Quantification of Enrichment Processes in Throughfall and Stemflow in a Mixed Temperate Forest

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Abstract

Forest ecosystems depend on throughfall and stemflow fluxes for both water and nutrient input. Spatial and temporal variability of throughfall and stemflow fluxes are large and differ between tree species. The nutrient fluxes that accompany throughfall and stemflow are affected by climate, precipitation intensity, the seasonality of dry deposition, and canopy exchange processes. The interdependence of these factors make it challenging to quantify changes in throughfall and stemflow amounts as well as their nutrient content. Here we provide observation-based evidence from 3.5 years of record with 222 rainfall events, of the seasonal variability of throughfall and stemflow magnitude and ion concentrations under a beech (*Fagus silvatica*) and spruce (*Picea abies*) tree. Interception and canopy cover were seasonally variable, average annual interception was 53% below beech, 61% below spruce and 68% below young spruce canopies. Further we assess seasonality of ionic nutrients such as NH $_4$ and NO $_3$ as well as Mg, Ca and K and their dependence on both dry deposition and canopy exchange. Throughfall and stemflow were enriched compared to precipitation, with large differences between ions and different months. Antecedent precipitation was a main control on throughfall and stemflow enrichment. We developed a conceptual model of the potential drivers of throughfall and stemflow enrichment based on our observations. While NH $_4$ and NO $_3$ enrichment are likely dominated by dry deposition and dew and fog accumulation, Mg, Ca and K were additionally affected by canopy exchange. Observation based studies such as this one are needed to understand precipitation and nutrient partitioning across forests, which enables to predict how changes in climate and forest composition will affect local hydrology and nutrient inputs into forest ecosystems.

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²⁶ 1 Introduction

Forests cover 38% of the habitable land area and have major impact on water and nutrient 27 fluxes between the lithosphere and the atmosphere (Betts et al., 2001; Bonan, 2002; Levia 28 and Frost, 2006; Veen et al., 1996). Ongoing climate change will affect the forest ecosystem 29 through changes in precipitation, air temperature and CO_2 concentrations (e.g. Bonan, 30 2002; Briggs, 2015; CH2018 - Climate Scenarios for Switzerland; Technical Report 2018; 31 Nabuurs et al., 2022). Climate change will also impact throughfall and stemflow by 32 which water and nutrients are distributed in the subcanopy and across forests, ultimately 33 affecting forest biogeochemistry (Adriaenssens et al., 2012; Fenn et al., 2013; Kumar 34 Gautam et al., 2017), local stand hydrology and biodiversity, depending on tree species 35 composition (De Schrijver et al., 2007; Levia and Frost, 2006; Nabuurs et al., 2022). 36

Most water enters the forest subcanopy and forest floor via throughfall (Bren, 2015; 37 Holko et al., 2009; Kofroňová et al., 2021; Krämer and Hölscher, 2009; Levia and Frost, 38 2006; Mahendrappa, 1990; Mindaš et al., 2018; Ringgaard et al., 2014; Rowe, 1983; Xiao 39 et al., 2000), with lesser contributions from stemflow (Brooks et al., 2012; Draaijers, 40 Van Eak, et al., 1992; Jost et al., 2004; Parker, 1983). This affects root growth of 41 understory vegetation as well as nutrient availability in forest soils (Levia and Frost, 42 2006; McDowell et al., 2020; Michel et al., 2013; Thimonier, Schmitt, Waldner, and 43 Rihm, 2005). The distribution of throughfall and stemflow is temporally and spatially 44 variable (Levia and Frost, 2006) and affected by precipitation amount (Brooks et al., 45 2012; Maniak, 1997; McDowell, 1998) and intensity (Brooks et al., 2012), as well as tree 46 type (Staelens, De Schrijver, Verheyen, and Verhoest, 2008), stand density (Macinnis-Ng 47 et al., 2012), and tree characteristics such as canopy cover, branch patterns and stem 48 roughness (Brooks et al., 2012; Macinnis-Ng et al., 2012; McDowell et al., 2020; Staelens, 49 De Schrijver, Verheyen, and Verhoest, 2008). As nutrient input fluxes for the forest 50 ecosystem throughfall and stemflow can on the one hand facilitate diverse ecosystem and 51 on the other hand harm the ecosystem, if certain nutrients become abundant (Eugster and 52 Haeni, 2013; Parker, 1983; Thimonier, Schmitt, Waldner, and Rihm, 2005), It is therefore 53 important to study nutrient inputs on both forest and stand scale (McDowell et al., 2020; 54 Thimonier, Schmitt, Waldner, and Rihm, 2005). Major ion inputs (Cl, Na, Mg, Ca, K, 55 NH_4 , NO_3 , and NO_2) stem from dry deposition (Andersen and Hovmand, 1999; Liu et 56 al., 2016; Lovett and S. E. Lindberg, 1984; McDowell, 1998; Sun et al., 2014), canopy 57 exchange (Brodo, 1973; Clark et al., 1998; Moffat et al., 2002) and inputs from fog and 58 dew (Groh, Pütz, et al., 2019; Klemm and Wrzesinsky, 2007), which all show distinct 59 seasonality and species dependence (Berger, Inselsbacher, et al., 2009; De Schrijver et al., 60 2007; Rothe et al., 2002). Although many of these processes are known individually, there 61 still remains a need for observation-driven evidence of the rates and seasonality of nutrient 62 enrichment by throughfall and stemflow in forests. 63

In this study we investigate climatic forcing of water and nutrient inputs into a forest ecosystem, as well as the species-specific influence of canopy cover on throughfall and stemflow amounts and seasonality. To this end, we compare throughfall and stemflow measurements under beech (*Fagus silvatica*) and spruce (*Picea abies*) to assess the differences between the locally most common deciduous and coniferous tree species in Switzerland.

