Exchangeable cations in deep forest soils: separating climate and chemical controls on spatial
and vertical distribution and cycling

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Abstract

The vertical distribution of soil exchangeable cations (Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+}) results from the integration of multiple processes: weathering of primary minerals, atmospheric input, leaching, and biological cycling. While weathering and atmospheric input affect the location of cation inputs to the soil system, leaching and biological cycling translocate cations in opposing directions within the profile. Little research has been conducted on deep soil relative to surface soil, and thus attempts to verify hypotheses about the drivers of exchangeable cation vertical distributions have not been possible on a broad scale. This study excavated soils down to 2.5 or 3 m at 22 sites across the coastal Pacific Northwest ranging from northern Washington to southern Oregon. Samples were analyzed for soil carbon (C), nitrogen (N), and exchangeable cations. PERMANOVA was used to evaluate the effect of soil chemical (C, N, and pH), environmental (climate, parent material, elevation), physical (texture) and spatial (horizon, depth) gradients on the distribution of exchangeable cation contents and stocks. The majority of exchangeable cation stocks are located in deeper soil horizons. On average, 66% of Ca^{2+} , 76% of Mg^{2+} , 57% of K^{+} , and 63% of Na^{+} stocks were below 1.0 m. Master soil horizon was the most significant predictor of the distribution of cations within the soil profile with substantial separation between A horizon samples and B and C horizon samples. There was a significant interaction between horizon and soil C, with higher soil C concentrations and stocks corresponding with lower Ca^{2+} and Mg^{2+} contents and stocks in horizons of the same type. Between sites, climate and cumulative carbon stocks were the dominant controls over cation distribution, with high C stocks and wet, cool climate leading to low exchangeable Ca^{2+} and Mg^{2+} . These results suggest that leaching with dissolved organic matter could be a driver of exchangeable Ca^{2+} and Mg^{2+} distributions in the

1 Pacific Northwest. On the other hand, K^+ and Na^+ were largely uncorrelated with these
2 environmental gradients. Biological uptake is a more important control over the distribution of
3 exchangeable K^+ , while atmospheric deposition drives the relatively uniform distribution of Na^+
4 both between sites and within profiles.

5 Keywords: Exchangeable Cations, Deep Soil, Calcium, Potassium, Magnesium, Soil Carbon

1. Introduction

As the interface between biosphere, lithosphere, hydrosphere, and atmosphere, soil is subjected to intense vertical exchange and transformation of materials that results in steep chemical and physical gradients from surface to bedrock (Jobbagy and Jackson, 2001). Stratification of soil into distinct horizons is a direct result of these gradients (Hilgard, 1906; Jenny, 1941), as is the vertical distribution of nutrients, including exchangeable cations such as Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+} (Jobbagy and Jackson, 2001). Four major processes shape the vertical distribution of exchangeable cations in soil: weathering, atmospheric deposition, leaching, and biological cycling (Trudgill, 1988). Release of exchangeable cations from weathering of primary minerals is generally slow (Simonsson et al., 2015), and atmospheric deposition - with the exception of Na^{+} - is typically small in the Pacific Northwest (Johnson, 1992). By contrast, rates of biological cycling and leaching can be relatively rapid (Aber and Melillo, 1991; Johnson and Lindberg, 1992).

The vertical transport of cations in soil is affected by plant uptake and leaching in opposite directions. In isolation, plant uptake moves nutrients upwards because a large proportion of nutrients absorbed in roots are transported aboveground, where they are recycled to the soil surface by litterfall, throughfall, and stemflow (Cole and Rapp, 1981; Stark, 1994; Trudgill, 1988). Leaching, on the other hand, moves nutrients downward. The dynamics of this downward cycling for exchangeable cations is complicated by interaction with cation exchange sites (CEC) on soil mineral surfaces that hold nutrients to the soil matrix itself. Consequently, the vertical distribution of nutrients can elucidate the extent to which uptake or leaching control the short-term chemical dynamics of exchangeable cations in soil. The extent to which cations are retained in surface soil and to which uptake controls the vertical distribution of cations can differ

by forest type and tree species. For example, Dijkstra and Smits (2002) found greater leaching of Ca^{2+} along with greater pumping of Ca^{2+} from deep soil in sugar maple compared to hemlock forests. In spruce and beech forests, considerably more leaching from surface soil occurs under spruce, and much greater subsurface uptake occurs under beech (Berger et al., 2006).

Soil solution studies suggest that charged chemical species - be they positive or negative - do not move in soil on their own, but instead require a charge balance in solution (Cole et al., 1975; Cole et al., 1967; Johnson and Cole, 1980; Likens et al., 1969). Consequently, the identity and quantity of mobile anions in soil solution controls cation leaching rates. Many anions can satisfy the positive charges of cations in solution, ranging from Cl^- to SO_4^{2-} to NO_3^- to HCO_3^- (Johnson and Cole, 1980). Ugolini and Sletten (1991) found a large deficit in negatively charged chemical species in soil solution when only Cl^- , SO_4^{2-} , and HCO_3^- were measured. Organic acids (along with NO_3^- in some cases) have long been hypothesized to fill the anion deficit in soil solution (Lundstrom, 1993), suggesting a fundamental control of cation dynamics by soil organic matter (SOM). The dynamics governing the behavior of SOM as it relates to exchangeable cations are complex. On the one hand, accumulation of SOM has been well established as a source of CEC sites in the solid phase (Kalisz and Stone, 1980). However, dissolved organic matter (DOM) and, in particular, low molecular weight (LMW) organic acids such as citric and oxalic acid have been identified as important compounds exuded by fungi and plants to induce destabilization of cations from organic complexes for later uptake (Clarholm and Skjellberg, 2013). Across six forest types, Dijkstra et al. (2001) found that between 25% and 43% of negative charge in soil solutions could be attributed to organic acids and implicated these acids as a primary driver of cation leaching from the forest floor into mineral horizons. DOM – especially those hydrophilic compounds rich in carboxylic and phenolic groups - may act as

mobile ligands for exchangeable cations that travel with water downward through soil (Johnson and Cole, 1980). Indeed, organic acids have been observed to be major cation leaching agents in acid soils from boreal to tropical/subtropical regions (Johnson et al., 1977; Ugolini et al., 1977). Thus different forms of organic matter are implicated both as a source of exchangeable cation retention and as a means by which nutrients stabilized in SOM are destabilized and subsequently mobilized for either uptake or leaching (Clarholm et al., 2015).

