DYNAMICS AND SEASONAL VARIATIONS IN BASE CATIONS OF A TEMPERATE BEECH FOREST AT TWO CLOSE-BY SITES

Master's thesis in the scientific program International Master of Science in Soils and Global Change (IMSOGLO) submitted to Georg-August Universität, Faculty of Geoscience and Geography

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Dedicated to

The defining moments of resilience
The Courage to continue
The love and support around me
The faith in the process
My family
Dr. Sunday Obalum
Dr. Ifeyinwa Uzoh
Dr. Tyler Anthony
&
All others who will inherit the responsibility from me

Abstract

The effect of phenological and climatic seasons on cation dynamics were assessed at two adjacent sites of a temperate beech forest from June 2017 to May 2021. The result shows significant and dynamic variations in the different pathways - stemflow, throughfall, precipitation and soil (15 cm, 30 cm, 50 cm and 70 cm depths). The behaviours of cations amongst throughfall, stemflow and precipitation showed divergent trend from that in soils. Cation concentrations were generally higher in stemflow compared to throughfall and precipitation. As conditioned by climatic factors, cation concentrations were largest during autumn and spring seasons in stemflow, throughfall and precipitation. The highest cation concentrations in the different pathways were observed during the growing season compared to the dormant season. Cation concentration in soil solutions displayed different behaviours at both slopes. However, the results generally showed that cation concentrations in soil were lowest during the winter season and highest during the autumn season. Generally, the result showed weak interlinkages between the cation concentration in the above-ground pathways and soil solution, with the most robust relationships observed between throughfall and soil solution concentrations at the 15cm depth during the autumn season. This study underscores the internal nutrient cycling in forest ecosystems and the role of stemflow, throughfall and precipitation in sustaining soil fertility.

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1. Introduction

The internal cycling of nutrients strongly determines forest productivity (Moffat *et al.,* 2002; Tobon *et al.*, 2004; Chuyong *et al*., 2004; Habashi *et al.*, 2019). Nutrient addition into forest ecosystems mainly occurs through precipitation and are transmitted in solution within forest ecosystems by throughfall or stemflow before reaching the forest floors and soils. While throughfall is the portion of precipitation that drips from the forest canopy before coming in contact with the forest floors, stemflow is the aspect of atmospheric precipitation that runs along the stems and trunks of trees. During this process, the chemical composition of the solutions in the different mediums is modified, and many authors have documented this. The chemical modification of these mediums depends on many factors, including the trees' physiology and prevailing climatic conditions. The interactions and balance between these sources of nutrient inputs determine the type of forests, degree of biomass growth and the long-term sustainability of forest ecosystems (de Schrijver *et al*., 2004; Hermann *et al.*, 2005; Zhang *et al*., 2006; Moslehi, 2016; Adedoyin and Adegbesin, 2012).

Ions usually exist in their particulate phase in the atmosphere, and their composition at any given time depends on the prevailing environmental conditions within an area, with reported variations in their concentrations at different times of the year. As such, the ionic concentration of precipitation is reported to be a function of seasonality (time of the year), distance to forest boundaries (Weathers *et al.* 2001), wind activities (Erisman *et al.*, 2001), proximity to oceans (Adedoyin and Adegbesin, 2012), and industrial activities adjacent to forest landscapes (Van Stan et al., 2012). A high concentration of Na, Mg and Cl in precipitation was observed in forest sites within kilometres from the ocean (Hermann *et al*., 2006; Adedoyin and Adegbesin *et al*., 2012). Marked differences have also been observed by Weather et al. (2001) on the chemistry of precipitation between forest centers and their boundaries.

The portion of precipitation that flows as stemflow or throughfall depends on the tree types, canopy structure, and densities and spatial distribution (Herrman *et al.* 2016). Several authors have reported significant differences in the chemical composition of throughfall and stemflow to that of precipitation (de Schrijver et al., 2004; Hermann *et al*., 2006; de Schrijver, 2007; Berger *et al*., 2009a; Návar *et al*. 2009; Chiwa *et al*., 2014; Moslehi *et al.*, 2016). The reported changes in the chemical concentrations along these mediums depend on several factors, including the physiological state of the trees, the ionic state of stems and leaves, and their permeability (Salehi *et al*., 2016; Muoghalu and Oakhumen, 2000). Additionally, the ionic concentration in these pathways has displayed variations due to the leaching of material from the internal plant tissues and the uptake of materials by foliage (Návar *et al*., 2009; Chiwa *et al*., 2014; Moslehi *et al.*, 2016). de Schrijver et al. (2007) reported a high leaching rate regarding Ca, Mg and K and observed that Na is comparably inert to leaching or uptake by the canopy of plants.

As a repository of nutrients, plants, rhizosphere and microbial ecosystems, forest soils provide nutrients for the growth and productivity of the living components that make up its biological diversity. Nutrient supply from stemflow, throughfall and precipitation may have a significant impact on the biogeochemistry cycling soil nutrients and affect important soil properties including acidity, cation exchange capacity, base saturation, pH, microbial immobilization and mineralization, etc. (Neirynck *et al*. 2000; Westling and Lovblad, 2004; Berger *et al.*, 2009b).

Moslehi et al. (2019) noted a higher cation concentration in soils around the canopies of beech forest than that of the forest gaps. They attributed this difference to influxes by stemflow and throughfall. Additionally, given the complexity of the soil-plant system, a linear relationship between nutrient inputs and soil contraction may not be easily directly established. Quite precisely, Berger *et al*. (2009a) noted that such nutrient cycling systems could not be perceived as a "wash-through system" as these relationships are influenced by complex processes within the plant-soil system. However, the biogeochemical cycling of nutrients needs to be continuously quantified, especially with phenoseasonal changes and interannual climatic variations.

As a result, many researchers have investigated the seasonal dynamics of nutrients in the aerial deposition in forest ecosystems. Habashi *et al*. (2019) reported significantly higher concentrations of cations, Ca, Mg and K (except Na) in all tree species during the growing seasons compared to the dormant season. Similarly, Moslehi *et al*. (2016) found a higher enrichment of cations (Fagus Orientalis Lipsky) during the growing season compared to the dormant season. These results were attributed to the marked defoliation of beech trees during the dormant season and significant flush of vegetative growth in the growing season. Additionally, Levia *et al*. (2011) reported that the phenoseasonal changes in forest trees composition does not only affect the dynamics of cations in the different pathways (precipitation, stemflow, throughfall and soil) but also affects the atmospheric deposition of tree canopies, the internal concentration of nutrients, and the leaching losses of cations from trees.

With exciting patterns and trends observed in the dynamics of cations in aerial forest depositions across a broad range of climates, just a few studies combine the investigation of both the soil and the aerial components of nutrient pathways as a factor of seasonality. Moreso, there is a deficit of literature that shows the dynamics of cations in the various media across the different climatic seasons of the year. Understanding the phenological responses of nutrient dynamics within the entire forest ecosystem provides quality insights into the apparent and potential effect of climatic variations in this regard.

European beech forests are one of the broadest distributions of forests within the continent, dominating large landscapes of the natural vegetation in western, southern and central Europe (Rötzer *et al.*, 2013). They play a crucial role in climate modification, air and water pollution, erosion control, carbon sequestration, maintenance of biodiversity etc. (Žemaitis *et al.*, 2018). Studies on the biogeochemical cycling of nutrients in this ecosystem will inform their management of forest vegetation and soil and the surrounding forest environment due to their impact on nutrient transport. This study addresses the effects of seasonality on the dynamics of base cations within the forest ecosystem by posing the following questions:

1. Do cation concentrations vary with the dormant and growing seasons of trees in throughfall, stemflow, precipitation and soil solution?
2. Do cation concentrations vary with annual climatic seasons?
3. Is there a direct impact on the concentration of cations in soil solution due to influx from throughfall, stemflow and precipitation?

We hypothesize that; *i)* higher concentrations of cations in stemflow compared to other media *ii)* higher cation concentrations in the growing season than in the dormant season *iii)* direct influence of nutrient input from precipitation, throughfall and stemflow on the concentration of soil cations. *iv)* differences in cation concentrations with the different seasons of the year. Consequently, the objective of this study is to assess the concentrations of base cations and show their relationships within the pathways of atmospheric precipitation, stemflow, throughfall and in the soil pool and also understand the impact of seasonality on cation concentrations in the different media.

2. Materials and methods

2.1 Study site

The study was conducted from June 2017 to May 2021 in a small valley near the village of Ebergotzen, which is approximately 15 km east of Gottingen (51°33'60.0"N 10°04'48.7"E) at an elevation 280 m above sea level (***Fig 1***). The experimental site is a beech forest (Fagus sylvatica), with the average age of the stands being about 50 years. The climate is warm and temperate, with rainfall experienced throughout the year with a mean annual precipitation of approximately 650 mm. The average yearly temperature is 8.3°C, with the warmest months in August (with an average maximum temperature of 22°C) and the coldest months in January (with an average maximum temperature of 1°C). The average relative humidity is 77.0%.
The soil is predominantly a cambisol, with active clay migration, acidification and incipient podzolization. The significant soil-forming process in the location is browning with a characteristic reddish-brown colouration, especially at the upper soil depths. The soil is derived from Triassic sandstone from the middle alps and contains periglacial loess admixture at the lower slopes.

Experimental plots were set up in the site at the two adjacent slopes (north- and south- oriented), with a wire net established around the plots to prevent the intrusion of humans and other large mammals. With reference to Rothe and Blinky (2001), we took advantage of the spatial scale of the interaction of trees at the two slopes without the need for replicated plot experiments. The soils of north and south slopes differ in their textural properties, soil depth, soil colour, degree of podzolization, leoss and organic matter content. ***Fig 2*** shows the soil profiles in both slopes. The north slope has a higher sand content and a higher degree of podzolization in the past compared to the south slope. Additionally, the south slope shows a higher intensity of browning, higher organic matter and leoss content relative to the north slope. The south slope shows a deeper soil profile and A horizon with a stony base below 6 m.

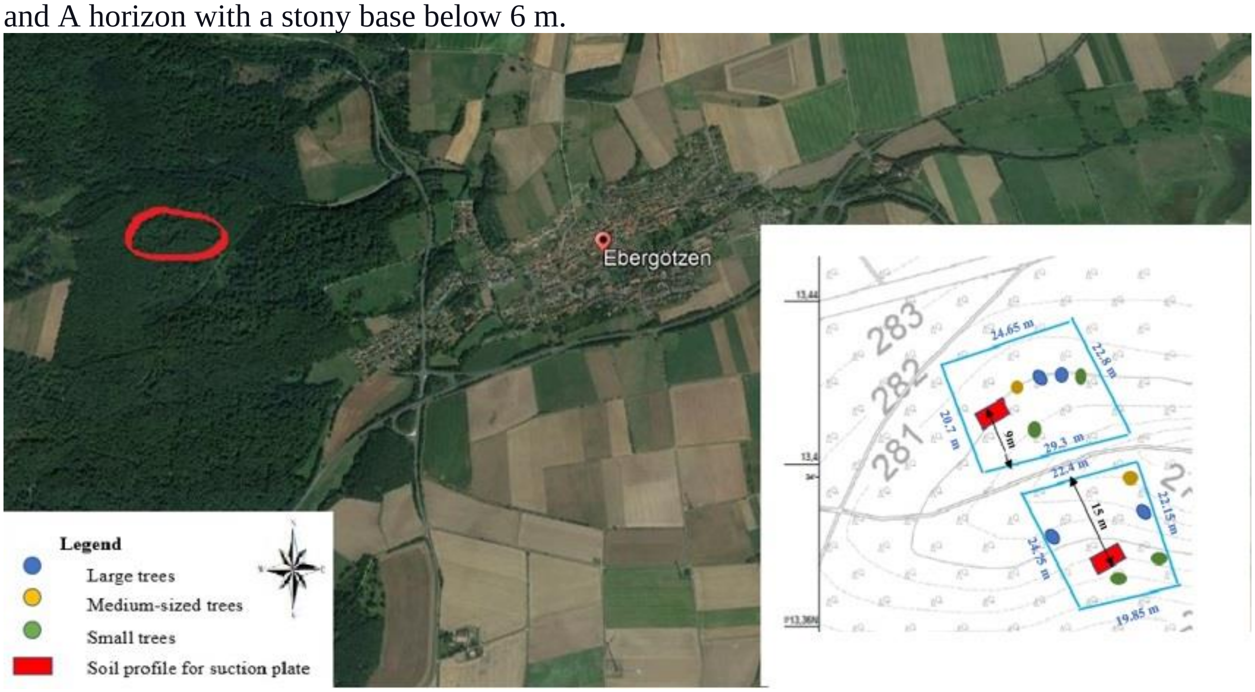

Figure 1: Map of study area showing the design of experimental site.

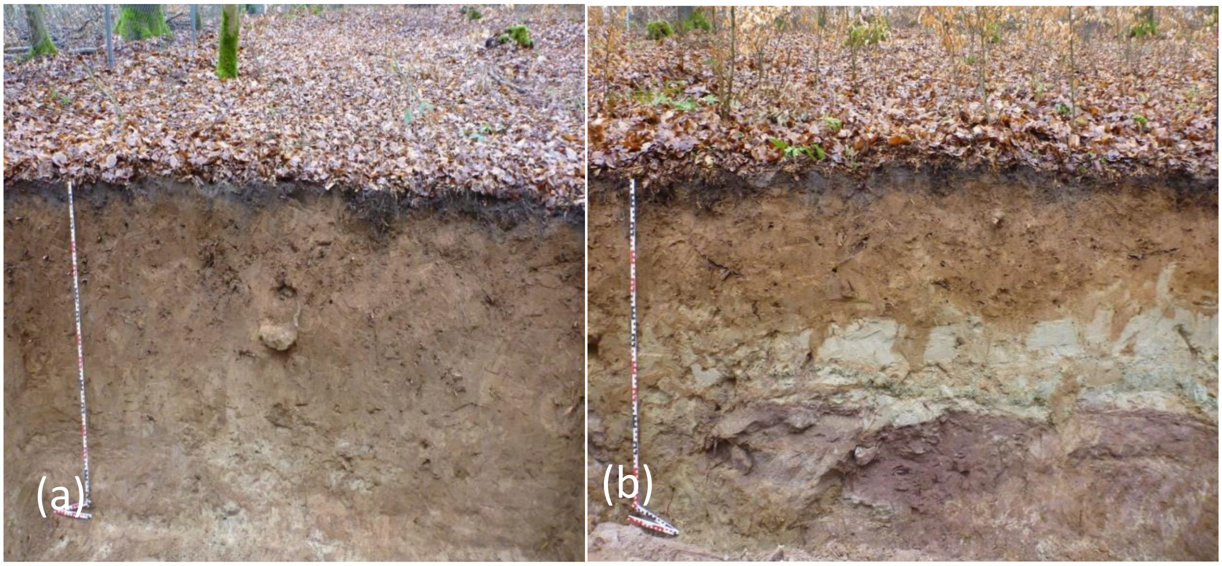

Figure 2: *South slope soil profile (a), and North slope profile (b)*

2.2 Sampling and analytical method

Twelve (12) suction plates connected to PE bottles were established at each slope to collect soil solution (***Fig 3a***). Soil solutions were pumped at four soil depths (15 cm, 30 cm, 50 cm and 70 cm) into PE bottles fitted with a 0.2 µm filter at the inlet to prevent the entrance of soil particles. Samples of soil solution are collected in three replications at every soil depth. The suction plates function at a matric potential of -150 hPa. Throughfall samples were collected in a tipping bucket connected to a water collector cup (***Fig 3b)***. The device is enclosed at the inlet with a nylon mesh to prevent the entrance of snails, insects and debris that could potentially contaminate the sample. Depending on the size of the tree, different sizes of tipping buckets were used for the collection of throughfall samples. The instrument is set up in such a way that excess water is let out when the collector cup is filled. Stemflow collection was also done through the collar method, where a spiral rubber was fitted around the trees, and the solution drained into tipping buckets (***Fig 3c)***. Samples for bulk precipitation were also collected from an adjacent weather station. All solute samples were collected on a biweekly basis and analyzed for base cations and pH. After collection of the samples, all collectors were rinsed with distilled water before reinstallation.

