



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



Jason James ^{*}, Kim Littke, Thiago Bonassi ¹, Rob Harrison

University of Washington, School of Environmental and Forest Sciences, Box 352100, Seattle, WA 98195, United States

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

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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

^{*} Corresponding author.

E-mail address: jjames@uw.edu (J. James).

¹ Present Address: University of Sao Paulo, Luiz de Queiroz College of Agriculture, Av. Pádua Dias, 11-Agronomia, Piracicaba, SP, 13418-900, Brazil.

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 Skjyllberg, 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 (Fig. 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, 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,

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