Acidic forest soils are a special subset of soils in which aluminum (Al) can complicate the interpretation of CEC and exchangeable cation extractions (Ross et al., 2008). Soil acidification can mobilize Al^{3+} , which blocks CEC sites from retaining base cations and has been implicated as a mechanism in forest soil Ca depletion (Lawrence et al., 1995). Mycorrhizal fungi take advantage of the affinity for Al^{3+} and LMW organic acids to form strong bridging complexation reactions by exuding LMW organic acids into soils, thus partially neutralizing soil acidity (Clarholm et al., 2015). At or below a pH of 4.5, Ross et al. (2008) argue that little Al^{3+} will be adsorbed to the soil solid phase, and that pH is modeled better if Al^{3+} is treated as a base cation. Consequently, base saturation in this range does not provide a useful metric (Ross et al., 2008).

Nitrogen may also be an important part of cation leaching under certain conditions. Nitrogen saturation is known to occur in forest ecosystems due to either large atmospheric inputs, weathering of N-bearing rocks (Dahlgren, 1994; Holloway and Dahlgren, 2002), or accumulation from N-fixing species (Aber et al., 1998; Aber, 1992; Aber et al., 1989). These phenomena result in increased N mineralization rates, followed by stripping of exchangeable cations from soil through nitrate leaching as the capacity of the ecosystem to take up excess N is overcome (Aber et al., 1989). In the coastal Pacific Northwest, early successional alder trees fix

large quantities of nitrogen through a symbiotic relationship with root-nodulating *Frankia* (Binkley et al., 1994), which can result in long-term acidification of soil and loss of exchangeable cations (Van Miegroet and Cole, 1984; Van Miegroet and Cole, 1985). Perakis et al. (2006; 2013) found that the distribution of N across the Pacific Northwest, which itself reflects forest disturbance and duration of alder colonization, acts as a primary control on exchangeable cation (particularly Ca^{2+}) availability to forest ecosystems. Many such studies focus on the horizontal rather than vertical distribution of nutrients in the soil profile (Perakis and Sinkhorn, 2011), and consequently do not explicitly consider the translocation of cations deeper into the soil profile.

Studies that examine exchangeable cation dynamics in forest soils often focus on the O horizon, or track changes with depth to only 50 or 100 cm. However, Douglas-fir and other dominant or co-dominant tree species in the region extend roots deeply (3+ m) into the soil profile (Stone and Kalisz, 1991). Little is known about the role of deep roots in the nutrition of forests, although maximum rooting depths between 2 and 20 m have been recorded for species from every major biome except for tundra (Canadell et al., 1996). Despite much lower density than surface roots, deep rooting may serve as a safety net by capturing nutrients leaching from surface soil horizons. Indeed, a tracer experiment found functional specialization of deep roots for the uptake of exchangeable cations (K^+ and Ca^{2+}) from deep regions of the soil (3 m) in highly productive Eucalyptus plantations in Brazil (da Silva et al., 2011). Whether similar rooting specialization exists in Douglas-fir or other forest types has not yet been widely studied.

Nutrient dynamics in deep soil are largely understudied (Harrison et al., 2011; James et al., 2015; Whitney and Zabowski, 2004). Two recent review papers on the impact of land use change on soil organic matter (Post and Kwon, 2000; West and Post, 2002) found that the

median depth of soil sampling was 20 cm, with 90% of the 360 referenced studies sampling to 30 cm or less. Consequently, testing the effects of environmental and chemical gradients on the vertical distribution of exchangeable cations deep into soil has not been possible on a broad spatial scale. Such tests often involve simple correlations between variables, which can fail to pick up on more complicated relationships governing changes that occur across the landscape and within the soil profile. Environmental variables are not often distributed normally, and thus techniques that go beyond parametric statistics are needed to evaluate the effects of these variables. The objectives of this paper are:

1. To introduce the use of permutational multivariate analysis of variance (PERMANOVA) and nonmetric multidimensional scaling ordination (NMDS) as tools to analyze complex soil chemical data.
2. To assess the impact of soil C, N and pH on the concentration, stocks and vertical distribution of soil exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) in deep forest soils.
3. To assess how other environmental gradients such as climate, horizonation, soil texture, parent material, and soil order affect the contents, stocks, and distribution of soil exchangeable cations.

2. Methods

2.1 Field sampling

Samples were collected from 22 sites in the coastal Pacific Northwest, ranging from the Pacific Ocean to the Cascade Range and from northern Washington to southern Oregon (Figure 1). All sites are intensively managed Douglas-fir stands that have been previously used to study forest response to nitrogen fertilization on individual trees (Littke et al., 2014a; Littke et al.,

2014c). One soil pit per site was excavated in unfertilized areas adjacent to fertilized stands. Bulk density samples were taken in the middle of regular depth intervals of 0-10 cm, 10-50 cm, 50-100 cm, 100-150 cm, 150-200 cm, 200-250 cm, and 250-300 cm (this depth only sampled at 6 sites). Major genetic horizon for each sample was assigned based upon field descriptions, which are detailed in James et al. (2015). Briefly, all 0-10 cm samples were taken from A horizons, while the 10-50 cm samples came from A horizons at six sites; the remainder of 10-50 cm samples were from B horizons, as well as eighteen of the twenty two 50-100 cm samples; and, finally, samples below 100 cm were from C horizons, except at three sites where the B horizon extended to roughly 200 cm.

2.2 Laboratory Analyses

Bulk density samples were sieved to 4.75 mm, ground to a fine powder, and analyzed for %C and %N using a PerkinElmer CHN analyzer. Complete explanations of methods and results for soil C and N at these sites can be found in James et al. (2014; 2015). Exchangeable cations (Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+} , as well as exchangeable Al^{3+}) were extracted by shaking samples with a 1 M solution of ammonium chloride for 2 hours. Sample solutions were filtered with Whatman 40 filter paper, and analyzed with an inductively coupled plasma mass spectrometer (ICP-MS). Soil stocks for soil C, N, and exchangeable cations were calculated as

$$\text{Stock}_M = [M] * D_b * H \quad (1)$$

where $[M]$ is the concentration of the element M , D_b is the bulk density, and H is the height of the soil layer for which the total stock is being calculated. The effective CEC (CECe) in each sample was calculated as the sum of exchangeable Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} , Al^{3+} , Fe^{2+} , Mn^{2+} , Zn^{2+} , and Cu^{2+} . Site level variables, including location (latitude and longitude), climate (temperature and precipitation for all four seasons), soil texture (percent sand and clay at 5 and 50 cm),

elevation, slope, aspect, and parent material were all collected by Littke et al. (2014b). Soil order was determined by comparing Web Soil Survey mapped soil series (Soil Survey Staff, 2014) with observed profiles and samples from the field (Table 1).