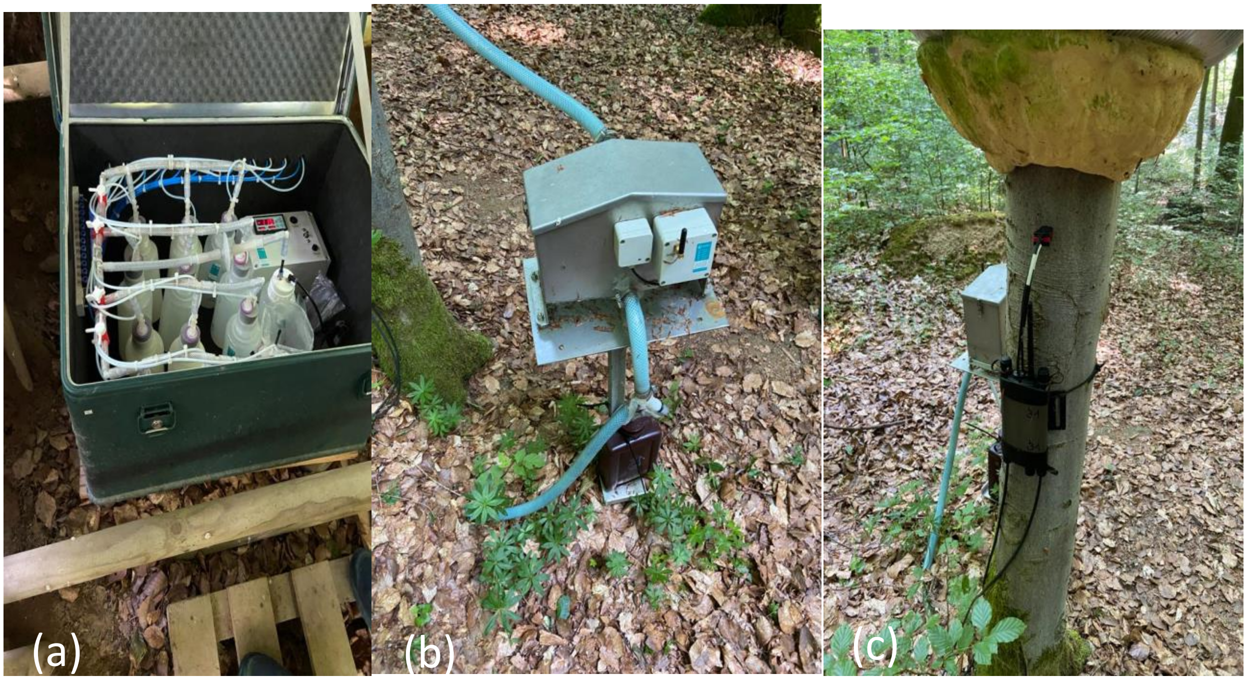

Figure 3. *PE bottles for soil solution collection (a), throughfall measurement and collection, and stemflow measurements*

2.3 Laboratory analysis

Laboratory analysis of samples was conducted at the Institute of Geography, George-August University, Gottingen. Solute samples of soil, precipitation, throughfall and stemflow were analyzed with an ICP-OES (inductive coupled plasma- optical emission spectrometer) for their base cation concentrations. Samples were placed into the analyzer where they were heated in a scorching plasma that excites the ions in the samples. The ions turn into light and are separated by the optical system of the analyzer. The wavelengths of the produced light provide information about the concentrations of cations in the sample. The pH ($CaCl_2$) was also analyzed for all the samples. The analysis was carried out in a volume ratio of 1:5 according to DIN ISO 10390. The pH values were automatically determined in sinking suspension using the pH meter. Before measurements, the pH meter was calibrated using pH 7 and pH 4 buffer solution to ensure a reliable measurement.

2.4 Statistical analysis

All preliminary analyses were performed using Microsoft excel 2019 to obtain an overview of the data. The data were partitioned by date into dormant seasons (November to April) and growing seasons (May to October) for further analysis based on phenological seasons. Additionally, the data were also divided into meteorological seasons for further analysis; Spring (March-May), Summer (June – August), Autumn (September – November) and winter (December – February). Statistical differences between cation concentrations in soil solutions, stemflow, throughfall and precipitation were tested using analyses of variance (ANOVA). Tukey's honestly significant difference test assessed the relationship between the means.   Correlation test matrix between the different media were established for individual cations across the different climatic seasons. Analyses of variance (ANOVA) and correlation tests were performed using R studio 4.1.0 for Windows (Released 18 May 2021).

3. Results

3.1 Soil solution concentration in north and south slopes

Table 1 shows the mean concentrations of cations in soil solution at the studied soil depths (15 cm, 30 cm, 50 cm and 70 cm) of the north and south slope. The ANOVA shows significant differences between the cation concentrations at the different soil depths ($P < 0.05$).

3.1.1 North slope soil

Generally, the highest cation concentrations were observed within the 15 cm soil depth. However, no clear trend was observed for the cation concentrations at the lower soil depths (30 cm, 50 cm and 70 cm). Al concentration in soil solution significantly decreased with depth, the with a highest concentration within 15 cm (0.46 mg/l) and the lowest concentration found within 50 cm (0.18 mg/l). Likewise, the highest concentration of Fe was observed in the top 15 cm (0.04 mg/l) and the lowest concentration within 50 cm depth (0.01 mg/l). Ca concentration significantly declined from the top 15 cm to the lower soil depths. The highest Ca concentration was observed in the top 15 cm soil depth (2.7 mg/l), with the lowest concentration found within 70 cm depth (1.38mg/l). The highest concentrations of divalent cations (Mg and Mn) were observed at the 50 cm depth of the soil and were significantly different from the concentration in other soil depths. The highest Na concentration (7.80 mg/l) was found within 70 cm soil depth, and this was more than two factors higher than the concentration in the top 15 cm soil depth (3.14 mg/l). The concentration of K in solution was also highest in the 15 cm soil depth but showed no statistical differences with their concentrations within 50 cm and 70 cm soil depth. P concentration in soil solution was deficient with a mean concentration of 0.01mg/l. S concentration significantly increased with soil depth, with the highest concentration of 5.02 mg/l at the 70 cm soil depths. The highest concentration of Zn was observed in 15 cm and 30 cm (0.24 and0.20 mg/l, respectively). There were no significant differences in the concentration of Si across the different soil depths. The soils displayed a slightly acidic property, with the highest pH observed at the 15 cm soil depth but showed no statistical difference from those of other depths.

3.1.2 South slope soil

In contrast to the soils of the north slopes, base cation concentrations showed unusual patterns in their distribution across soil depths in the south slope. The highest concentration of Ca was observed at the 70 cm soil depth (2.32 mg/l), with the concentrations at other soil depths showing no statistical differences. K concentration was highest at the 50 cm depth of the soil (0.47 mg/l), with the topmost soil depth showing very low concentrations (0.13 mg/l). Likewise, soil Mg concentration was highest at 30 cm and 70 cm depth (1.72 mg/l and 1.68 mg/l) with lower concentrations observed at 15 cm and 30 cm depths (1.27 mg/l and 1.33 mg/l). The highest Na concentration was observed in the 70 cm depth; however, this was not significantly different from the concentration at other depths. Similar to Fe dynamics in soil solution, the soil displayed low P concentrations, showing no statistical difference across the depths. Similar to the soils of the north slope, the highest S concentration was observed at the 70 cm depth (4.33 mg/l), while other depths showed no statistical differences in their S concentration. Zn concentration was highest at the 15 cm and 70 cm depth (0.19 mg/l and 0.18 mg/l respectively), with the lowest concentrations of 0.07 mg/l observed in the 50 cm depths. The soils also displayed a slightly acidic behaviour, with the soil pH showing no statistical differences across the depths.

3.2 Variation in concentration of selected cations in soils as a factor of phenological seasons
Two distinct phenological seasons have been identified during the life cycle of beech trees; growing season (spring and summer) and dormant season (late fall and winter). Table 2 shows the distribution of selected soil cations with regard to these phenological seasons. These cations (Ca, Mg, Na and K) have been selected because of their essential roles in plant physiology and their relevance in neutralising soil acidity. In addition to their acid neutralising effects within the soil, they serve as fundamental building blocks for plant tissues and chlorophyll (Dessert et al., 2019).

Ca concentration was significantly higher in the 15 cm depth of the soil in both slopes during the dormant season (***Fig 4a***). However, Ca concentration showed differing behaviours in both slopes during the growing season. Ca concentration was lowest in the 70 cm soil in the north slope, while the concentration was higher and not significantly different at the other depths. During the growing season, soil Ca concentration in the south slope showed an opposite trend from the observation in the north slope soils, with the highest concentration recorded in the 70 cm depth. Ca concentration only showed significant differences between phenological seasons at the 30 cm and 70 cm soil depths within the north slope. Ca concentration was only statistically different in the south slope between phenological seasons in the 15 cm depth, with the highest ionic concentration observed during the growing season.

Soil Mg dynamics showed almost similar trends as in Ca dynamics in both slopes. The lowest Mg concentration observed during the dormant season in the north slope was at the 70 cm soil depth (1.20 mg/l), with concentrations at 15 cm (2.77 mg/l), 30 cm (2.38 mg/l) and 50 cm (2.08 mg/l) displaying higher mean values, nonetheless showing no statistical differences (***Fig 5a***). During the growing season, soils of the north slope showed no statistical differences in their concentration across the soil depth. Furthermore, Mg concentrations were statistically similar in both dormant and growing seasons in all soil depths within the north slope. Mg concentration showed similar trends in both dormant and growing seasons for south slope soils. The lowest Mg concentration recorded in both seasons was observed within the 15 cm and 50 cm depths, while the most significant concentrations were noted in the 30 cm and 70 cm depths.

The soil K concentration displayed very low mean values in both slopes (***Fig 6a***). Within the north slope, soil K concentration showed no statistical differences across the depths in both phenological seasons. Also, the highest concentration of soil K between both seasons in the north slope occurred within the 70 cm depth, with the largest concentration found during the growing season (0.20 mg/l). The most significant soil K concentration within the south slope was recorded in the 50 cm depth in both seasons (0.30 mg/l for dormant season and 0.79 mg/l for growing season). This was closely followed by the 70 cm soil depth concentration (0.23 mg/l for dormant season and 0.46 mg/l for growing season), with the lowest ionic concentration observed in the 15 cm soil depth (0.10 mg/l for dormant season and 0.19 mg/l for growing season). Between both phenological seasons, the concentration of K was statistically different in all soil depths of the south slope, with higher concentrations recorded during the growing seasons.

The highest Na concentration was observed in the 70 cm depth for both slopes and phenological seasons (***Fig 7a***). Additionally, the ionic concentration of Na was statistically different between dormant and growing seasons for all four soil depths. The largest Na concentration was recorded during the growing season in the north slope. The concentration of Na in the south slope were also statistically different in all soil depths except at the 70 cm soil depth.

3.3 Variation in cation concentration in throughfall, stemflow and precipitation as a factor of phenological seasons

Table 3 shows the distribution of selected cations in stemflow, throughfall and precipitation with regards to the phenological stages of forest trees. The effect of seasonality was significant, with a higher concentration of cations in stemflow during the two distinct phenological seasons in both slopes. Ca concentration in stemflow, throughfall and precipitation were significantly higher during the growing season compared to the dormant season. K concentration showed a similar dynamic and seasonal pattern as Ca concentrations in both slopes. However, the concentrations of Mg in stemflow and throughfall showed no statistical differences for both slopes during the dormant season, with the concentration in precipitation exhibiting lower values. Mg concentration in stemflow were also significantly higher than the concentrations of throughfall and precipitation during the growing season in both slopes. Mg concentrations in stemflow and precipitation were also considerably higher during the growing season than in the dormant season for both slopes. Throughfall concentration of Mg was not statistically different for both growing and dormant seasons within the north slope, with only weak differences observed in their concentration in the south slope.

Similarly, Na was higher in stemflow than in throughfall for both phenological seasons within the two slopes. Unlike the trends observed in the seasonal variations of other cations, stemflow concentrations of Na within the north slope were larger during the dormant season than in the growing season. No significant differences were recorded in the Na stemflow concentration for the south slope. However, the concentration of Na displayed significant differences in throughfall and precipitation with significantly higher levels during the dormant season compared to the growing season in both slopes.

3.4 Dynamic variations in selected soil cations within yearly meteorological seasons

Table 4 provides detailed information of the dynamics of soil cations at the different depths within individual meteorological seasons throughout the study period. Statistical differences in cation concentration in the different soil depths are denoted by letters in superscripts, while subscripts indicate differences among similar depths in the various seasons.

Ca concentration were consistently higher in the 15 cm and 30 cm depth for both north and south slopes during the spring period. The Mg concentration declined with soil depth within the north slope, with differing behaviours observed in the south slopes. In soils of the south slope, the highest concentration was recognised at the 30 cm and 70 cm depths, while the lowest concentrations were found in the 15 cm and 50 cm depths. The concentration of K showed no statistical differences during the spring period for the soils in the north slope, with differing behaviours observed in the south slopes' soils, where the highest K concentration was recorded in the 50 cm depth of the soil. The highest Na concentration was also observed in the lowest depth studied in both slopes during the spring season.

