didn't systematically change with the age of the surface. This was in contrast to a chronosequence study by Harrison *et al*. (1990) which showed consistent increases in extractable Al (1 M KCl extracted Al) concentration and decreases in pH for soils on progressively older landforms along two development sequences. Potential explanations for the contrasts is the lack of uniformity of other soil forming factors (e.g. slope, aspect) and erosion/depositional history that were more tightly controlled in the chronosequence study.

Differences in pH among landform types were found, in contrast to no difference in Al (0.02 M $CaCl_2$) concentrations, which was an unexpected finding (Table 2). The only landform-related distinction was a higher pH on alluvial fans, which is presumably related to the relative youth of these landforms compared to glacial-age moraines and outwash terraces.

Rainfall was an important factor for pH and Al (0.02 M $CaCl_2$) values in this catchment. However, the relationship was weak and showed the opposite trend to that in other New Zealand climosequence studies. Webb *et al*. (1986) and Harrison *et al*. (1990) reported declines in soil pH and increases in soil Al (1 M KCl extracted Al) concentration with increasing rainfall for a transect of moraines near Lake Pukaki (640-2000 mm/year) and two chronosequences under different rainfall on moraine and terrace soils near Craigieburn, Canterbury. Increased soil acidification and Al (1 M KCl extracted Al) was observed at the higher rainfall sites in these two studies, which was linked to more intense weathering, greater soil development, leaching and the reduction in bases on the cation exchange sites. Current results are attributed to a relatively narrow range of rainfall in the study area (ca 450 mm) and the rainfall being above the threshold (800 mm/year) at which a major shift in soil leaching and weathering occurs (Dixon *et al.* 2016). Thus, the relationship between MAR-pH and MAR-Al identified here may be simple correlation due to some indirect relationship, not causation.

Decision tree analysis used only the 20 cm depth zone data to remove any influence of strong depth variation of pH and extractable Al. Distinct areas with higher extractable Al concentrations were identified that seem to mirror the areas identified as most acidic in the catchment (Figure 2). Rainfall (≥1174 mm/year) at sites located at lower elevations in the catchment (<699 m a.s.l) and southerly aspects, had more acidic soils with more Al (0.02 M $CaCl_2$) in the 20 cm depth zone. Rainfall was important and trends were similar to those found in the studies discussed above (Figure 2). The influence of aspect on acidity and Al concentration is consistent with other findings (Eger & Hewitt 2008). Their study found stronger leaching, enhanced weathering and acidification on south-facing slopes and higher oxalate extractable Al concentrations. Their measure of Al was different to the Al (0.02 M $CaCl_2$) used in this study; however, the expectation is that the Al (0.02 M $CaCl_2$) is higher at the lower pH sites (south-facing) under greater weathering conditions, although this was not tested.

Decision tree analysis suggests, that when the overwhelming depth variability of extractable Al was isolated, then the variability of Al was spatially structured according to landscape and environmental attributes (rainfall, elevation, aspect). Although the characteristics of the spatial structure may be unique to the Ashburton Lakes area, or limited to a subset of the South Island high-country, this study provides support for continuing this line of research. Landscape models of extractable Al in a range of settings would provide a valuable decision support mechanism for farmers when determining which areas could be targeted for development and which are unsuitable, either by avoiding or mitigating soil Al concentrations.

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