2.3 Statistical Analysis

Principal component analysis (PCA) was used to build a synthetic climate index based upon 8 climate variables – the temperature and precipitation for spring, summer, autumn, and winter seasons. The first and second principal components of the PCA were subsequently used to test the effect of climate on the differences in exchangeable cations between sites. PCA was also used to create a synthetic index for soil texture for each site, which was derived from the percent sand and clay at 5 and 50 cm depths. The first principal component was used to test for the effect of texture on the distribution of exchangeable cations between sites. Texture data was not available for all soil depth samples, and consequently texture was only analyzed for differences between sites, not for changes in cation vertical distribution within the soil profiles.

Permutational multivariate analysis of variance (PERMANOVA) was used to examine the effects of environmental, chemical, physical, and spatial variables on exchangeable base cation concentrations and total stocks both within the soil profile and between sites. To our knowledge, this technique has not been used before in the soil literature outside of microbiology, and a brief explanation should make clear both how this technique works and why it was used here. The PERMANOVA approach is commonly used to statistically assess the effects of experimental or uncontrolled environmental gradients on the overall distribution of ecological communities, which can be made up of hundreds to thousands of biological species (McArdle and Anderson, 2001). Rather than assess the effect of these environmental gradients on one species at a time, PERMANOVA instead analyzes these gradients against a distance matrix that

is the product of the differences between sites for all these species at the same time (Anderson, 2001; Anderson and Ter Braak, 2003; McCune and Grace, 2002). The analyses in this paper use Euclidean distance to produce the distance matrix, which is an application of the Pythagorean theorem. To understand how this is done, consider a study in which n number of species are measured at p number of sites, which produces a $p \times n$ data matrix. Euclidean distance calculates the distance (D_p) between each site using the equation

$$D_p(q, r) = \sqrt{(q_1 - r_1)^2 + (q_2 - r_2)^2 + \dots + (q_i - r_i)^2 + \dots + (q_n - r_n)^2} = \sqrt{\sum_{i=1}^n (q_i - r_i)^2}$$

where q and r are separate species measured at each site. This produces a $p \times p$ distance matrix that quantitatively expresses the differences between sites regardless of the number of species measured at each site. PERMANOVA then compares explanatory variables to this distance matrix by permuting the explanatory data many times and comparing the observed test statistic (*Pseudo-F*) to the distribution of *Pseudo-F* values derived from the many possible permutations of the data. Each permutation in the data is made by swapping two (or more) values of the explanatory variables under the null hypothesis that they have no effect on the response variables. In univariate cases where the assumptions of parametric ANOVA are met, PERMANOVA and ANOVA produce identical F -statistics and asymptotically similar p -values, except that PERMANOVA does not require the assumption that explanatory data is normally distributed (Anderson and Ter Braak, 2003). This paper uses PERMANOVA to examine exchangeable base cation species (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) in an analogous way to biological species.

PERMANOVA assumes that the permuted data is exchangeable under a true null hypothesis, and consequently the precise interpretation of PERMANOVA tests depend upon the

1 method used to control how the data is permuted (Anderson and Ter Braak, 2003). This study
2 employs a nested design in which we are interested in both factors that explain differences in
3 exchangeable cations between sites (i.e. different soils) and factors that explain the vertical
4 distribution of exchangeable cations in repeated measurements within each site (i.e. samples
5 down the soil profile). Consequently, modeling the effects of explanatory variables between sites
6 must be done separately from testing the effects of explanatory variables on the vertical
7 distribution (within-site variability) in soil exchangeable cations. When testing the effects of
8 between-site variables – which include climate PC1 and PC2, soil texture PC1, parent material
9 (sedimentary, igneous, or glacial), total C, total N, mean pH, and soil order (Alfisol, Andisol,
10 Inceptisol, or Ultisol) – PERMANOVA was allowed to freely permute data between each of the
11 22 sites. The response matrix used for testing between-site explanatory variables was composed
12 of the distances between the site centroids (mean exchangeable base cation values at each site),
13 and thus limited the tests of between-site variables to 21 total degrees of freedom. On the other
14 hand, soil samples in the profiles are repeated spatial measurements and care must be taken to
15 preserve the spatial structure of this sampling scheme. Thus, for testing within-site variables –
16 which include soil C, N, exchangeable Al^{3+} , pH, horizon (A, B, or C), and depth – data were
17 permuted to preserve the spatial ordering (moving either up or down the profile) and were not
18 permuted between sites. Because the primary interest was to test for effects on the vertical
19 distribution of base cations within whole profiles, a site factor was used as the first term in
20 within-site tests to control for the differences between sites. Variables that are statistically
21 significant for between-site tests do not imply control over the vertical distribution of
22 exchangeable cations but only control over differences in mean exchangeable cations across the
23 landscape; likewise, significant within-site explanatory variables are those which differentiate

patterns in the vertical distribution of profiles, but not differences between sites. Due to the high variability between sites in both soil base cation content and stocks, soil chemical data was ln-transformed prior to analysis.

The order in which explanatory variables appear in PERMANOVA is important, and the *pseudo-F* statistic and R^2 values for variables change depending on whether they are included first or later in the model (Anderson, 2001). The final PERMANOVA models were built stepwise by adding only the explanatory variable with the highest R^2 at each step. Final p-values for both within- and between-site tests were calculated based upon a *pseudo-F* distribution derived from 10,000 permutations. Variables were only added to the model if they were significant at $\alpha = 0.05$. Analysis of multivariate homogeneity of dispersions (PERMDISP) was used to test for differences due to dispersion for statistically significant grouping factors in the final PERMANOVA models (Anderson et al., 2006; Anderson and Walsh, 2013). Between-site and within-site models for base cation contents ($\text{cmol}_c \text{ kg}^{-1}$) and total stocks ($\text{kmol}_c \text{ ha}^{-1}$) were computed separately. Soil content variables were not crossed with soil stock variables either as response or explanatory variables (e.g. %C was used to test models for exchangeable cation contents, but C stocks were used in models of exchangeable cation stocks).