Compared to the spring season, the soils showed relatively lower concentrations of soil cations during the summer season. The highest Ca concentration was observed at the top 15 cm depth for soils of the north slopes, while there were no statistical differences observed for south slope soils in summer. Also, Mg concentration showed no statistical differences for soils in both slopes during this period. Similar to the spring season, the highest Na concentration was observed at the 70 cm soil depth in both slopes. The level of concentration also showed similar patterns as spring, with apparent differences in their concentrations. K concentration showed no statistical differences in the soil contraction across the depths during the summer; however, the highest concentrations were observed in the 70 cm and 50 cm. Soil Na concentrations also followed similar trends in the spring, with the highest concentration observed at the 70 cm depth for both slopes.

During the autumn season, the largest recorded Ca concentrations were observed in the 15 cm and 30 cm depth for the north slope soils, with no statistical differences observed in their concentration in soils of the south slope. Na concentration showed no statistical differences in their concentrations in soils of both slopes during this season. The highest concentration of Mg was also observed at the lowest soil depth for both slopes in autumn, with the lowest concentration recorded at the 15 cm soil depth. Similarly, the highest K concentration in soils was observed at the lowest soil depth for both slopes. Other soil depths in the north slope showed no statistical differences in their mean values, and the lowest concentration were recorded at the 15 cm soil depth for the south slopes.

The Table 4 also shows that the concentrations of soil cations were low in the winter seasons. The largest concentration of Ca was observed at the topsoil depth in the north slope, with no statistical differences observed in their concentrations across soil depths in the south slope. K concentration also showed no differences in their mean values across soil depths in both slopes. Additionally, very low concentrations were observed in Mg concentrations in the soils of the north slope, with the largest concentration recorded at the lowest depth and no statistical differences in the concentrations at other depths during the winter season. The highest Mg concentration was also observed at the 30 cm depth in the south slope. There were no statistical differences in Na concentration in the 15 cm, 30 cm and 50 cm depths in both slopes, with highest mean values of Na observed at the 70 cm depths in both slopes during the winter season.

Table 1: Mean base cation concentration (mg/l) at various soil depths within the north and south slope

	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Si	Zn	pH
North slope												
15	0.46^{d}	2.70^{c}	0.04^{c}	0.11^{b}	0.98^{a}	0.04^{b}	3.14^{b}	0.01^{a}	1.73^{a}	5.74^{a}	0.24^{b}	5.61^{a}
	(0.01)	(0.12)	(0.00)	(0.02)	(0.05)	(0.00)	(0.21)	(0.00)	(0.16)	(0.24)	(0.03)	(0.03)
30	0.35^{c}	2.26^{b}	0.02^{b}	0.02^{a}	0.98^{a}	0.06^{c}	2.44^{ab}	0.01^{a}	1.84^{a}	5.58^{a}	0.20^{b}	5.42^{a}
	(0.02)	(0.05)	(0.00)	(0.05)	(0.02)	(0.00)	(0.10)	(0.00)	(0.05)	(0.19)	(0.03)	(0.03)
50	0.18^{a}	2.13^{b}	0.01^{a}	0.12^{b}	1.03^{b}	0.08^{d}	2.23^{a}	0.01^{a}	2.51^{b}	5.97^{a}	0.13^{a}	5.36^{a}
	(0.01)	(0.05)	(0.00)	(0.03)	(0.02)	(0.00)	(0.07)	(0.00)	(0.04)	(0.17)	(0.01)	(0.03)
70	0.28^{b}	1.38^{a}	0.02^{b}	0.13^{b}	0.89^{a}	0.10^{a}	7.80^{c}	0.01^{a}	5.02^{c}	5.57^{a}	0.15^{a}	5.50^{a}
	(0.01)	(0.07)	(0.00)	(0.03)	(0.04)	(0.00)	(0.41)	(0.00)	(0.33)	(0.20)	(0.01)	(0.04)
South slope												
15	0.23^{c}	2.14^{a}	0.01^{a}	0.13^{b}	1.27^{a}	0.11^{b}	2.72^{a}	0.01^{a}	2.29^{a}	5.31^{b}	0.19^{c}	5.61^{a}
	(0.01)	(0.04)	(0.00)	(0.02)	(0.03)	(0.01)	(0.09)	(0.00)	(0.10)	(0.17)	(0.02)	(0.04)
30	0.15^{b}	2.36^{b}	0.00^{a}	0.21^{b}	1.72^{b}	0.11^{b}	3.04^{a}	0.01^{a}	3.35^{a}	5.40^{b}	0.14^{b}	5.56^{a}
	(0.01)	(0.06)	(0.00)	(0.02)	(0.04)	(0.01)	(0.21)	(0.00)	(0.12)	(0.21)	(0.05)	(0.04)
50	0.08^{a}	2.13^{a}	0.00^{a}	0.47^{c}	1.33^{a}	0.08^{a}	2.59^{a}	0.01^{a}	2.53^{a}	4.53^{a}	0.07^{a}	5.65^{a}
	(0.01)	(0.14)	(0.00)	(0.10)	(0.07)	(0.01)	(0.07)	(0.00)	(0.10)	(0.17)	(0.00)	(0.04)
70	0.21^{c}	2.32^{b}	0.01^{a}	0.32^{b}	1.68^{b}	0.22^{c}	4.47^{a}	0.01^{a}	4.33^{b}	5.09^{b}	0.18^{c}	5.44^{a}
	(0.01)	(0.07)	(0.00)	(0.04)	(0.05)	(0.02)	(0.57)	(0.00)	(0.37)	(0.20)	(0.02)	(0.04)

A One-way ANOVA (factor soil depth) was performed for each slope and results of the Tukey test are given only, if differences were significant (different letters indicate significant differences, $p<0.05$; a represents the lowest mean). Standard deviations in bracket.

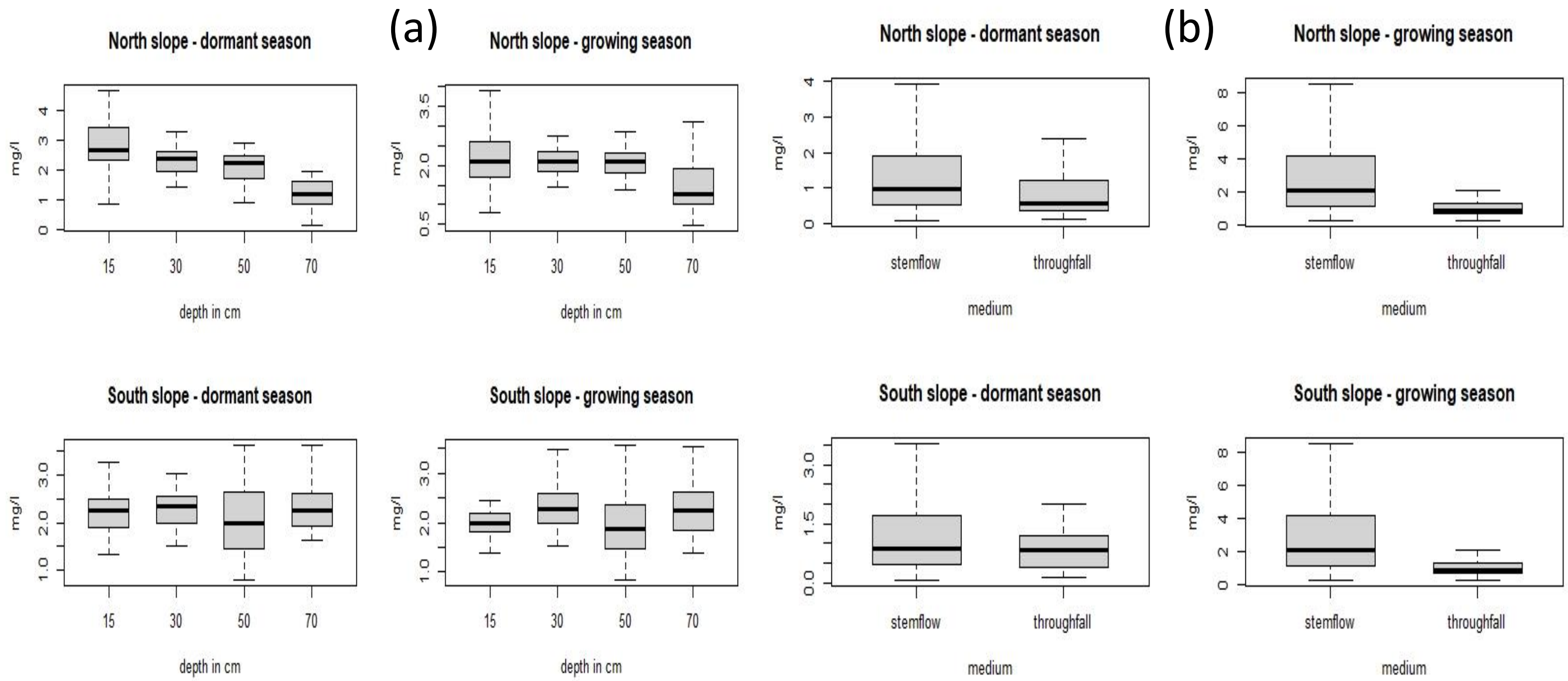

Figure 4: Calcium concentration in (a) soil and (b) stemflow and throughfall during the dormant and growing seasons

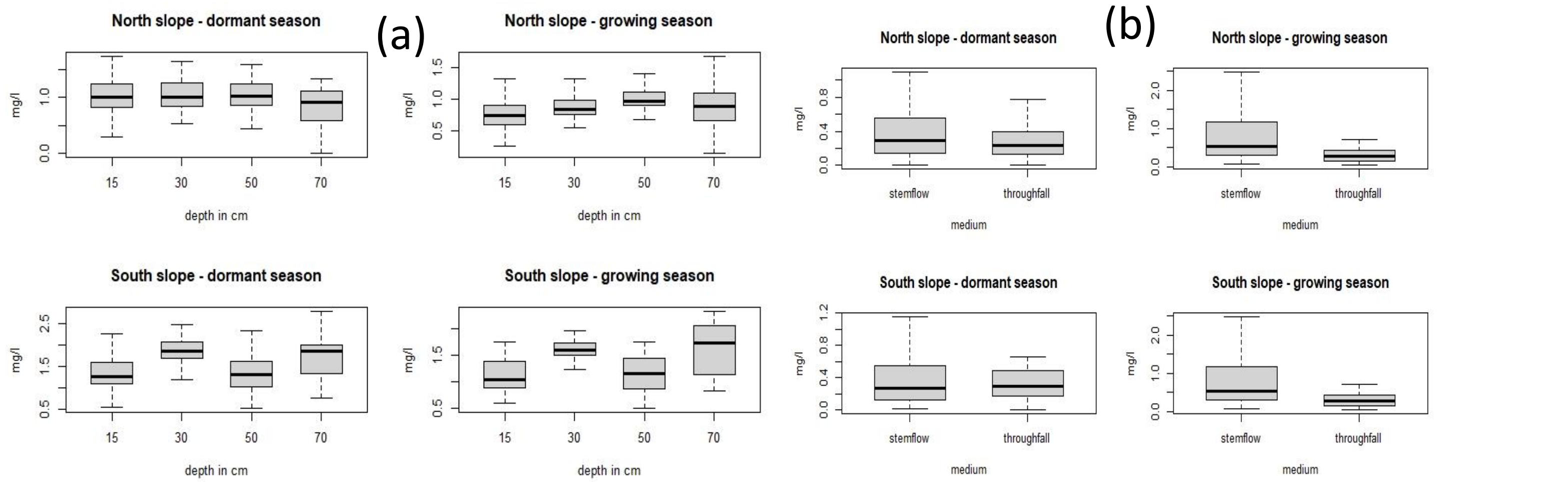

Figure 5: Magnesium concentration in (a) soil and (b) stemflow and throughfall during the dormant and growing seasons

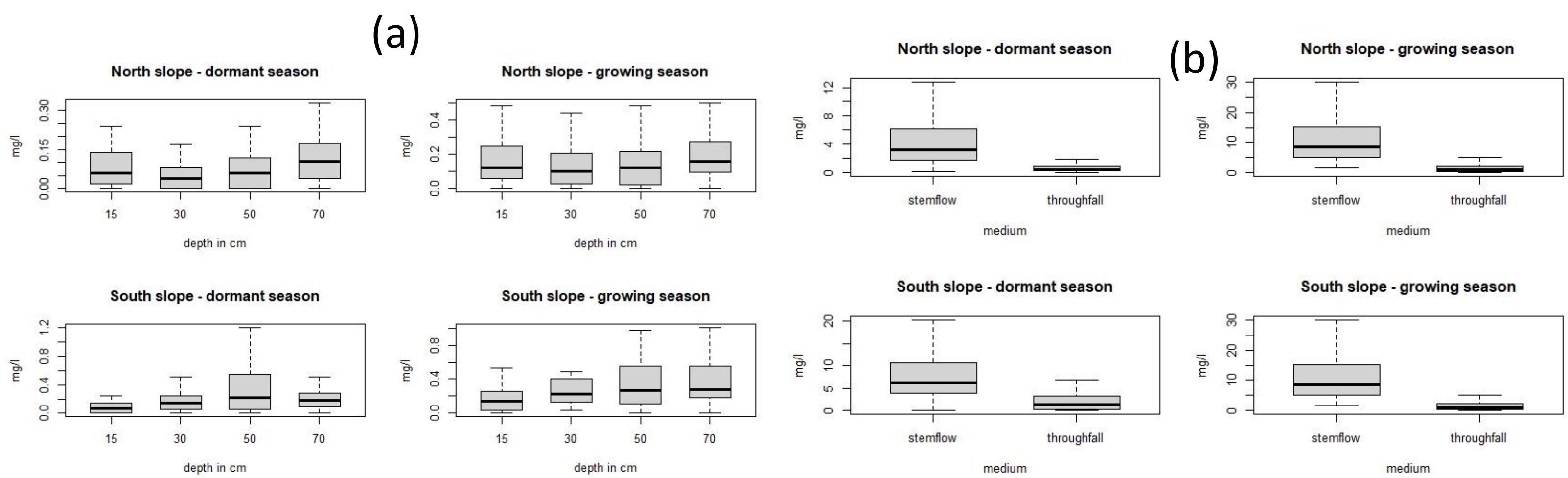

Figure 6: Potassium concentration in (a) soil and (b) stemflow and throughfall during the dormant and growing seasons