⁶⁹ We collected 222 precipitation, throughfall and stemflow samples at our study site ⁷⁰ in a mixed temperate forest in Zurich, Switzerland, over the course of 3.5 years. We analysed throughfall and stemflow under a beech, spruce and young spruce canopy each
quantitatively and measured the ion concentration in all collected samples to answer the
following questions:

- How large is the seasonal variation of throughfall and stemflow under beech and spruce species and to which extent is this variability linked to precipitation intensity and seasonality of canopy cover?
- What are the nutrient enrichment rates of throughfall and stemflow compared to precipitation?
- What are the seasonal dynamics of different nutrient inputs to the forest and which
 factors explain the seasonality of nutrient enrichment?

2 Study Area and Methods

Our experimental site is a 1.5 km^2 large temperate mixed forest dominated by beech (Faque 82 silvatica) and spruce (*Picea abies*) located at the edge of the city of Zurich (Switzerland), 83 47°N 8°E, embedded in the larger "Waldlabor Zurich" initiative. The study plot lies in the 84 Holderbach catchment at a mean elevation of 510 m a.s.l. on a hillslope of 20° inclination 85 with a mean annual temperature of 9.3 °C and mean annual precipitation of 1134 mm. 86 Observations from March 2020 until November 2022 are analysed here. During this 87 time, we measured all relevant climate variables just outside the forest with a compact 88 all-in-one weather station (Meter Group - Atmos41) approximately 150 m away from our 89 study site. In the forest, we partitioned our study plot into three subplots: mature beech 90

(B), mature spruce (mS) and young spruce (yS) figure 1a. We measured throughfall (TF) 91 at all three sections and stemflow (SF) at B and mS, as the young spruces at yS do 92 not have stem diameters where stemflow measurements were feasible. Throughfall was 93 measured with 2 m long and 10 cm wide precipitation gutters installed at 1 m distance 94 from the tree stem leading into tipping precipitation gauges with 2 l bottles attached 95 for water sampling. To prevent contamination with organic material, nets were installed 96 at the end of the precipitation gutters to keep larger particles out and to prevent the 97 tipping rain gauges from clogging. Stemflow was measured with a flexible precipitation 98 gutter installed around the tree stem which led into a tipping precipitation gauge and a 99 2 bottle for water sampling. We collected samples of precipitation (outside the forest at 100 the meteostation), throughfall and stemflow water, directly after each precipitation event 101 > 3 mm.102

To measure canopy cover (CC), i.e. the amount of sky covered by the canopies as seen 103 from the ground, photographs were taken weekly with a DSL camera at the three 104 plots. Per plot 12 photographs were taken approximately 1 m above ground vertically 105 upwards according to Chianucci (2016) and Chianucci and Cutini (2013) in mode Av 106 (automatic exposure), aperture set to F = 10, a focal length of 55, as well as a exposure 107 correction of -1. From these images the CC was calculated with an automatic threshold 108 function implemented in R following Chianucci and Cutini (2013) with the program in 109 appendix A.1. 110

Stemflow was measured in volume per time, and in order to compare these measurements with throughfall and precipitation (measured in mm/10 min), the area of the tree canopy needed to be estimated. We followed Hemery et al. (2005) who found a linear relationship between tree diameters at breast height (DBH) > 20 cm and the canopy diameter (DC). For beech the linear fit was determined by Hemery et al. (2005) and Sharma et al. (2017) found values for beech as well as spruce which are reproduced in equations (6) to (7) in appendix A.2. From the canopy diameter the area of the canopy was calculated and measured stemflow volume was transformed to mm/10 min.

Overall we collected samples for 222 precipitation events in the March 2020 to November 119 2022 observation period, resulting in 607 throughfall samples (n = 210 for B, 198 for mS, 120 199 for yS) and 380 stemflow samples (209 for B, 171 for mS). All water samples were 121 stored at 4 °C until analysis, filtered using 0.45 μ m PTFE Syringe filters (Simplepure, 122 USA) and acidified to a pH between 2 and 3 using 1M HCl. We measured the concentration 123 of major ions Cl⁻, Na⁺, Mg²⁺, Ca²⁺, K⁺, NH₄⁺, NO₃⁻, and NO₂⁻, further reported as Cl, 124 Na, Mg, Ca, K, NH₄, NO₃, and NO₂. For all samples we conducted ion chromatography 125 analyses in the Environmental Engineering Laboratory of ETH Zürich (Metrohm Compact 126 IC 761, Metrohm Schweiz AG, Switzerland). 127

For both beech and mature spruce, event interception (IC) in percent was calculated as the fraction of the measured precipitation outside the forest (PR) which was not reaching the forest floor by throughfall or stemflow, as follows:

$$IC [\%] = 100 \frac{PR - TF - SF^1}{PR}$$

$$\tag{1}$$

¹³¹ ¹ for young spruce no stemflow was measured.