2.4 Data Visualization

Non-metric multidimensional scaling (NMDS) ordination was used to visualize the significant effects of environmental, chemical, and spatial variables on the distribution of exchangeable base cations. Separate ordinations were computed for exchangeable cation contents and stocks, but only results from the soil stocks ordination are presented here to prevent redundancy. The NMDS ordinations were computed in two dimensions using Euclidean distances between ln-transformed exchangeable cation variables. New random sets of starting

coordinates were used for each run of the monoMDS engine until convergence criteria were reached (instability less than $1e^{-5}$). The final ordination converged after 3 runs, with final stress = 0.0305, non-metric $R^2 = 0.999$, and linear $R^2 = 0.997$. Overlaying external environmental variables on the points in NMDS space can visually show their effects on exchangeable cations. When displaying factors that explain differences between sites, the site centroids (average value of exchangeable cations across all depths) are shown, leaving 22 points. However, when displaying the effects of variables that explain the vertical distribution of cations within soil profiles, the full 136-sample dataset is shown. For grouping factors such as soil horizon (where samples are either from A, B, or C horizons in this dataset), there are frequently multiple samples from each horizon in a single soil profile because samples were taken by standard depth intervals.

All models were run in R version 3.1.2 (R Core Team, 2015). Principal components analysis (PCA) for climate and texture data was performed using the `princomp()` function within the base stats package. The `adonis()`, `betadisper()`, and `metaMDS()` functions from the vegan package (version 2.2-1) were used for PERMANOVA, PERMDISP, and NMDS, respectively (Oksanen et al., 2015).

3. Results and Discussion

3.1 Synthetic Climate and Texture Variables

The climate in the coastal Pacific Northwest is characterized by generally warm, dry summers and wet, cool winters. Substantial variation in climate occurs across sites in this study due to wide latitudinal separation between sites, as well as the influence of the Olympic, Coast, and Cascade mountain ranges on precipitation (rain shadow effects) and temperature (elevation

effects). Principal Components Analysis (PCA) of climate data reveals that two component axes explain 87% of the variation in climate between sites. The first principal component (PC1) explains 57% of the variance and consists of roughly equivalent loadings for each of the 8 climate variables (TWIN, TSPR, TSUM, TAUT, PWIN, PSPR, PSUM, PAUT) with precipitation negatively weighted and temperature positively weighted (Figure 2, Table 2). This principal component represents an index of climate running from cold and wet to warm and dry, and follows the trend from high to low leaching rates. In the context of soil taxonomic moisture regimes, climate PC1 could be interpreted as differentiating between more udic conditions (where there is little to no moisture deficit - low PC1 scores) and more xeric conditions (where there is some moisture deficit during the year - high PC1 scores). Differences in temperature between sites were not large enough to span different taxonomic temperature regimes. The second principal component (PC2), which explains an additional 29% of the variance, excludes the summer temperature and precipitation variables and has slightly higher loadings for winter variables (Figure 2, Table 2). This climate index runs from cool and dry to warm and wet for autumn, winter, and spring seasons, and captures changes in wet season leaching rates. Climate PC2 does not fit patterns recognized as separate soil moisture and temperature regimes. These two indices were subsequently used to examine the impact of climate and leaching on exchangeable cation distribution.

The PCA for soil texture yielded a single dominant component that explains 81% of the variance in the 4 texture and depth variables (Clay_5, Clay_50, Sand_5, Sand_50). The loadings for this component are roughly equal for each variable, with negative loadings for clay at 5 and 50 cm depth and positive loadings for sand at 5 and 50 cm depth (Figure 3, Table 3). This principal component runs from fine texture to coarse texture and captures all four variables into a

single texture index, which was used to test for texture effects on exchangeable cation distribution.

3.2 Exchangeable base cation contents

Results of PERMANOVA for both between- and within-site tests appear in Table 4. The distribution of exchangeable base cation contents between sites is significantly predicted by climate PC1, which accounts for 19% of the between-site variation ($pseudo-F = 4.59$, $p < 0.05$), while climate PC2 was not a significant predictor. Climate PC1 runs generally from cool, wet conditions to hot, dry conditions, and in the context of exchangeable cation cycling can be thought of as an index of leaching. Temperature and precipitation will also affect decomposition rate, leading to variation in the quantity and quality of organic matter at each site. Other variables tested at the between-site level explain relatively large portions of the variation but are not significant or even marginally significant ($p > 0.1$). For example, soil order explains 20% of the variation between sites, but is not significant ($p \approx 0.17$). Neither soil texture PC1 ($R^2 = 0.06$, $p \approx 0.22$) or the average effective CEC ($R^2 = 0.02$, $p \approx 0.75$) were significant. One possible reason for this is the relatively small number of sites (22) and limited degrees of freedom to test for significant effects. These results show that climate (and the associated leaching force associated with different climates) is a primary driver of the differences in exchangeable cation contents between different soils across the landscape.

The site factor – which controls for differences between sites when testing for changes in vertical distribution within the soil profile – is very large, accounting for 73% of the variation (Table 4). Nonetheless, soil horizon and an interaction term between horizon and %C are both significant. The soil horizon groupings (A, B, or C horizon) do not differ in their dispersion ($F = 3.02$, $p > 0.05$), and thus the significance of this term can be safely interpreted to be the result of

differences between group centroids. In particular, A horizon samples appear distinctly separated from B and C horizon samples with lower concentrations of exchangeable base cations (particularly Ca) in the A horizon compared to B and C horizons. While %C is not a significant predictor of the distribution of soil exchangeable cation contents on its own, within each master horizon the areas with higher %C tend to have fewer exchangeable base cations. This is counter-intuitive given the role of soil organic matter (SOM) as a source of exchange sites in the solid phase. One hypothesis to explain this observed relationship is that the C that reaches the subsoil has been broken down into tiny pieces or even monomers that can be mobile in soil solution. While SOM in the solid phase is considered a source of CEC sites, LMW organic acids in soil solution are mobile anions that can promote leaching loss of exchangeable cations. The role of organic acids as a component of base cation leaching has long been recognized in soil solution studies (Johnson and Cole, 1980; Johnson, 1992; Johnson et al., 1977; Ugolini and Sletten, 1991). These results suggest that pedogenic accumulation and cycling of organic matter may be an important control on the distribution of exchangeable cation contents within acidic forest soils. Detailed soil solution study at these sites would provide additional data to directly observe this phenomenon, but is beyond the purview of this study.