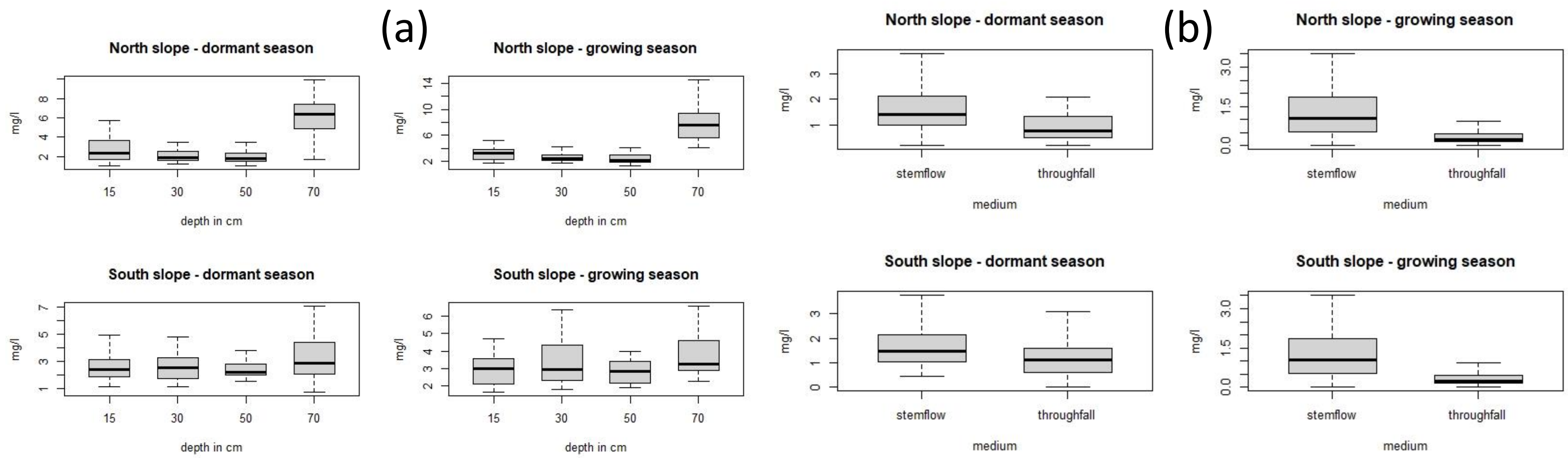

Figure 7: Sodium concentration in (a) soil and (b) stemflow and throughfall during the dormant and growing seasons

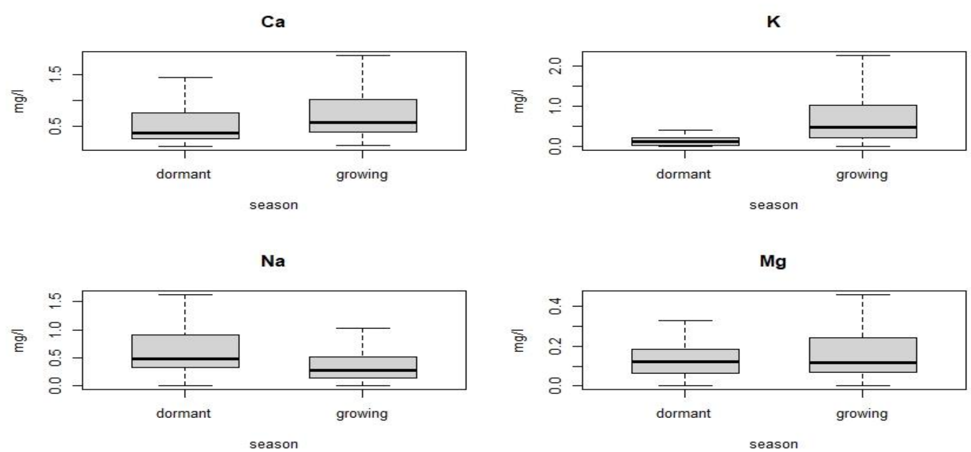

Figure 8: Cation concentrations in precipitation during the dormant and growing seasons

Table 2: Concentrations of base cations (mg/l) in the dormant and growing seasons

	Ca	K	Mg	Na	Ca	K	Mg	Na
	North slope				**South slope**			
Dormant season								
15	2.77^{d}	0.08^{a}	1.03^{b}	2.66^{b}	2.22^{b}	0.10^{a}	1.35^{a}	2.59^{a}
	(0.11)	(0.03)	(0.05)	(0.13)	(0.06)	(0.02)	(0.04)	(0.12)
30	2.38^{c}	0.04^{a}	1.05^{b}	2.23^{ab}	2.37^{b}	0.17^{ab}	1.78^{b}	2.67^{a}
	(0.07)	(0.08)	(0.03)	(0.11)	(0.06)	(0.03)	(0.05)	(0.15)
50	2.08^{b}	0.09^{a}	1.04^{b}	2.03^{a}	2.03^{a}	0.30^{c}	1.34^{a}	2.42^{a}
	(0.06)	(0.04)	(0.03)	(0.09)	(0.09)	(0.04)	(0.05)	(0.08)
70	1.20^{a}	0.17^{a}	0.83^{a}	6.39^{c}	2.31^{b}	0.23^{bc}	1.72^{b}	4.34^{b}
	(0.06)	(0.05)	(0.05)	(0.28)	(0.08)	(0.03)	(0.07)	(0.83)
Growing season								
15	2.47^{b}	0.17^{a}	0.91^{a}	3.96^{a}	2.00^{a}	0.19^{a}	1.134^{a}	2.94^{a}
	(0.25)	(0.03)	(0.11)	(0.15)	(0.05)	(0.03)	(0.05)	(0.14)
30	2.06^{b}	0.14^{a}	0.88^{a}	2.77^{a}	2.34^{ab}	0.28^{b}	1.57^{b}	3.81^{b}
	(0.04)	(0.02)	(0.03)	(0.16)	(0.09)	(0.05)	(0.06)	(0.56)
50	2.18^{b}	0.16^{a}	1.02^{a}	2.45^{a}	2.30^{ab}	0.79^{d}	1.31^{a}	2.91^{a}
	(0.08)	(0.03)	(0.03)	(0.10)	(0.38)	(0.27)	(0.18)	(0.14)
70	1.54^{a}	0.20^{a}	0.94^{a}	9.06^{b}	2.34b^{c}	0.46^{c}	1.62^{b}	4.66^{c}
	(0.11)	(0.02)	(0.06)	(0.70)	(0.11)	(0.08)	(0.08)	(0.72)
Factor season								
15	ns	*	ns	**	*	*	**	*
30	***	ns	ns	**	ns	*	**	*
50	ns	ns	ns	**	ns	*	*	**
70	*	ns	ns	***	ns	*	ns	ns

A One-way ANOVA (factor soil depth) was performed for each season and results of the Tukey test are given only, if differences were significant (different letters indicate significant differences, $p<0.05$; a represents the lowest mean). A T-test (factor slope) was done to test mean differences between the dormant and growing seasons for the different soil depths; level of significance is shown as: ns: not significant, $p>0.10$; (*), $p<0.10$; *$p<0.05$; **$p<0.01$; ***$p<0.001$. Standard deviations in bracket.

Table 3: Concentration of base cations (mg/l) in stemflow, throughfall and precipitation

	Ca	K	Mg	Na	Ca	K	Mg	Na
North slope					**South slope**			
Dormant season								
Stemflow	1.48[b]	5.24[b]	0.47[b]	1.78[b]	1.25[c]	9.01[c]	0.45[b]	1.74[c]
	(0.10)	(0.36)	(0.04)	(0.10)	(0.07)	(0.63)	(0.03)	(0.06)
Throughfall	0.86[a]	1.75[a]	0.42[b]	1.08[a]	1.07[ab]	3.53[b]	0.45[b]	1.35[b]
	(0.09)	(0.53)	(0.06)	(0.14)	(0.14)	(0.88)	(0.06)	(0.15)
Precipitation	0.57[a]	0.05[a]	0.15[a]	0.72[a]	0.57[a]	0.05[a]	0.15[a]	0.72[a]
	(0.08)	(0.17)	(0.02)	(0.12)	(0.08)	(0.17)	(0.02)	(0.12)
Growing season								
Stemflow	3.38[b]	11.95[b]	0.95[b]	1.50[b]	3.23[c]	19.7[c]	1.08[c]	1.81[b]
	(0.23)	(0.72)	(0.07)	(0.12)	(0.22)	(1.17)	(0.08)	(0.13)
Throughfall	1.16[a]	2.32[a]	0.34[a]	0.37[a]	2.17[b]	5.59[b]	0.66[b]	0.60[a]
	(0.12)	(0.41)	(0.04)	(0.06)	(0.26)	(0.93)	(0.09)	(0.09)
Precipitation	0.79[a]	0.92[a]	0.18[a]	0.30[a]	0.79[a]	0.92[a]	0.17[a]	0.30[a]
	(0.09)	(0.29)	(0.03)	(0.08)	(0.08)	(0.17)	(0.02)	(0.12)
Factor season								
Stemflow	***	***	***	ns	***	***	***	ns
Throughfall	(*)	**	ns	***	**	(*)	(*)	***
Precipitation	**	***	(*)	(*)	**	***	(*)	(*)

A One-way ANOVA was performed for each season and results of the Tukey test are given only, if differences were significant (different letters indicate significant differences, $p<0.05$; a represents the lowest mean). A T-test was done to test mean differences between the dormant and growing seasons for stemflow, throughfall and precipitation; level of significance is shown as: ns: not significant, $p>0.10$; (*), $p<0.10$; *$p<0.05$; **$p<0.01$; ***$p<0.001$. Standard deviations in bracket.

Table 4: Concentrations of base cations (mg/l) in the different meteorological seasons

	Ca	K	Mg	Na	Ca	K	Mg	Na
	North				**South**			
Spring								
15	2.72^{c}_{a}	0.12^{a}_{a}	1.03^{c}_{a}	2.75^{b}_{a}	2.14^{b}_{b}	0.07^{a}_{a}	1.37^{a}_{b}	2.74^{a}_{a}
	(0.21)	(0.05)	(0.09)	(0.16)	(0.07)	(0.01)	(0.05)	(0.12)
30	$2.32b^{c}_{a}$	0.12^{a}_{a}	1.04^{b}_{b}	2.14^{a}_{a}	2.29^{b}_{a}	0.14^{b}_{a}	1.85^{b}_{bc}	2.76^{a}_{a}
	(0.06)	(0.05)	(0.04)	(0.08)	(0.08)	(0.02)	(0.06)	(0.24)
50	2.17^{b}_{a}	0.15^{a}_{a}	1.09^{b}_{a}	2.15^{a}_{a}	1.95^{a}_{a}	0.28^{d}_{a}	1.31^{a}_{a}	2.57^{a}_{a}
	(0.07)	(0.07)	(0.04)	(0.10)	(0.08)	(0.04)	(0.05)	(0.09)
70	1.19^{a}_{a}	0.19^{a}_{a}	0.83^{a}_{a}	6.28^{c}_{a}	2.28^{b}_{a}	0.19^{b}_{a}	1.80^{b}_{a}	3.53^{b}_{a}
	(0.07)	(0.07)	(0.06)	(0.26)	(0.07)	(0.03)	(0.08)	(0.19)
Summer								
15	2.83^{c}_{a}	0.27^{a}_{b}	1.07^{a}_{a}	5.07^{b}_{b}	1.99^{a}_{a}	0.27^{a}_{b}	1.09^{a}_{a}	3.07^{a}_{a}
	(0.58)	(0.05)	(0.24)	(1.12)	(0.07)	(0.04)	(0.07)	(0.21)
30	2.01^{b}_{a}	0.17^{a}_{a}	0.83^{a}_{a}	3.18^{a}_{b}	2.39^{a}_{a}	0.34^{b}_{b}	1.50^{a}_{a}	4.38^{a}_{b}
	(0.06)	(0.03)	(0.03)	(0.26)	(0.15)	(0.08)	(0.08)	(0.94)
50	2.29^{b}_{a}	0.22^{a}_{a}	1.04^{a}_{a}	2.71^{a}_{b}	2.71^{a}_{b}	1.30^{c}_{c}	1.43^{a}_{a}	3.09^{a}_{b}
	(0.14)	(0.05)	(0.05)	(0.16)	(0.72)	(0.51)	(0.34)	(0.23)
70	1.67^{a}_{b}	0.24^{a}_{a}	0.98^{a}_{a}	9.90^{c}_{b}	2.51^{a}_{b}	0.66^{b}_{b}	1.61^{a}_{a}	5.43^{b}_{a}
	(0.19)	(0.03)	(0.11)	(1.19)	(0.18)	(0.13)	(0.11)	(1.27)
Autumn								
15	2.37^{b}_{a}	0.10^{a}_{a}	0.83^{ab}_{a}	3.25^{a}_{a}	2.20^{a}_{b}	0.17^{a}_{b}	0.97^{a}_{a}	2.26^{a}_{a}
	(0.15)	(0.02)	(0.05)	(0.32)	(0.13)	(0.01)	(0.08)	(0.21)
30	2.35^{b}_{a}	0.02^{a}_{a}	0.89^{b}_{ab}	2.85^{a}_{a}	2.58^{a}_{a}	0.43^{b}_{b}	1.68^{c}_{ab}	2.41^{a}_{a}
	(0.26)	(0.04)	(0.06)	(0.38)	(0.09)	(0.03)	(0.05)	(0.31)
50	2.03^{a}_{a}	0.11^{a}_{a}	0.94^{b}_{a}	2.16^{a}_{a}	2.05^{a}_{ab}	0.40^{b}_{b}	1.06^{b}_{a}	2.47^{a}_{a}
	(0.07)	(0.02)	(0.02)	(0.15)	(0.38)	(0.27)	(0.14)	(0.27)
70	1.66^{a}_{b}	0.21^{b}_{a}	1.05^{c}_{a}	9.59^{b}_{b}	2.66^{a}_{b}	0.59^{c}_{b}	1.35^{b}_{a}	3.12^{a}_{a}
	(0.10)	(0.01)	(0.05)	(0.88)	(0.26)	(0.20)	(0.22)	(0.38)
Winter								
15	2.70^{c}_{a}	0.05^{a}_{a}	1.00^{b}_{a}	2.57^{a}_{a}	2.20^{b}_{b}	0.13^{a}_{a}	1.34^{a}_{b}	2.64^{a}_{a}
	(0.11)	(0.02)	(0.04)	(0.18)	(0.08)	(0.04)	(0.06)	(0.20)
30	2.32^{b}_{a}	0.08^{a}_{a}	1.05^{b}_{b}	2.17^{a}_{a}	2.36^{a}_{a}	0.17^{a}_{a}	1.71^{c}_{ab}	2.79^{a}_{a}

Table 4 cont'd

	(0.07)	(0.01)	(0.04)	(0.14)	(0.10)	(0.04)	(0.07)	(0.20)
50	1.99^{b}_{a}	0.01^{a}_{a}	1.01^{b}_{a}	1.92^{a}_{a}	2.06^{a}_{a}	0.29^{a}_{a}	1.34^{a}_{a}	2.36^{a}_{a}
	(0.09)	(0.03)	(0.04)	(0.11)	(0.14)	(0.05)	(0.07)	(0.12)
70	1.12^{a}_{a}	0.10^{a}_{a}	0.77^{a}_{a}	6.25^{b}_{a}	2.18^{a}_{a}	0.22^{a}_{a}	1.61^{b}_{a}	5.57^{c}_{a}
	(0.08)	(0.03)	(0.06)	(0.34)	(0.14)	(0.03)	(0.12)	(1.86)

A One-way ANOVA (factor soil depth) was performed for each climatic season and results of the Tukey test are given only, if differences were significant (different letters indicate significant differences, $p<0.05$; a represents the lowest mean). A T-test (factor slope) was done to test mean differences between the dormant and growing seasons for the different soil depths; level of significance is shown as: ns: not significant, $p>0.10$; (*), $p<0.10$; *$p<0.05$; **$p<0.01$; ***$p<0.001$. Standard deviations in bracket.

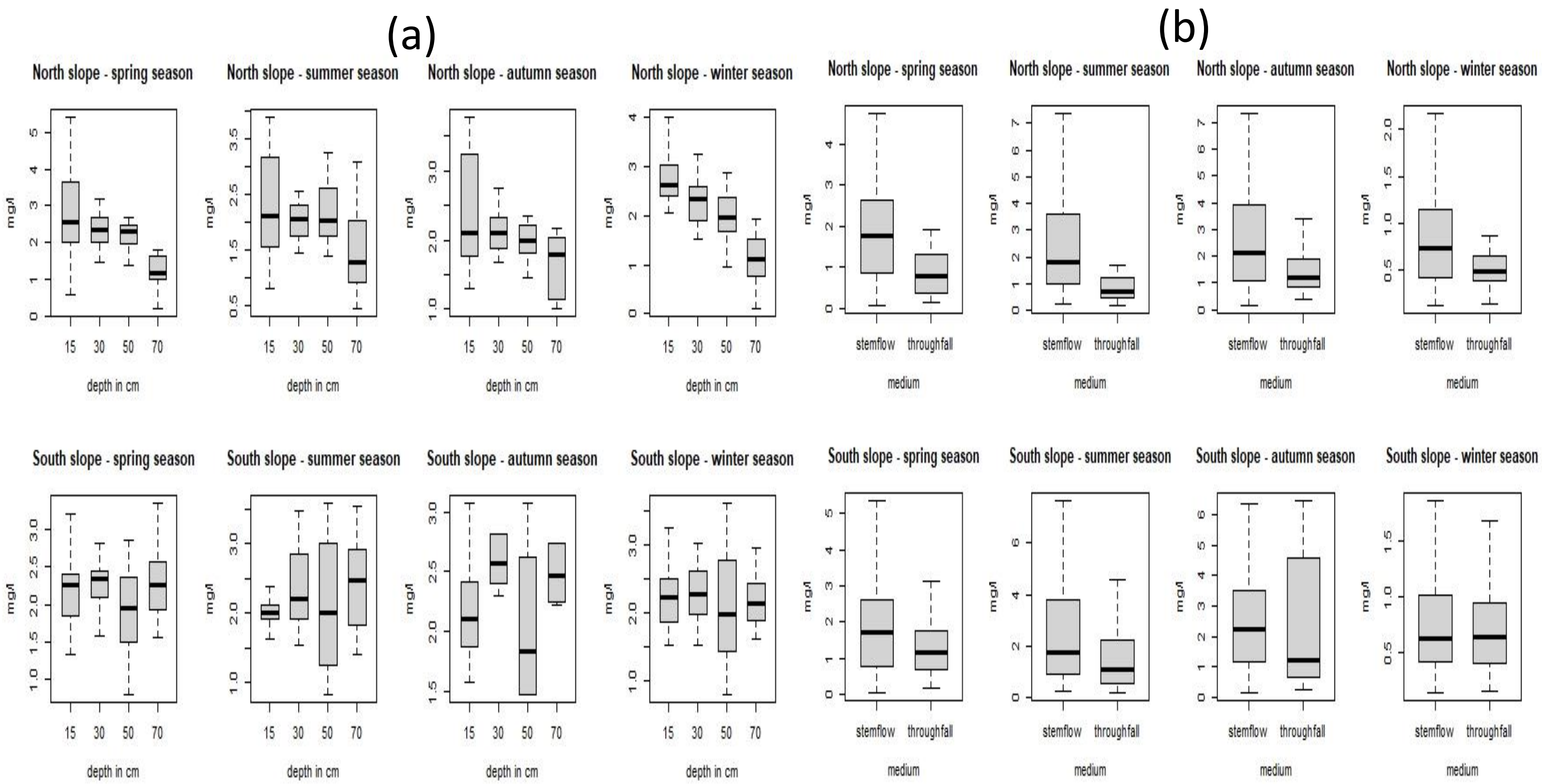

Figure 9: Calcium concentration in (a) soil and (b) stemflow and throughfall in the different annual meteorological seasons

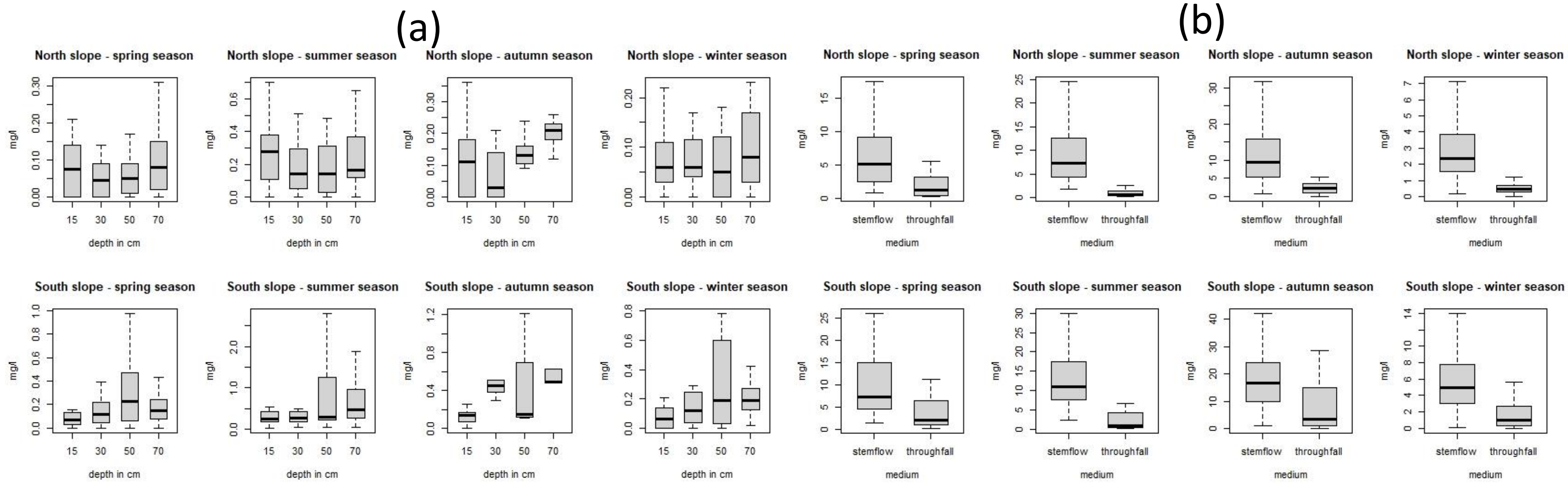

Figure 10: Potassium concentration in (a) soil and (b) stemflow and throughfall in the different annual meteorological seasons

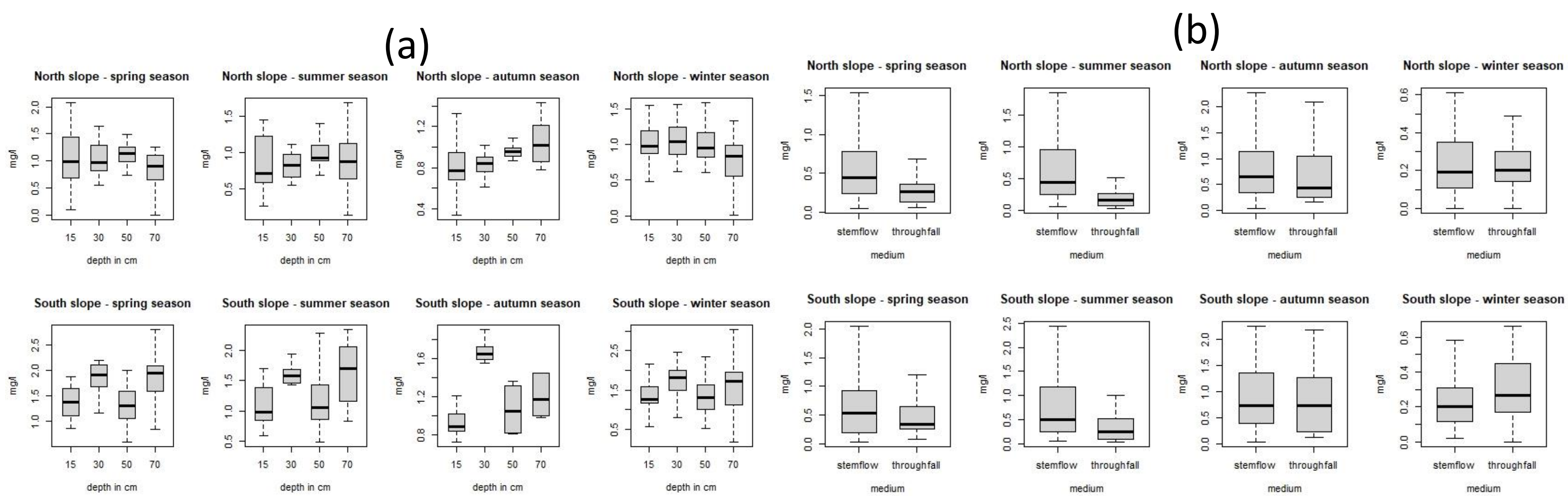

Figure 11: Magnesium concentration in (a) soil and (b) stemflow and throughfall in the different annual meteorological seasons

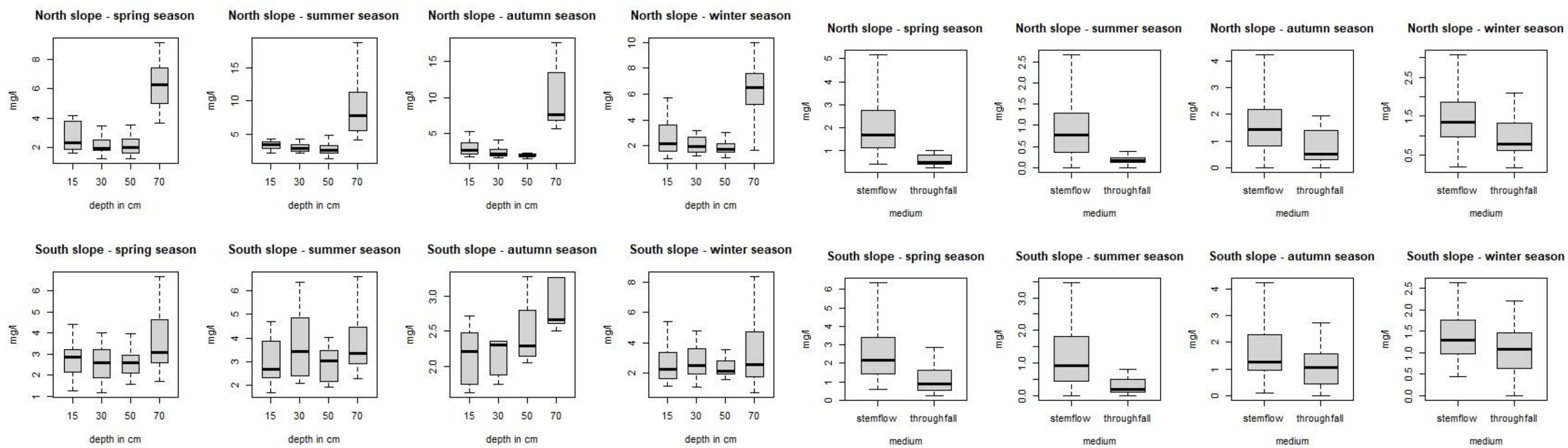

Figure 12: Sodium concentration in (a) soil and (b) stemflow and throughfall in the different annual meteorological seasons

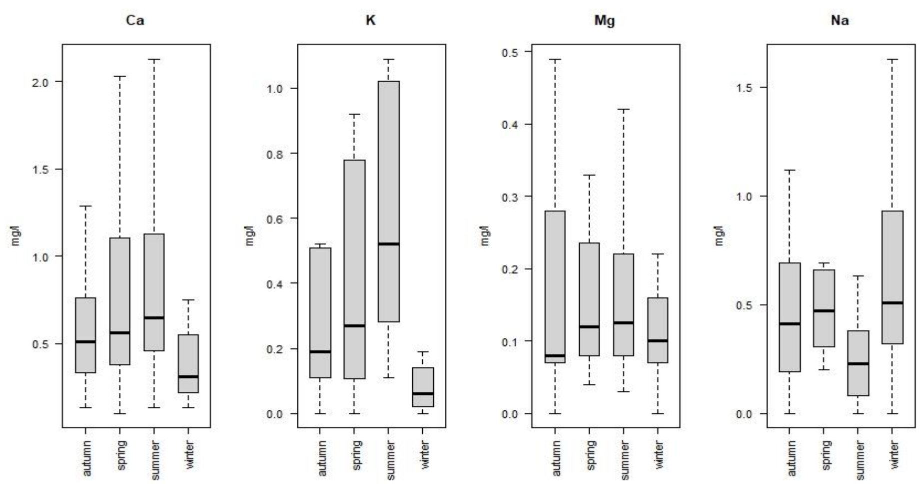

Figure 13: Cation concentrations in precipitation in the different annual meteorological seasons

Table 5: Concentrations of base cations (mg/l) in stemflow, throughfall and precipitation in the different meteorological seasons