The vertical distribution of C concentration and exchangeable cation contents are shown in Figure 4. In sites with high surface and particularly subsurface (50+ cm) soil C concentrations, exchangeable base cation contents remain low throughout the profile (Figure 4a). At some sites with moderately high C concentrations - particularly below 100 cm - the concentrations of exchangeable Ca^{2+} and Mg^{2+} begin to increase in the subsurface (Figure 4b). Sites with moderately low surface and subsurface soil C tend to have higher surface and subsurface concentrations of Ca^{2+} and Mg^{2+} (Figure 4c). Finally, at sites with low soil C concentrations,

particularly below 50 cm, exchangeable Ca^{2+} and Mg^{2+} increase dramatically with depth (Figure 4d). Very little regular change in exchangeable K^+ or Na^+ can be observed with depth in response to soil C concentration changes. Exchangeable cation contents (especially Ca^{2+} and Mg^{2+}) tend to be lower in A horizons than they are in subsurface horizons, and within each major horizon (A, B, or C) areas with lower %C tend to have higher concentrations of exchangeable Ca^{2+} and Mg^{2+} . This can most dramatically be seen comparing the subsurface (>1 m) samples (corresponding with the B and C horizons) between Figure 4a and 4d. Between 100 cm and 250 cm depth, soils in Figure 4a average 0.477% C by mass, whereas the soils in Figure 4d average 0.106% C by mass. Exchangeable Ca^{2+} and Mg^{2+} concentrations, meanwhile, are nearly an order of magnitude less in Figure 4a than in 4d within the same depth interval.

The change in the concentration of exchangeable Al with depth across sites is not consistent. It does not increase with depth as soil C decreases, as with Ca^{2+} and Mg^{2+} , nor does it remain consistent with depth, as with K^+ and Na^+ (Figure 5). At most sites, exchangeable Al remains low throughout the profile. However, substantial concentrations that generally increase with soil depth can be observed at 5 sites, indicating long-term acidification. These sites are some of the oldest in this dataset, representing Ultisols (Windygap, Honeygrove), Alfisols (Melbourne), and Andisols (Tolovana, Hoquiam) developed on old alluvium or sedimentary parent materials with ash influence in the surface. High exchangeable Al^{3+} may indicate greater prevalence of Al and dearth of other cations in parent materials at these sites. The soil pH across the sites in this study ranged from slightly to extremely acidic (Table 1). Consequently, fixation of Ca by soil available P is unlikely to drive Ca cycling in this region.

3.3 Exchangeable cation stocks

Stocks of soil exchangeable Ca^{2+} , Mg^{2+} , K^+ , and Na^+ are shown in Figure 6, as well as the relative contribution of each sampling interval to the total stock at each site. On average there are 762 $\text{kmol}_c \text{ ha}^{-1}$ of Ca (ranging from 21 to 2981 $\text{kmol}_c \text{ ha}^{-1}$), 496 $\text{kmol}_c \text{ ha}^{-1}$ of Mg (range 11 to 1876 $\text{kmol}_c \text{ ha}^{-1}$), 48 $\text{kmol}_c \text{ ha}^{-1}$ of K (range from 11 to 128 $\text{kmol}_c \text{ ha}^{-1}$), and 261 $\text{kmol}_c \text{ ha}^{-1}$ of Na (range 41 to 484 $\text{kmol}_c \text{ ha}^{-1}$) total across all 22 sites. Subsurface (>1 m depth) stocks represent the majority of the total pool; 66% of exchangeable Ca^{2+} , 76% of exchangeable Mg^{2+} , 57% of exchangeable K^+ , and 63% of exchangeable Na^+ are located deeper than 1 m, on average. Douglas-fir can be very deeply rooted, with reports of maximum rooting depth greater than 3 m in many locations (Stone and Kalisz, 1991). Subsoil nutrient stocks are likely a key resource for Douglas-fir growing in this region, and may help explain the increase in forest productivity with increasing effective soil depth (Steinbrenner, 1979).

The underlying distribution of base cation quantities in NMDS space is presented in Figure 7. All soil chemical data (cations as well as C and N) were ln-transformed prior to analysis, so apparent linear correlations evident in the ordinations are non-linear in nature. Each point in space represents the same rank-order as the distance matrix of exchangeable cations, rather than the actual metric distances. Hulls are drawn around the distribution of points within each major horizon (discussed in detail below). Stocks of Ca^{2+} and Mg^{2+} increase in nearly the same direction, while K^+ and Na^+ are more similar to each other. The labeled vectors show that K^+ and Na^+ increase orthogonally to Ca^{2+} and Mg^{2+} , indicating that these two sets of cations change independently of each other and, furthermore, that different factors are the dominant controls over their distributions in soil. Environmental and chemical gradients overlain on the NMDS distribution help to visualize the statistical effects seen in PERMANOVA and can aid in interpreting which of the exchangeable cations respond to each gradient.

Both total C and Climate PC1 are significant predictors of the distribution of exchangeable cations between sites (Table 5). Cumulative soil C explains 20% of the variation, with an additional 12% explained by Climate PC1. These effects can be seen on the distribution of cations in NMDS space in Figure 8. The points in these plots are the site centroids – the point of mean distance between exchangeable cation stocks within each site. Sites with high total soil C tend to occur where exchangeable Ca^{2+} and Mg^{2+} are low (Figure 8a). This result is unexpected given the well-recognized positive relationship between SOM and CEC sites (Kalisz and Stone, 1980). One hypothesis to explain this difference between observation and theory is that in sites as acidic as these (Table 1) the pH dependent charges on SOM will be mostly protonated or occupied by Al^{3+} (Gruba and Mulder, 2008), while simultaneously, the sites with high C stocks are likely to release more dissolved organic matter (DOM), which can act as mobile anions that exacerbate leaching loss (Johnson and Cole, 1980; Johnson, 1992). Further reinforcing this hypothesis is our finding that sites with warm, dry climates tend to have larger quantities of Ca^{2+} and Mg^{2+} (Figure 8b). The soils that experience less rainfall and higher temperatures have less leaching force exerted on the system, producing less translocation and loss of cations to groundwater. These results suggest that increased leaching accompanied by greater SOM buildup and associated DOM movement could be a fundamental control over the distribution of exchangeable cations across the landscape, particularly for Ca^{2+} and Mg^{2+} . The direction of linear correlation for K^{+} and Na^{+} is nearly perpendicular to the direction of change in both total C and climate PC1, indicating that other processes are dominant controls for these base cation species between sites.