	Ca	K	Mg	Na	Ca	K	Mg	Na
North					**South**			
Spring								
Stemflow	2.73 $^{a}_{b}$	10.19 $^{b}_{b}$	0.89 $^{b}_{b}$	2.38 $^{b}_{c}$	2.70 $^{a}_{b}$	15.28 $^{b}_{b}$	1.03 $^{a}_{b}$	2.81 $^{b}_{b}$
	0.34	1.41	0.13	0.24	0.35	1.86	0.15	0.24
Throughfall	1.06 $^{ab}_{b}$	3.24 $^{a}_{c}$	0.38 $^{ab}_{a}$	0.67 $^{a}_{bc}$	1.65 $^{a}_{b}$	5.48 $^{a}_{c}$	0.69 $^{a}_{bc}$	1.13 $^{a}_{b}$
	0.20	0.94	0.08	0.09	0.30	1.41	0.15	0.14
Precipitation	0.82 $^{a}_{c}$	1.35 $^{a}_{c}$	0.20 $^{a}_{c}$	0.68 $^{a}_{c}$	0.82 $^{a}_{c}$	1.35 $^{a}_{c}$	0.20 $^{a}_{c}$	0.68 $^{a}_{c}$
	0.16	0.65	0.06	0.19	0.16	0.65	0.06	0.19
Summer								
Stemflow	2.90 $^{b}_{b}$	9.42 $^{b}_{b}$	0.73 $^{b}_{b}$	0.94 $^{b}_{a}$	2.82 $^{b}_{b}$	14.68 $^{b}_{b}$	0.84 $^{b}_{b}$	1.27 $^{b}_{a}$
	0.26	0.61	0.07	0.07	0.26	1.02	0.08	0.10
Throughfall	1.01 $^{a}_{b}$	1.06 $^{a}_{b}$	0.22 $^{a}_{a}$	0.19 $^{a}_{a}$	1.79 $^{ab}_{b}$	2.71 $^{a}_{b}$	0.41 $^{a}_{b}$	0.30 $^{a}_{a}$
	0.16	0.20	0.03	0.07	0.32	0.66	0.08	0.09
Precipitation	0.87 $^{a}_{c}$	0.85 $^{a}_{b}$	0.17 $^{a}_{b}$	0.19 $^{a}_{a}$	0.87 $^{a}_{c}$	0.85 $^{a}_{b}$	0.17 $^{a}_{b}$	0.19 $^{a}_{a}$
	0.13	0.18	0.03	0.12	0.13	0.18	0.03	0.12
Autumn								
Stemflow	3.08 $^{b}_{b}$	11.52 $^{b}_{b}$	0.92 $^{b}_{b}$	1.72 $^{b}_{b}$	2.60 $^{b}_{b}$	20.94 $^{b}_{c}$	0.93 $^{b}_{b}$	1.64 $^{b}_{a}$
	(0.27)	(0.72)	(0.08)	(0.17)	0.19	1.62	0.07	0.10
Throughfall	1.46 $^{a}_{bc}$	4.03 $^{a}_{d}$	0.68 $^{ab}_{b}$	0.90 $^{a}_{c}$	2.56 $^{b}_{b}$	9.27 $^{a}_{d}$	0.92 $^{b}_{bc}$	1.41 $^{b}_{b}$
	0.14	0.94	0.10	0.18	0.43	2.20	0.15	0.31
Precipitation	0.64 $^{a}_{b}$	0.16 $^{a}_{a}$	0.17 $^{a}_{b}$	0.59 $^{a}_{b}$	0.64 $^{a}_{b}$	0.16 $^{a}_{a}$	0.17 $^{a}_{b}$	0.59 $^{a}_{b}$
	0.10	0.30	0.04	0.18	0.10	0.30	0.04	0.18
Winter								
Stemflow	1.00 $^{b}_{a}$	3.33 $^{b}_{a}$	0.30 $^{a}_{a}$	1.62 $^{a}_{b}$	0.83 $^{b}_{a}$	6.38 $^{b}_{a}$	0.28 $^{b}_{a}$	1.51 $^{b}_{a}$
	0.09	0.30	0.03	0.10	0.06	0.58	0.03	0.08
Throughfall	0.59 $^{a}_{a}$	0.36 $^{a}_{a}$	0.26 $^{a}_{a}$	1.08 $^{a}_{c}$	0.74 $^{ab}_{a}$	2.14 $^{a}_{a}$	0.33 $^{a}_{a}$	1.19 $^{b}_{b}$
	0.07	0.13	0.05	0.20	0.07	0.48	0.04	0.14
Precipitation	0.45 $^{a}_{a}$	0.11 $^{a}_{a}$	0.13 $^{a}_{a}$	0.60 $^{a}_{b}$	0.45 $^{a}_{a}$	0.11 $^{a}_{a}$	0.13 $^{a}_{a}$	0.60 $^{a}_{b}$

Table 5 cont'd

	0.07	0.03	0.02	0.09	0.07	0.03	0.02	0.09

A One-way ANOVA was performed for each season and results of the Tukey test are given only, if differences were significant (different letters indicate significant differences, p<0.05; a represents the lowest mean). Another One-way ANOVA was done to test mean differences between the different climatic seasons for stemflow, throughfall and precipitation; level of significance is shown as: ns: not significant, p>0.10; (*), p<0.10; *p<0.05; **p<0.01; ***p<0.001. Standard deviations in bracket.

3.5 Inter-seasonal variation in the concentration of selected cations for individual soil depths

Table 4 also shows the inter-seasonal variations in the concentration on soil cations for the different soil depth (statistical differences denoted with letters in subscripts).

Within the north slope, the concentrations of soil Ca showed no statistical differences in mean values at the 15 cm, 30 cm, and 50 cm soil depths in all four meteorological seasons of the year, with the highest concentration at the 70 cm soil depth. Ca concentration was lowest for the soils in the south slope during the summer while showing no statistical differences in the concentrations between other seasons at the 15 cm depth. Ca concentration was also not significantly different across all seasons at the 30 cm depth. Also, the highest soil Ca concentration recorded in the 50 cm, and 70 cm depths of the south slope were in the summer and autumn seasons.

Soil K concentration displayed less variations especially at the north slopes. The soils within the north slope showed no variability in their K concentrations at the 30 cm, 50 cm and 70 cm depths across the seasons. However, K concentration was highest during the summer for the 15 cm soil depth at the north slope, with other depths showing no statistical differences. K concentration showed the largest mean values within the south slope during the summer and autumn at all depths. Additionally, the lowest soil K concentration was consistently observed during the winter and spring seasons at all soil depths.

Between both slopes, the largest concentration of Mg in soil solution was observed in the 15 cm and 30 cm depths, with no significant differences observed in the 50 cm and 70 cm depth across all meteorological seasons. Within the north slope, the lowest Mg concentration in the 15 cm depth was recorded during the winter season, with no significant differences in that of other seasons. However, differing results were observed in the opposite slope, where the highest concentrations were observed in both spring and winter seasons. At the 30 cm depth, soil Mg concentration exhibited the largest fconcentration in the summer and autumn at the north slope, with the largest concentrations observed in the spring seasons at the south slope.

Unlike other cations, Na concentrations in soil solution showed very weak inter-seasonal variations. Asides from the 70 cm depth, the soil Na concentration at the north slope was consistently higher in the summer season, with no significant differences observed in their concentration in the other seasons. Na concentration was highest at the 70 cm soil depth at the summer and autumn seasons in the north slope. Almost similar results were also observed in the south slope. There were no significant differences in the soil Na concentration at the 15 cm and 70 cm depths across all seasons in the soils of the south slope. However, the largest soil Na concentration in the 30 cm and 50 cm depths was observed during the summer seasons. The concentrations at these depths showed no statistical differences across other seasons.

3.6 Dynamic variations of selected cations in stemflow, throughfall and precipitation within yearly meteorological seasons

Table 5 provides detailed information of the dynamics of cations in stemflow, throughfall and precipitation within individual meteorological seasons throughout the study period.

At the north slope, the largest cation concentrations were observed in the stemflow (2.73 mg/l) compared to throughfall (1.06 mg/l) and precipitation (0.82 mg/l) during the spring. The cation concentration also showed no statistical differences between throughfall and precipitation in the spring season. At the south slope, bivalent cations (Ca and Mg) displayed different trends from the monovalent cations during the spring season. Ca and Mg concentrations in stemflow, throughfall and precipitation were not statistically different during the spring season. The largest concentrations of K and Na at the south slope were also observed in the stemflow compared to throughfall and precipitation.

Displaying similar behaviours as in the spring season, cations concentration in the autumn season were predominantly largest in the stemflow at the north slope, with no significant differences observed in the concentrations between throughfall and precipitation. The concentration of Ca, Mg and Na showed a similar trend in these aerial depositions during the autumn season at the south slope. The concentrations of these cations were largest in both stemflow and throughfall and were not statistically different. However, stemflow (20.94 mg/l) K concentration at the south slope during the autumn season was significantly higher than throughfall (9.27 mg/l) and precipitation (0.16 mg/l).

During the summer, the highest concentration of all cations was observed in the stemflow on both slopes. Also, the concentrations of cations in precipitation and throughfall showed no statistical differences in both slopes. Similarly, the stemflow cation concentration was generally higher compared to throughfall and precipitation in both slopes.

In the winter season, the concentration of Ca and K were significantly higher in stemflow in both slopes. At the same time, Na and Mg showed no statistical differences in their concentrations in stemflow, throughfall and precipitation within the north slopes. Na concentrations in stemflow and throughfall were higher and significantly different from that in precipitation within the south slope. The Mg concentration were also larger in stemflow during the winter seasons in the south slope.

3.7 Inter-seasonal variation in the concentration of selected cations in stemflow, throughfall and precipitation

Table 5 also shows the inter-seasonal variations in the concentrations of cations in stemflow, throughfall and precipitation (statistical differences denoted with letters in subscripts). Cation concentrations in stemflow were generally lower during the winter seasons. The concentrations of cations showed no statistical differences in spring, autumn and summer. However, very high K concentrations in stemflow were observed during the autumn season. Cation concentrations in throughfall also displayed the largest concentrations in the autumn seasons, with the lowest concentrations observed in the winter. Generally, concentrations of cations exhibited the largest concentrations during the spring season compared to other seasons.

3.8 Interannual variation in soil cations across the different seasons within the north slope

Table 6 and 7 shows the interannual concentrations of soil Ca and K within both slopes across the different seasons of the year. Bearing in mind the significant role of K and Ca in the productivity of forest and the hazy trends of these cations in the different mediums during the growing and dormant seasons and their relatively lower dynamics across the different meteorological seasons, both cations have been selected for a more profound investigation into their concentrations in different the years. Additionally, their contrasting behaviour among throughfall, stemflow and precipitation makes these two cations interesting to understand in forest soils. The result shows interesting dynamic variations for soil cations across the same seasons for the different years. Generally, the highest cation concentrations were observed in the year 2018 for all seasons.

Significant differences in the cation concentrations were observed across the years. However, within the north slope (Table 4), the soil cations did not significantly differ during the winter seasons of the different years. Quite interestingly, the largest concentrations of Ca and K at the 15 cm and 30 cm soil depths at both slopes were observed during the summer season in 2018. The table also shows that the cation concentrations displayed similar trends between the spring and autumn seasons of the year in the 15 cm and 30 cm soil depth.

Table 6: Concentration of soil cations (mg/l) on an interannual and seasonal basis within the north slope

	Spring		Summer		Autumn		Winter	
	Ca	K	Ca	K	Ca	K	Ca	K
15 cm								
2018	3.93^{b}	0.12^{a}	3.32^{c}	0.35^{b}	2.29^{a}	0.14^{b}	2.90^{a}	0.09^{a}
	(0.23)	(0.02)	(0.75)	(0.05)	(0.16)	(0.03)	(0.13)	(0.02)
2019	2.36^{b}	0.04^{a}	2.04^{b}	0.09^{a}	2.63^{a}	0.06^{a}	2.51^{a}	0.06^{a}
	(0.08)	(0.02)	(0.25)	(0.04)	(0.42)	(0.00)	(0.17)	(0.01)
2020	1.09^{a}	0.18 ^{a}	0.84^{a}	0.04^{a}	N/A	N/A	2.20^{a}	0.04^{a}
	(0.14)	(0.08)	(0.01)	(0.08)			(0.55)	(0.01)
30 cm								
2018	2.57^{b}	0.03^{a}	2.13^{b}	0.26^{b}	2.10^{a}	0.10^{b}	2.56^{c}	0.09^{b}
	(0.09)	(0.02)	(0.07)	(0.03)	(0.09)	(0.03)	(0.09)	(0.01)
2019	2.44^{b}	0.05^{a}	1.80^{a}	0.06^{a}	2.04^{a}	0.00^{a}	2.38^{b}	0.04^{a}
	(0.09)	(0.02)	(0.08)	(0.01)	(0.19)	(0.00)	(0.13)	(0.01)
2020	1.99^{a}	0.13^{b}	1.84^{a}	0.06^{a}	4.28^{b}	0.00^{a}	2.02^{a}	0.03^{a}
	(0.09)	(0.04)	(0.13)	(0.03)	(2.10)	(0.00)	(0.10)	(0.02)
50 cm								
2018	2.41^{b}	0.07^{a}	2.57^{b}	0.30^{b}	2.01^{b}	0.13^{b}	2.23^{b}	0.10^{b}
	(0.04)	(0.01)	(0.18)	(0.07)	(0.05)	(0.01)	(0.10)	(0.01)
2019	2.29^{b}	0.08^{a}	1.79^{a}	0.02^{a}	2.18^{b}	0.00^{a}	1.95^{a}	0.00^{a}
	(0.10)	(0.01)	(0.11)	(0.00)	(1.20)	(0.00)	(0.80)	(0.00)
2020	1.94^{a}	0.11^{a}	1.77^{a}	0.08^{a}	0.00^{a}	0.00^{a}	1.95^{a}	0.04^{b}
	(0.12)	(0.04)	(0.09)	(0.05)	(0.00)	(0.00)	(0.05)	(0.02)
70 cm								
2018	1.49^{c}	0.07^{a}	2.22^{b}	0.33^{b}	1.66	0.21	1.35^{c}	0.17^{b}
	(0.07)	(0.02)	(0.27)	(0.04)	(0.10)	(0.01)	(0.09)	(0.03)
2019	1.06^{b}	0.03^{a}	0.85^{a}	0.13^{a}	N/A	N/A	1.04^{b}	0.04^{a}
	(0.05)	(0.01)	(0.08)	(0.04)			(0.16)	(0.01)
2020	0.93^{b}	0.20^{b}	0.90^{a}	0.13^{a}	N/A	N/A	0.58^{a}	0.02^{a}
	(0.16)	(0.05)	(0.07)	(0.04)			(0.01)	(0.01)

A One-way ANOVA (factor year) was performed for each soil depth and results of the Tukey test are given only, if differences were significant (different letters indicate significant differences, $p<0.05$; a represents the lowest mean). Standard deviations in bracket

Table 7: Concentration of soil cations (mg/l) on an interannual and seasonal basis within the south slope

	Spring	Summer	Autumn	Winter

	Ca	K	Ca	K	Ca	K	Ca	K
15 cm								
2018	2.23^{a}	0.08^{ab}	2.10^{b}	0.40^{b}	2.14^{a}	0.17^{b}	2.23^{ab}	0.12^{b}
	(0.15)	(0.02)	(0.10)	(0.03)	(0.16)	(0.01)	(0.11)	(0.01)
2019	2.19^{a}	0.05^{a}	1.96^{ab}	0.13^{a}	2.35^{b}	0.00^{a}	2.56^{b}	0.00^{a}
	(0.07)	(0.01)	(0.10)	(0.04)	(0.13)	(0.00)	(0.12)	(0.00)
2020	1.83^{a}	0.13^{b}	1.74^{a}	0.14^{a}	N/A	N/A	2.18^{a}	0.03^{a}
	(0.14)	(0.06)	(0.16)	(0.04)			(0.14)	(0.01)
30 cm								
2018	2.45^{a}	0.23^{b}	2.83^{b}	0.50^{b}	2.58	0.43	2.60^{c}	0.23^{b}
	(0.19)	(0.03)	(0.16)	(0.12)	(0.09)	(0.03)	(0.12)	(0.01)
2019	2.34^{a}	0.07^{a}	2.03^{a}	0.18^{a}	N/A	N/A	2.82^{c}	0.04^{a}
	(0.06)	(0.02)	(0.07)	(0.03)			(0.60)	(0.01)
2020	2.03^{a}	0.12^{a}	1.73^{a}	0.13^{a}	N/A	N/A	2.45^{b}	0.07^{a}
	(0.17)	(0.03)	(0.10)	(0.05)			(0.20)	(0.02)
50 cm								
2018	2.21^{c}	0.45^{c}	3.93^{b}	2.36^{b}	2.05	0.40	2.54^{c}	0.43^{b}
	(0.13)	(0.11)	(1.35)	(0.89)	(0.38)	(0.27)	(0.15)	(0.06)
2019	2.02^{b}	0.24^{b}	1.68^{a}	0.29^{a}	N/A	N/A	N/A	N/A
	(0.11)	(0.04)	(0.23)	(0.08)				
2020	1.56^{a}	0.16^{a}	1.11^{a}	0.12^{a}	N/A	N/A	1.76^{b}	0.14^{a}
	(0.15)	(0.04)	(0.14)	(0.05)			(0.24)	(0.05)
70 cm								
2018	2.21^{a}	0.23^{b}	2.87^{c}	0.95^{b}	2.66	0.59	2.22^{b}	0.26^{b}
	(0.14)	(0.07)	(0.22)	(0.16)	(0.26)	(0.20)	(0.13)	(0.04)
2019	2.36^{a}	0.18^{a}	2.17^{b}	0.24^{a}	N/A	N/A	N/A	N/A
	(0.11)	(0.03)	(0.22)	(0.02)				
2020	2.20^{a}	0.13^{a}	1.64^{a}	0.21^{a}	N/A	N/A	2.44^{b}	0.10^{a}
	(0.13)	(0.04)	(0.17)	(0.07)			(0.15)	(0.03)

A One-way ANOVA (factor year) was performed for each soil depth and results of the Tukey test are given only, if differences were significant (different letters indicate significant differences, $p<0.05$; a represents the lowest mean). Standard deviations in bracket

4. Discussion

4.1 Do cation concentration vary with dormant and growing seasons?

Seasonality imposed by the phenology of forest trees influences cation fluxes and concentrations within the forest ecosystem. This study shows that stemflow concentration were significantly enriched in cations compared to throughfall and precipitation in both seasons. Averaged over both slopes, Ca concentrations in stemflow (1.48 mg/l in north slope and 1.25 mg/l in south slope) was approximately two factors higher than the concentration in throughfall (0.86 mg/l in north slope and 1.07 mg/l in south slope) and precipitation (0.57 mg/l) during the dormant season. During the growing season, Ca concentration in stemflow (3.38 mg/l in north slope and 3.23 mg/l in south slope) was about two and four folds higher than their concentrations in throughfall (1.16 mg/l in north slope and 2.17 mg/l in south slope) and precipitation (0.79) respectively. However, Mg concentration did not show large differences in throughfall, stemflow and precipitation in both seasons, with the concentrations in stemflow not showing statistic differences from that in throughfall during the dormant season. Averaged over both slopes, Na concentrations in stemflow (1.50 mg/l in north slope and 1.81 mg/l in south slope) during the growing season were over two and four folds higher in throughfall (0.37 mg/l in north slope and 0.60 mg/l in south slope) and precipitation (0.30 mg/l), respectively. However, only close differences were observed among the ariel pathways in Na concentration during the dormant season. This result was similar to findings by Van Stan *et al.*, (2012) where K exhibited the largest differences in cation concentrations (compared to Na, Ca, and Mg) among the ariel depositions.

The higher concentrations of cations observed in stemflow and throughfall were primarily due to exchange processes that occur as water percolates down the tree surfaces. Additionally, with the higher contact area of stemflow solutions with tree surfaces and resultant bark leaching, they exhibit a higher concentration of cations than throughfall whose contact are only limited to the tree canopy (Staelens *et al*., 2007). Observations by Lu *et al.* (2017) showed that the largest concentrations of cations (recorded in volume-weighted mean solute concentrations) were in stemflow compared to throughfall and precipitation. Van Stan *et al*. (2012) observed the highest concentrations of Mg, K and Ca were recorded in throughfall compared to precipitation. However, the results observed under different climates and locations show other trends. Chiwa *et al*. (2003) noted that cation concentrations were largest in throughfall compared to stemflow and rainfall in areas with low urban influence in the humid-cold climate of Japan. Similarly, Rodrigo *et al*. (2003) observed higher cation concentrations in throughfall than in stemflow in sheltered areas characterised by low pollution under the Mediterranean climate of northeast Spain. However, Berger and Glatzel (1998) reported lower calcium exchange in throughfall during the leafless (dormant) season compared to leafed (growing) season in Austrian oak forest (under similar climate).

Depending on the mobility of cations, processes such as leaching of nutrients from the internal plant tissues, washing of cations from plants surfaces and their absorption into internal tissues may alter the chemistry of solution in throughfall and stemflow (Moslehi *et al*. 2019). In both seasons, the concentration of K was very high in stemflow compared to throughfall and precipitation. This could be ascribed to the very high mobility, and easier leachability of K compared to other cations (Balestrini and Tagliaferri, 2001; Hermann *et al.*, 2006; Andre *et al*., 2008). This is because K is located in the cytoplasm of plant cells and is not strongly bound to plant enzymes or structural tissues of plants (Tobón *et al.* 2004; Andre *et al.*, 2008). Findings by Baestrini and Tagliaferri (2001) showed that K concentration was over was more prominent in throughfall and over 30 factors higher than the concentrations in bulk precipitation (averaged over the study period). On the other hand, the lower concentrations of Ca may be ascribed to their tight binding to the cell walls of plants and chlorophyll and other molecular complexes in plants, thus having a very high resorption rate (Habashi *et al*., 2019). Similarly, plant demand for Mg and Na is relatively low, hence their lower availability at the foliar and stem surfaces and leaching capacity. Although significantly different, the concentrations of selected cations in stemflow and throughfall showed very similar trends, with K concentrations being the largest, while Mg concentrations were the lowest. This was in alignment with findings by Staelens et al. (2003), André et al. (2008), Van Stan *et al*. (2012), Habashi *et al*. 2019 and Moslehi *et al*. (2019).

With changes in forest canopy structure and density due to phenological seasons, the concentrations of cations in throughfall, stemflow and precipitation showed significant variations. The concentrations of Ca, K and Mg in stemflow were over two factors higher in the growing season compared to the dormant seasons. The differences observed in cations concentrations in throughfall and precipitation were relative lower in magnitude compared to their concentrations in stemflow across both seasons. Unparallel to findings by Staelens (2007), cation concentration in rainfall was significantly higher in the growing (leafed) season than in the dormant (leafless season). Reported in $mmol_c.m^{-2}$, results by Stalens *et al.*, (2007) showed that the concentrations of cations (Ca and Mg) in stemflow were five folds higher than that in throughfall and precipitation during the growing seasons. The higher concentrations observed during the growing season could be attributed to the higher vegetation surface area, canopy density, and aerial moisture that allows leaching and interception processes to occur (Duchesne *et al*., 2001; Habashi *et al*., 2019).

The establishment of chemical equilibrium and nutrient availability within the mineral soil is affected by many factors. The soil - a multipart environment consisting of solid, liquid and gaseous phases, with an active biological component - may alter the equilibrium of nutrient inputs via precipitation, throughfall and stemflow through chemical reactions at the cation exchange complex. The cation exchange complex presents a huge reactive surface for the adsorption and release of nutrients within the soil (Evangelou and Phillips, 2005; Moslehi *et al.,* 2019). Microbial mineralisation and immobilisation are also factors that could affect the concentration of nutrients in soil solution (Fujinuma *et al*., 2005; Pumpanen *et al*., 2012). This study shows that soil cation concentrations were significantly different at various depths during both seasons, with dissimilar trends observed at both slopes. The unparallel observations in both slopes may be due to the predominating physical, chemical and biological processes predominating within the soil. However, this study shows that Na concentration in soil solution was consistently largest at the lowest soil depth in both slopes. This is likely due to the lower demand of plants and soil biota for Na and its weak interaction between solution and soil surfaces (Verstraeten *et al*., 2012; Moslehi *et al.*, 2019).

The results explicitly show that soil cation concentrations were generally higher during the growing season. This may be due to the higher availability of water during the early growing season and higher soil temperatures, providing ideal conditions for microbial activities and the mineralisation of nutrients. The dormant season is characterised by lower soil temperature and freezing conditions, which may perpetuate quiescence among soil microbial communities, thus lowering the nutrient concentration in soil solution. In addition, freeze and thawing cycles of the dormant season may also alter the hydrological cycles in soils leading to and the leaching of water-soluble nutrients (Jiang *et al*., 2016). Additionally, the differences in the concentrations of inputs such as throughfall, stemflow and litter flow during the two phenological seasons could result in this disparity in concentrations of cations in soil solution. Unlike other cations, Na concentrations were significantly different between seasons across all depths in both north and south slope. This may be attributed to the higher mobility of monovalent cations compared to bivalent cations.

Averaged over the soil depths, the concentrations of Ca, Mg and Na were higher in the soil in both seasons compared to stemflow, throughfall and precipitation. This may be ascribed to the ability of the ability of the soil exchange sites to hold these cations for tree uptake. Our findings were similar to those of Moslehi *et al.,* (2019), where the concentrations of Ca, Mg and Na were two, four and three factors higher in the top soil compared to the concentrations in stemflow. Unlike other cations, K concentrations in soils were deficient and several magnitudes lower than that in throughfall and stemflow. Our results also showed that the of cations in precipitation were generally lower than in soil solution.

4.2 Do cation concentration vary with climatic seasons?

Since the transport of cations within the forest ecosystem is mediated by water from precipitation, alteration in hydrological cycles imposed by the different climatic seasons will impact the biogeochemical cycling of nutrients. Similar to the dynamics of cations due to tree phenology, concentrations of cations in stemflow were predominantly higher than in precipitation and throughfall in the different meteorological seasons. Averaged over the entire seasons, Ca concentration in stemflow was two and three folds higher than the concentrations in throughfall and stemflow respectively. Similarly, K concentrations in stemflow was over ten and four factors higher in precipitation and throughfall respectively across all seasons. Comparable trend of results was also observed with the concentrations of Mg and Na with the largest magnitude of differences observed in the aerial depositions during the winter season. As earlier discussed, the relatively higher concentrations in stemflow amongst the aerial depositions can be ascribed to the higher contact of stemflow solution with tree barks leading to a more significant alteration in their solution chemistry (Staelens *et al*., 2007). In all meteorological seasons, the concentration of K was highest in stemflow, with Na exhibiting the lowest concentrations (K > Ca > Na > Mg). Cation concentrations in throughfall and precipitation followed similar patterns (K > Ca > Mg > Na). This is in agreement with previous findings by Staelens *et al.* (2003), André *et al*. (2008), Van Stan *et al.* (2012), Habashi et al. (2019) and Moslehi *et al*. (2019).

The concentrations of cations in stemflow and throughfall were significantly higher during the autumn and spring seasons at both slopes. Stemflow concentrations of Ca and K during the winter seasons were two and three factors higher than their concentrations in the spring and autumn seasons. This result was also similar to findings by Lu *et al*. (2017) and Moslehi *et al*. (2016) where they noted the highest concentrations of Ca, Mg, Na and K in stemflow and throughfall during the early spring season. These periods coincide with the high degree of vegetative growth and availability of precipitation which allows the wash down of nutrients on foliar and bark surfaces into the forest. The high concentration of cation during the autumn season may be as a result of nutrient release with canopy senescence before the leaves are lost as litter to the forest floor. The low cation concentrations observed during the winter season is likely due to the lower availability of precipitation and the dormancy of trees during this period. Nutrient exchange on canopy and stem surfaces is also limited in the winter seasons because of lower soil moisture availability, limited nutrient uptake, and lower vegetative growth. Cation concentrations in precipitation were also highest during the spring season. This period coincides with the highest annual precipitation, hence the higher likelihood of ionic inputs in their particulate phases in the atmosphere.

Within each season, the concentration K, Mg and Na in soil solution showed no clear pattern between the two slopes. This is in alignment to conclusions by Berger *et al.,* (2009a) where they reported cation cycling within forests are dependent on the site, individual element and associated processes. The highest concentrations of Ca within the soil system were generally observed at the top 15 cm depths for individual seasons. This is possibly due to the direct effect of the chemistry of solutions from stemflow, throughfall and precipitation on the topsoil. The high concentrations at the topsoil relative to the lower soil depth may also be attributed to the activity of mineralisers on forest litter and litter flow solution, which we did not consider in this study (Tobón *et al.*, 2004; Ndakara, 2012). Quite interestingly, K concentration in solution did not change across the soil depths for individual seasons at the north slope, with soil solution concentration at the south slope displaying higher concentrations compared to the lower depths for each season. While the concentrations of the cations displayed diverse behaviours in different soil depths and seasons, the lowest concentrations of all cations were consistently observed during the winter seasons. This may be attributed to the lower cation inputs from stemflow, precipitation and throughfall in the winter season. This may also be due to the limited activities of mineralisers due to the impact of freeze-thaw events and their consequent dormancy. (Lemma *et al*., 2007; Jiang *et al*., 2016). Also, the smaller concentrations of cations in soil solution may be attributed to the limited mobility of water during the winter seasons due to freezing at or near the soil surfaces, restricting the mobility of cations in soil solutions, hence, their low concentrations (Cho et al., 2016). Similar findings were also reported by Jaing *et al*. (2016) and Habashi *et al.* (2019). These authors attributed their results to the lower input of cations from throughfall and the reduced microbial activities due to limited soil moisture and lower temperatures during the winter.