There are large differences between sites – accounting for 58% of the variation within the soil profiles – which must be controlled for prior to testing the effects of environmental gradients

1 on the vertical distribution of cations. This large site effect is expected given the vast differences
 2 between soils, and allows subsequent explanatory variables to be tested for their ability to
 3 explain the vertical distribution of exchangeable cations regardless of soil type. Soil horizon
 4 along with both soil C and soil N are significant predictors of the distribution of exchangeable
 5 cations (Table 5). Master soil horizon, on its own, explains 21% of the variation and is
 6 statistically a much stronger predictor of cation distribution than is soil depth on its own. The
 7 significance of soil horizons could be partially explained by differences in soil volume – the
 8 surface stocks (0-50 cm depth) are thinner than subsurface stocks (>50 cm depth), with
 9 thicknesses of 10 or 40 cm rather than 50 cm in the subsurface. However, soil horizon is also a
 10 significant predictor of cation concentration (Table 4), which is independent of soil stock
 11 calculations. Furthermore, A horizons are frequently thinner than B and C horizons in the field,
 12 as was the case in all sites sampled for this study. Horizon development is driven by pedogenic
 13 and biogeochemical mechanisms that have advanced to various depths in different soils, and thus
 14 stocks of soil nutrients will naturally vary based upon the volume of each horizon. The
 15 significant separation in the distribution of A horizon samples from B and C horizon samples can
 16 be seen in Figure 8. There was a significant interaction between soil horizon and both soil C (R^2
 17 = .021, $p < .05$) and depth ($R^2 = .014$, $p < .05$). Within each horizon, samples with less soil C
 18 tend to have more exchangeable base cations, particularly Ca^{2+} and Mg^{2+} (Figure 8c). Vectors for
 19 K^+ and Na^+ are orthogonal to soil C, suggesting lack of a relationship. Likewise, within each
 20 major horizon, deeper samples tend to have more base cations (Figure 8e). The interaction
 21 between horizon and soil carbon stock reinforces the hypothesis that DOM can be a control over
 22 the distribution of exchangeable cations. Not only is soil C a significant control on exchangeable
 23 cations between different soils, it is partly responsible for the vertical distribution within each

soil. In particular, within each master horizon group (A, B, or C) those samples with higher C tend to contain less exchangeable Ca^{2+} and Mg^{2+} than those with lower C. The interaction of horizon and depth makes intuitive sense given that leaching appears to be a major force acting on the vertical distribution of exchangeable cations, resulting in greater exchangeable cation stocks (particularly Ca^{2+} and Mg^{2+}) in deeper parts of soil horizons.

Soil N has a significant effect on exchangeable cation distribution, second only to horizon (Figure 8d). This effect only explains a small portion of the variation, however ($R^2 = 0.011$, $p < .05$). Larger quantities of N occur where exchangeable cations are lower, particularly Ca^{2+} (Figure 8d). The finding that exchangeable cations decrease as soil N increases agrees with other studies in the region, most notably Perakis et al. (2006; 2011; 2013). Because N is found in many different forms in soil, this effect could be due to NO_3^- leaching as well as leaching via DOM that has N incorporated in the molecular structure. Soil C and N are highly correlated across all samples in this dataset ($R^2 = 0.71$), though there is surprisingly no significant interaction between these terms in the PERMANOVA model. Though the data presented here cannot tease apart these two mechanisms, most likely both are operating in these soils. Soil N distribution is very surficial compared to exchangeable cations at these sites (31% below 1 m relative to 57-76% below 1 m for exchangeable cations), suggesting that N is more limiting to plant growth and that it is recycled more efficiently within coastal Pacific Northwest ecosystems.

Soil theory states that the dominant role of soil organic matter in cycling of exchangeable cations is as a source of CEC sites in the solid phase that hold these nutrients and keep them from leaching. However, the PERMANOVA results presented here reveal a contrary result: that there is more exchangeable Ca^{2+} and Mg^{2+} in soils with less soil C and in the parts of soil horizons with less C. How might this reconcile with well-established theory? Almost all of these

soils are highly acidic (Table 1), which causes the carboxylic and phenolic functional groups that contribute the most to pH-dependent charge to remain protonated or to be occupied by Al^{3+} (Gruba and Mulder, 2008). Consequently, the ability of SOM to retain base cations in these soils is limited. In this context, the role of dissolved organic matter becomes magnified. DOM has been highlighted as an important vector by which C migrates from O and A horizons to subsurface B and C horizons (Kaiser and Kalbitz, 2012). As more complex, surface reactive DOM is retained by sorption to soil minerals, the lighter, more soluble compounds continue into subsoil (Guggenberger and Kaiser, 2003). The DOM likely to reach the deep subsurface horizons include hydrophilic compounds that contain more functional groups and few hydrophobic aliphatic chains, as well as low molecular weight (LMW) organic acids. These compounds could essential serve as mobile CEC sites that gradually leach exchangeable cations deeper into soils as they become mobilized in solution. Scott and Rothstein (2014) hypothesize that DOM in soil is in dynamic exchange, whereby highly sorptive, hydrophobic compounds displace previously sorbed, N-rich hydrophilic compounds on soil surfaces. Several studies have recognized that dissolved organic nitrogen (DON) can leak from terrestrial ecosystems due to its low biodegradability (Hedin et al., 1995; Neff et al., 2003; Perakis and Hedin, 2002), and thus could also serve as a mobile ligand for cations.

The distributions of K^+ and Na^+ differ considerably from Ca^{2+} and Mg^{2+} . The fact that K^+ follows a different trajectory in its vertical distribution – and does not appear to follow soil C, N or horizon as closely as Ca^{2+} and Mg^{2+} – suggests that processes other than leaching are more dominant controls. Jobbagy and Jackson (2001) suggest that at the global scale plant uptake and cycling are more important drivers of K^+ distribution than leaching, despite K^+ being more poorly held to CEC sites than Ca^{2+} and Mg^{2+} . K^+ is found in high concentrations in plant tissues,

1 and there are typically limited supplies available in soil. Consequently, the particular importance
2 of upward translocation through biological cycling of K^+ seems a reasonable hypothesis for the
3 differences in vertical distribution seen here. Based upon the stoichiometry of cation exchange,
4 the release of cations into soil solution is a function of both leaching rate and the total ionic
5 concentration (Johnson and Lindberg, 1992). This relationship is dependent on the charge (and
6 associated hydrated radius) of cations, which implies that K^+ and Na^+ release into solution will
7 be least affected by increases in total anion or cation leaching rate (Johnson, 1992).