With the shifts in climatic conditions due to climate change, we attempted to elucidate this impact on the biogeochemical cycling of nutrients within the soils of our experimental site. The rationale for this assessment was due to the significant climatic shifts observed during this period and their impact on the forest ecosystem (Schuldt et al., 2020). Environmental impact, especially with the parched summer and heatwave of 2018, has been reported to affect forest health resulting in drought stress, premature leaf shedding and widespread leaf discolouration (Henal *et al.,* 2018; Schuldt et al., 2020). Our results showed significant variations in the concentration of soil cations (Ca and K) in the different seasons of the three years (2018, 2019, and 2020) at both slopes. Patterns of cation variation were more explicit in the soils at the north slope, where the highest concentrations of cations were generally observed in all meteorological seasons of the year 2018. Particularly, the concentrations of cation in soil solution during the summer period of 2018 (with notable heatwaves) was higher in soils compared to other years. Incongruous to our expectation, this result implies that the forest environment was not severely affected with regards to the biogeochemical cycling of nutrients. While the exact reasons for this annual and seasonal changes in soil cation concentration may not be easily suggested, variations in the levels of climatic variables in the different years will affect forest ecosystems. Lu *et al.,* (2017) reported cation concentrations in stemflow, throughfall and precipitation showed differences in the years 2011, 2012 and 2013 (the last extreme summer drought prior to 2018 was recorded in 2013). This will affect the input of cations into forest soils. The temperature within the soil is also positively correlated with atmospheric temperature (Pumpanen *et al.*, 2012), which could impact microbial activity (Barreiro *et al.*, 2020). as well as solute transport at different soil depths (Mon *et al.,* 2016).

4.3 Relationship between solution chemistry of the different medium

Correlation tables showing the relationships between cation concentrations in the different mediums and seasons are shown in appendixes 1, 2, 3 and 4 for Ca, K, Mg and Na respectively. Generally, the results show very weak relationships between the concentrations in the aerial pathways (stemflow, throughfall and precipitation) and soil individual cations in the different climatic seasons. Quite distinctively, the impact of throughfall solution was more prominent than that of rainfall and stemflow on soils. The results show that this relationship between throughfall and soil solution at the 15 cm depth was strongest during the autumn seasons, with r^2 ranging between 0.39 -0.41 during the autumn seasons for Ca, K and Mg. The positive correlations observed at the topsoil do not present a surprise as most of the significant processes that occur during the passage of nutrients into the deeper soils occur at the topsoil (Berger *et al.*, 2009b). However, a similar relationship could not be established for Na concentrations in different medium. Additionally, one may not alienate the fact that the robust relationship observed particularly in autumn seasons conforms to the times of the year with the a relatively high preponderance of litterfall. The litter, which previously make up the canopy during the leafy seasons and the resulting litter solution are biochemically more similar to throughfall solution. This could an added reason that contributes to the strong relationship between top soil solution and that of throughfall.

Conversely, soil nutritional properties influence the chemistry of stemflows and throughfall. Duchesne *et al.*, (2001) showed generally higher resorption of cations in leaves of trees during the growing stages, with variations in their rates in different times of the year. They reported that a high resorption rate of Ca and Mg in soils coincided with limited availability of these cations in soils. Commensurate to findings by Duchesne *et al.*, (2001), Hegan-Thorn *et al.*, 2006, showed that the closed-cycle of nutrient accretion, resorption and losses depends on both the soil properties and the time of the year. Therefore, one could also suggest that the leaching of throughfall and stemflow in our study could be as a result of the soil property and biogeochemical cycling of nutrient that we have already shown to be established during the autumn season.

Unparallel to findings by Lu *et al.* (2017), our results showed very weak relationships between rainfall, throughfall and precipitation. These authors reported that Ca, Mg, and K concentrations showed very significant relationships between throughfall, stemflow and precipitation in their study, with no significant correlation found between throughfall and stemflow. These authors did not take into account the influence of these aerial depositions on soil solution chemistry. This result is also similar to the report of Berger *et al.* (2009a) where they found that the correlations between throughfall chemistry and that of soils were not significant for all studied cations, except for Mn (r^2: 0.42; $p < 0.001$). The stronger relationship between throughfall and soil solution chemistry may be attributed to its greater spatial influence over the soil than the equally chemically modified stemflow solution. The influence of stemflow may be more robust around the stem of trees where their aerial reach is primarily limited. The very weak relationship between precipitation and soil solution may also be attributed to the occlusion of their direct impact and modification of their chemistry by tree canopy. This impact may also be more dominant during the summer and autumn seasons, where forest canopy growth is at its peak during the year. The peak in canopy growth during the autumn seasons relative to other seasons of the year may also be the dominating factor as to why the stronger relationships were observed for Ca, K and Mg.

5. Conclusion

The result of this study shows interesting variations in the concentrations of cations in stemflow, throughfall, precipitation and soil solutions (at different depths – 15 cm, 30 cm, 50 cm, 70 cm). The dynamics of cations in stemflow, throughfall and precipitation showed different trends from their behaviour in soil solution. Ionic concentrations in stemflow were higher than in precipitation and throughfall due to the higher contact time and consequent bark leaching as the solution moves down the stem. Due to their mobility and leachability, the concentration of K in throughfall and stemflow was higher those of other cations. The concentration of cations was also higher during the growing season as well as the autumn and spring seasons. These periods were identified to coincide with the times of peak vegetative growth and moisture availability.

Together with the influence of seasonality on soil hydrological cycle, nutrient inputs in soils are influenced by the parent material, activity of soil biota, cation exchange capacity and soil acidity. The results of this study showed very different observations in the concentrations of cations in the different soil depths at both slopes. However, soil cations were generally higher in the autumn season and lower during the winter season. This result was attributed to the dormancy of mineralisers and freezing of water near the soil surface during winter. The high cation concentrations in autumn were largely due to the high inputs of cations from aerial depositions and the prevalence of soil conditions that favours nutrient release from litter. This result of this study also showed a generally weak relationship between soil cations and aerial depositions (stemflow, throughfall and precipitation). However, the most robust influence on soil cation concentration were from throughfall during the autumn season.

This study accentuates the widely accepted knowledge of the internal nutrient cycling in forest ecosystems and underscores the role of stemflow, throughfall and precipitation in improving the fertility of forest soils and the overall productivity of forest ecosystems. Additionally, the result also provides important information to forest managers that are necessary to guide their actions in maintaining a nutrient-enriched ecosystem via the returns of nutrients from precipitation, stemflow and throughfall into the soil. This results also highlights the variations in cations with forest phenology and meteorological changes during the year.

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Appendices

Appendix 1: Correlation matrix between calcium concentrations in the different medium across different seasons

	15 cm - SD	30 cm - SD	50 cm - SD	70 cm - SD	stemflow	throughfall	precipitation
Spring							
15 cm - SD	1.00						
30 cm - SD	0.10	1.00					
50 cm - SD	-0.64	-0.19	1.00				
70 cm - SD	-0.16	-0.33	0.43	1.00			
stemflow	-0.13	0.27	0.09	0.10	1.00		
throughfall	0.24	-0.24	-0.12	0.09	0.00	1.00	
precipitation	-0.17	0.16	-0.29	-0.11	0.03	-0.40	1.00
Summer							
15 cm - SD	1.00						
30 cm - SD	-0.20	1.00					
50 cm - SD	-0.02	-0.04	1.00				
70 cm - SD	-0.34	0.49	0.51	1.00			
stemflow	0.08	0.02	0.21	0.11	1.00		
throughfall	0.15	-0.43	-0.19	-0.14	0.06	1.00	
precipitation	-0.21	0.19	-0.17	-0.01	0.36	-0.14	1.00
Autumn							
15 cm - SD	1.00						
30 cm - SD	0.04	1.00					
50 cm - SD	-0.18	-0.27	1.00				
70 cm - SD	0.18	0.08	0.07	1.00			
stemflow	-0.43	0.07	-0.08	0.30	1.00		
throughfall	0.41	-0.21	0.11	0.30	0.04	1.00	
precipitation	0.01	0.23	0.17	-0.15	0.00	-0.33	1.00

Appendix 1 cont'd

Winter

15 cm - SD	1.00						
30 cm - SD	0.47	1.00					
50 cm - SD	0.11	-0.48	1.00				
70 cm - SD	-0.21	-0.39	0.45	1.00			
stemflow	-0.38	-0.13	-0.01	0.21	1.00		
throughfall	0.01	0.02	-0.24	0.24	-0.35	1.00	
precipitation	-0.30	0.06	-0.40	-0.17	0.02	0.14	1.00

SD = soil depth

Appendix 2: Correlation matrix between potassium concentrations in the different medium across different seasons

	15 cm - SD	30 cm - SD	50 cm - SD	70 cm - SD	stemflow	throughfall	precipitation
Spring							
15 cm - SD	1.00						
30 cm - SD	0.14	1.00					
50 cm - SD	0.63	0.08	1.00				
70 cm - SD	0.28	0.19	0.49	1.00			
stemflow	-0.13	0.10	-0.07	-0.10	1.00		
throughfall	-0.76	-0.25	-0.33	-0.21	-0.22	1.00	
precipitation	0.07	0.17	0.09	0.20	0.15	-0.09	1.00
Summer							
15 cm - SD	1.00						
30 cm - SD	0.05	1.00					
50 cm - SD	0.29	-0.02	1.00				
70 cm - SD	0.15	-0.16	0.41	1.00			
stemflow	0.13	-0.13	0.07	0.38	1.00		
throughfall	-0.44	-0.28	-0.01	0.08	-0.19	1.00	
precipitation	0.04	0.15	-0.16	-0.13	-0.17	-0.24	1.00
Autumn							
15 cm - SD	1.00						
30 cm - SD	-0.17	1.00					
50 cm - SD	0.45	-0.08	1.00				
70 cm - SD	0.39	-0.13	0.24	1.00			
stemflow	-0.43	0.38	-0.09	-0.08	1.00		
throughfall	**0.41**	-0.10	0.17	0.53	-0.16	1.00	
precipitation	-0.09	0.28	-0.34	0.17	0.08	-0.04	1.00
Winter							
15 cm - SD	1.00						

Appendix 2 Cont'd

30 cm - SD	0.46	1.00					
50 cm - SD	-0.50	-0.05	1.00				
70 cm - SD	0.31	0.18	-0.25	1.00			
stemflow	0.56	0.20	-0.05	0.30	1.00		
throughfall	0.28	-0.02	-0.23	0.85	0.23	1.00	
precipitation	-0.56	-0.44	0.63	-0.04	-0.16	-0.05	1.00

SD = soil depth

Appendix 3: Correlation matrix between magnesium concentrations in the different medium across different seasons

	15 cm - SD	30 cm - SD	50 cm - SD	70 cm - SD	stemflow	throughfall	precipitation
Spring							
15 cm - SD	1.00						
30 cm - SD	-0.14	1.00					
50 cm - SD	-0.43	0.17	1.00				
70 cm - SD	-0.09	0.00	-0.24	1.00			
stemflow	-0.11	0.17	0.04	-0.01	1.00		
throughfall	-0.09	-0.18	-0.16	0.36	0.12	1.00	
precipitation	-0.05	-0.10	-0.32	0.33	-0.17	-0.06	1.00
Summer							
15 cm - SD	1.00						
30 cm - SD	-0.21	1.00					
50 cm - SD	-0.08	0.00	1.00				
70 cm - SD	-0.14	0.60	0.10	1.00			
stemflow	0.12	-0.11	0.16	0.10	1.00		
throughfall	0.07	-0.37	-0.17	-0.29	0.06	1.00	
precipitation	-0.11	0.45	0.01	0.15	0.09	-0.24	1.00
Autumn							
15 cm - SD	1.00						
30 cm - SD	0.25	1.00					
50 cm - SD	-0.43	-0.06	1.00				
70 cm - SD	0.23	0.22	-0.47	1.00			
stemflow	-0.06	0.14	0.05	0.21	1.00		
throughfall	**0.39**	-0.03	-0.14	-0.12	-0.22	1.00	
precipitation	-0.20	0.10	-0.01	0.24	0.16	-0.61	1.00

Appendix 3 Cont'd

Winter							
15 cm - SD	1.00						
30 cm - SD	-0.28	1.00					
50 cm - SD	0.27	-0.42	1.00				
70 cm - SD	0.45	-0.48	0.42	1.00			
stemflow	-0.18	-0.16	-0.04	0.20	1.00		
throughfall	**0.44**	0.17	-0.25	0.02	-0.35	1.00	
precipitation	-0.27	0.15	-0.12	-0.18	-0.18	-0.08	1.00

SD = soil depth

Appendix 4: Correlation matrix between magnesium concentrations in the different medium across different seasons

	15 cm - SD	30 cm - SD	50 cm - SD	70 cm - SD	stemflow	throughfall	precipitation
Spring							
15 cm - SD	1.00						
30 cm - SD	-0.06	1.00					
50 cm - SD	0.38	0.15	1.00				
70 cm - SD	-0.33	0.19	-0.38	1.00			
stemflow	0.44	0.20	0.03	-0.24	1.00		
throughfall	-0.27	-0.02	-0.67	0.05	-0.15	1.00	
precipitation	-0.23	-0.02	-0.24	0.08	-0.18	0.16	1.00
Summer							
15 cm - SD	1.00						
30 cm - SD	0.24	1.00					
50 cm - SD	0.24	0.79	1.00				
70 cm - SD	0.07	-0.02	0.07	1.00			
stemflow	-0.14	0.02	0.22	0.19	1.00		
throughfall	0.22	0.02	-0.06	-0.26	-0.17	1.00	
precipitation	-0.02	0.16	0.16	0.44	0.17	-0.27	1.00
Autumn							
15 cm - SD	1.00						
30 cm - SD	-0.26	1.00					
50 cm - SD	0.29	-0.40	1.00				
70 cm - SD	0.04	-0.35	0.40	1.00			
stemflow	-0.19	-0.03	0.01	-0.47	1.00		
throughfall	-0.01	-0.04	-0.37	-0.01	-0.26	1.00	
precipitation	-0.01	-0.07	0.15	-0.09	0.07	-0.46	1.00

Appendix 4 Cont'd

Winter							
15 cm - SD	1.00						
30 cm - SD	0.10	1.00					
50 cm - SD	-0.35	-0.11	1.00				
70 cm - SD	-0.25	-0.14	-0.30	1.00			
stemflow	0.15	0.01	-0.15	-0.14	1.00		
throughfall	0.25	0.19	-0.11	-0.17	-0.30	1.00	
precipitation	-0.16	-0.27	0.61	-0.25	0.07	-0.19	1.00

SD = soil depth

Affirmation

Name: Enemo David Chukwuebuka, Matriculation No.: 21743337
Degree Course: International Master of Science in Soils and Global Change (IMSOGLO) Module: Master-

I, hereby confirm that this thesis entitled with "Dynamics and seasonal variations in base cations of a temperate beech forest at two close-by sites" is done in partial fulfilment of the requirements for the degree of Master of Science in Soils and Global Change. I declare that this work is done exclusively by me under the supervision of my supervisors and no other sources were used except from secondary literature which are accordingly cited. I have complied with the guidelines on good academic practice at the University of Göttingen. I am aware that failure to comply with these principles will result in the examination being graded "nicht bestanden", i.e. failed. I take full responsibility for this work.

Göttingen, September, 2021.

Enemo David Chukwuebuka