8 The lack of correlation between Na^+ distribution and Ca^{2+} and Mg^{2+} distributions is
9 surprising, since this element is least likely to be cycled upward through biological uptake and
10 most likely to be leached deeper into the profile. There are two conceivable explanations for the
11 uniformity of exchangeable Na^+ stocks both between different soils as well as in its vertical
12 distribution. First, while Na^+ is not recognized as an essential soil nutrient, it has been
13 hypothesized that Na^+ can fill some small roles in plant nutrition usually fulfilled by K^+ ,
14 including the passive regulation of osmotic pressure across cell walls (Subbarao et al., 2003).
15 This explanation seems unlikely, however, because K^+ concentrations in Douglas-fir foliar
16 tissues are typically an order of magnitude larger than Na^+ (Goodrich and Jacobi, 2012),
17 indicating selective exclusion of Na^+ from uptake. The second, more likely explanation is that
18 increased atmospheric deposition of Na^+ due to proximity to the ocean is driving the more
19 surficial distribution within sites and uniform distribution between sites. Na^+ deposition rates in
20 the coastal Pacific Northwest can be quite high (Cole and Rapp, 1981; Edmonds et al., 1995;
21 Johnson and Lindberg, 1992), resulting in persistent seeping of exchangeable Na^+ through soil.
22 Finding uniform quantities with depth could imply that these soils have reached equilibrium
23 between persistent atmospheric deposition and leaching of Na^+ .

This analysis can help guide future research into the mechanisms of these relationships, particularly examining the interplay between cation release from weathering and leaching. Soil solution studies at these sites could help elucidate the chemical speciation of soil C and N that directly results in cation leaching, as well as quantifying other negatively charged species like HCO_3^- , Cl^- and SO_4^{2-} . Across the Pacific Northwest, leaching (possibly via mobile organic acids) is a primary driver of Ca^{2+} and Mg^{2+} differences both between soils across the landscape and within soil profiles, while biological cycling and weathering release from primary and secondary minerals control the distribution of K^+ .

4. Conclusions

1. Over 50% of all exchangeable base cations are found below 1 m, on average.
2. Leaching is a primary control over exchangeable Ca^{2+} and Mg^{2+} distribution between sites in the Pacific Northwest, possibly with assistance from mobile organic acids.
3. Soil horizon development substantially affects the distribution of exchangeable base cations within the soil profile, with lower contents and stocks of cations in A horizons relative to B and C horizons. Within horizons, exchangeable Ca^{2+} and Mg^{2+} increase as soil C decreases and depth increases.
4. Exchangeable K^+ is less deeply distributed than Ca^{2+} or Mg^{2+} , indicating plant uptake as a more dominant control.
5. Exchangeable Na^+ is relatively evenly distributed both between soils and within the soil profile in the Pacific Northwest, likely due to persistent atmospheric deposition along with leaching.

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Figures Captions

Figure 1. Locations of 22 sampling sites in western Washington and Oregon. Symbol colors correspond with site scores on a climate index (Climate PC1, Figure 2) running from wet and cool to warm and dry.

Figure 2. Principal components analysis of climate variables. Component 1 (PC1) is composed of roughly equal loadings for all 8 variables (temperature and precipitation for 4 seasons). PC1 runs from generally cool and wet conditions to hot and dry conditions. Component 2 (PC2) is composed of loadings from only autumn, winter, and spring variables. PC2 runs from cool and dry conditions to warm and wet conditions. See Table 2 for loadings for each principal component.

Figure 3. Principal components analysis of soil texture variables. Component 1 (PC1) is composed of roughly equal loadings for all 4 texture variables (Table 3) and runs generally from fine texture to coarse texture.

Figure 4. The change in exchangeable cation concentrations with depth at 22 soils in the Pacific Northwest split into groups by (a) high soil C concentration, (b) moderately high soil C, (c) moderately low soil C, and (d) low soil C concentration. As soil carbon concentrations decrease, particularly in subsurface horizons, exchangeable Ca^{2+} and Mg^{2+} increase.

Figure 5. The change in exchangeable Al^{3+} with depth, split into groups as in Figure 4 for ease of interpretation.

Figure 6. Total soil stocks and relative contribution by sampling layer for (a) exchangeable Ca^{2+} , (b) exchangeable Mg^{2+} , (c) exchangeable K^{+} , and (d) exchangeable Na^{+} . The soils are ordered from largest total C stocks (Hk) at left to smallest total C stocks (Sm) at right.

Figure 7. Non-metric multidimensional scaling (NMDS) ordination for total soil exchangeable cation data fit in 2 dimensions using a Euclidean distance measure. Data was ln-transformed prior to analysis. NMDS converged on a solution after 3 runs using random starting locations. Final stress = 0.0305. Vectors indicate the direction and magnitude of positive correlation for (a) total exchangeable Ca^{2+} , (b) total exchangeable Mg^{2+} , (c) total exchangeable K^{+} , and (d) total exchangeable Na^{+} . These vectors will be used in the later figures to show the direction of increase for each exchangeable cation. Point symbols represent the horizon from which the sample was taken, and hulls are drawn around the distribution of each horizon in the ordination space.

Figure 8. Relationships between total soil exchangeable cations and (a) cumulative soil C at each site, (b) climate PC1 for site centroids, (c) soil C, (d) soil N, and (e) soil depth. These environmental gradients visually show the statistically significant relationships observed in Table 5. Soil chemical values (soil C stocks, and soil N stocks) were ln-transformed. For full description of NMDS ordination, refer to Figure 7. Vectors indicate positive correlation if they point in the same direction, negative correlation if they point away from each other, and lack of correlation if they are perpendicular. In (a) and (b) plotted points are the centroids of the

- 1 exchangeable cation stocks for each site. Symbols correspond to the major soil horizon for each
- 2 sample in (c), (d) and (e).
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1 Tables

Table 1. Soil series, map symbol, subgroup, and texture for 22 forest soils in western Washington and Oregon

Soil Series	Map Symbol	Subgroup ^a	Texture	Mean pH ^b (range)	Mean CEC ^c (range)
Astoria	A	Andic Humudept	Clay loam	4.9 (4.5 - 5.3)	4.1 (1.2 - 7.4)
Barneston 1	Bn1	Typic Vitrixerand	Gravelly sandy loam	5.4 (5.2 - 5.5)	7.6 (3.7 - 17.2)
Barneston 2	Bn2	Typic Vitrixerand	Gravelly sandy loam	5.3 (5.0 - 5.8)	2.4 (1.6 - 3.3)
Blachly	Bl	Humic Dystrudept	Clay loam	4.8 (4.3 - 5.1)	3.5 (1.7 - 5.0)
Cloquallum	C	Aquandic Dystrudept	Sandy loam	5.4 (4.7 - 6.0)	6.5 (3.5 - 12.7)
Hoko	Hk	Aquic Durudand	Gravelly clay loam	4.5 (3.9 - 4.9)	2.9 (0.9 - 6.0)
Honeygrove	Hg	Typic Palehumult	Gravelly silty clay loam	4.7 (4.5 - 5.0)	11.6 (8.7 - 15.7)
Hoquiam	Ho	Typic Fulvudand	Clay	4.7 (4.4 - 5.0)	11.8 (7.3 - 23.7)
Jory	J	Xeric Palehumult	Silty clay	4.6 (4.4 - 4.8)	4.3 (3.5 - 5.2)
Kinney	K	Andic Humudept	Sandy clay	5.3 (5.0 - 5.9)	10.1 (3.7 - 21.1)
Lemolo	L	Typic Humaquept	Sandy clay loam	5.7 (5.1 - 6.2)	9.2 (7.4 - 10.8)
Melbourne	M	Ultic Palexeralf	Clay	4.6 (4.3 - 4.8)	19.3 (6.5 - 30.3)
O'Brien	Ob	Typic Fulvudand	Sandy clay loam	5.0 (4.3 - 5.2)	2.3 (1.3 - 5.4)
Olete	Ol	Vitrandid Haploxerept	Gravelly loam	6.0 (5.3 - 6.4)	24.5 (8.3 - 50.8)
Ovall	Ov	Andic Humixerept	Gravelly sandy clay loam	4.7 (4.2 - 5.0)	6.9 (2.3 - 12.4)
Ragnar	R	Vitrandid Dystroxerept	Fine loamy sand	5.3 (4.7 - 5.7)	1.5 (0.7 - 3.1)
Scamman	Sm	Aquic Palexeralf	Sandy clay loam	5.2 (4.5 - 5.7)	19.1 (8.3 - 22.9)
Shelton	Sh	Typic Haploxerand	Gravelly loam	5.4 (4.8 - 6.2)	14.9 (5.1 - 25.4)
Tokul	Tk	Aquic Vitrixerand	Gravelly clay loam	5.8 (4.5 - 6.8)	5.4 (3.3 - 6.8)
Tolovana	Tv	Typic Fulvudand	Clay loam	4.2 (4.0 - 4.3)	14.2 (8.8 - 20.3)
Vailton	V	Alic Hapludand	Loam	5.1 (4.7 - 5.3)	3.2 (1.0 - 9.3)
Windygap	W	Xeric Haplohumult	Loam	4.7 (4.5 - 5.1)	15.9 (10.3 - 20.2)

^a Data from Natural Resources Conservation Service 2012.

^b pH measured as saturated paste; mean across all depths

^c effective CEC (eCEC) calculated as the sum of exchangeable Ca²⁺, Mg²⁺, K⁺, Na⁺, Al³⁺, Fe³⁺, Mn²⁺, Zn²⁺, and Cu²⁺

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Table 2: Loadings for Principal Component Analysis of Climate Variables			
Loadings:		Comp. 1	Comp. 2
Winter Precipitation	PWIN	-0.320	0.440
Spring Precipitation	PSPR	-0.371	0.368
Summer Precipitation	PSUM	-0.369	
Autumn Precipitation	PAUT	-0.395	0.319
Winter Temperature	TWIN	0.221	0.514
Spring Temperature	TSPR	0.396	0.288
Summer Temperature	TSUM	0.390	
Autumn Temperature	TAUT	0.332	0.448

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Table 3: Loadings for Principal Component Analysis of Soil Texture Variables		
Loadings:		Comp. 1
Clay 5 cm depth	Clay_5	-0.483
Clay 50 cm depth	Clay_50	-0.507
Sand 5 cm depth	Sand_5	0.478
Sand 50 cm depth	Sand_50	0.530

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Table 4: PERMANOVA results for distribution of exchangeable cation contents (<i>P</i> -value calculated with 10,000 permutations)						
		Df	SS	<i>Pseudo-F</i>	R ²	<i>P</i> (>F)
Between Site Variation	Climate PC 1	1	23.16	4.59	0.187	0.019
	Residuals	20	101.01		0.813	
	Total	21	124.17			
Within Site Variation	Site ID	21	655.26	19.10	0.725	< 0.0001
	Horizon	2	42.22	12.92	0.047	< 0.0001
	% Carbon	1	3.04	1.86	0.003	0.2591
	Horizon % C	2	25.60	7.84	0.028	0.0004
	Residuals	109	178.03		0.197	
	Total	135	904.14			

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**Table 5: PERMANOVA results for distribution of exchangeable cation stocks
(*P*-value calculated with 10,000 permutations)**

		Df	SS	<i>Pseudo-F</i>	R^2	$P(>F)$
Between Site Variation	Total C	1	30.58	5.69	0.203	0.0024
	Climate PC 1	1	18.15	3.38	0.120	0.0342
	Residuals	19	101.96		0.677	
	Total	21	150.69			
Within Site Variation	Site ID	21	658.17	19.55	0.583	< 0.0001
	Horizon	2	237.21	73.98	0.210	< 0.0001
	Nitrogen	1	12.94	8.07	0.011	0.0035
	Carbon	1	9.21	5.74	0.008	0.0115
	Depth	1	3.27	2.04	0.003	0.1775
	Horizon Carbon	2	23.86	7.44	0.021	0.0006
	Horizon Depth	2	16.04	5.00	0.014	0.0169
	Residuals	105	168.34		0.149	
	Total	135	1129.03			

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Exchangeable Al
($\text{cmol}_c \text{ kg}^{-1}$)

Figure 7

Figure 8