Most results are presented as boxplots, whereas the middle horizontal line of the box-132 plots indicates the median, the box represents the inter-quartile range, and the whiskers 133 extend to 1.5 times inter-quartile range from the first and third quartiles. The black + 134 signs represent outliers. The numbers in blue below the boxplots indicate the number 135 of samples used to derive the boxplot. We use the Spearman rank correlation to obtain 136 the correlation coefficient rS and p-value statistics to test the significance of the obtained 137 correlations. We use the Wilcoxon-test statistics to analyse significant differences between 138 two groups of samples. We report results as statistically significant when p < 0.05. 139

¹⁴⁰ **3** Results and Discussion

¹⁴¹ 3.1 Quantitative Observations of Interception, Throughfall and ¹⁴² Stemflow

Interception and stemflow as a function of precipitation per event is shown in Figure 2. Throughfall started after less input precipitation below beech (B) than below mature (mS) and young spruce (yS) trees (mean canopy storage of 1.84 mm for beech and 2.79 mm and 2.84 mm for mature and young spruce, respectively) as indicated by the dashed vertical lines in figure 2a). Eaton et al. (1973) and Maniak (1997) found between 0.5 mm up to 2.5 mm canopy storage for beech and between 1.8 mm up to 4 mm canopy storage for spruce, which are magnitudes comparable to our study results.

Total interception decreased with increasing total precipitation amount as indicated by the logarithmic fit in figure 2a) (see equations (2) to (5) in appendix A.2).



(a) Schematic of our experimental site.



Figure 1: Location of "Waldlabor Zürich" study site in Zurich, Switzerland, (b) and a schematic of our experimental site at its eastern border (a), indicating the location of single trees (beech, mature and young spruce and other in orange, dark and light green and grey, respectively) and the three subplots (B, mS, yS). The weather station is located outside the forest, approximately 150 m from our experimental site.

Example of two photographs used for canopy cover estimation under mature spruce in early April (c) and in late May (d).

Average event interception is biased towards precipitation events which occur more frequently (i.e., small precipitation events). Average per event interception rates (such as shown in figure 2) are 56 % for beech, 57 % for mature spruce and 63 % for young spruce. If precipitation, throughfall and stemflow are integrated over a whole year interception values are 53 % for beech, 61 % for mature spruce and 68 % for young spruce. As interception is measured directly below one respective canopy each, values are not representative for the entire forest stand.

Stemflow amounts are small, with only few events > 1% of total precipitation (as shown in figure 2b)). Beech stemflow showed a mean of 1 % of precipitation and a median of 0.7 %, however for some events there were up to 3.6 % stemflow of total precipitation. Mature spruce showed a mean stemflow of 0.4 %, a median of 0.03 % and a maximum of 3.7 % of total precipitation.



Figure 2: a) Interception as a function of precipitation for beech (B - orange), mature spruce (mS - dark green) and young spruce (yS - light green)). The lines indicate the statistically significant inverse logarithmic fit for beech as well as mature and young spruce for all three species separately and combined (blue line). The vertical dashed lines show the means of the throughfall threshold, which is the mean amount of input precipitation needed to create throughfall, for beech (orange) and mature and young spruce (dark and light green). b) Stemflow as a function of precipitation for B and mS. The lines indicate the statistically significant linear fits, respectively.

Interception is therefore mainly affected by throughfall, which in turn is affected by leaf type, leaf and branch surface area, stem roughness and canopy shape (Brooks et al., 2012; Macinnis-Ng et al., 2012; McDowell et al., 2020) as well as intensity and distribution of precipitation (Brooks et al., 2012) and thus shows high spatial and temporal variability (Levia and Frost, 2006). Before reaching the soil the forest-floor litter layer further intercepts precipitation (Brooks et al., 2012; Floriancic et al., 2022).

Previous studies found stemflow to be between 1 and 10 % of annual precipitation (Bren, 2015; Brooks et al., 2012; Draaijers, Van Eak, et al., 1992; Jost et al., 2004). Stemflow under deciduous trees is generally larger than under coniferous trees (Levia, Keim, et al., 2011; Ponette-González et al., 2020; Van Stan and Stubbins, 2018), being affected by branch altitude, the shape of crown or canopy structure and the roughness of bark (Brooks et al., 2012; M. S. Johnson and Lehmann, 2006; Levia, Nanko, et al., 2019). Beech having smoother bark and a more funnel shaped canopy than spruce could therefore contribute to the differences in stemflow. Overall, we found that stemflow volume is negligible, but differs between beech and spruce and should be evaluated for different tree species separately. The possible relevance as input for nutrients is discussed in section 3.3.1.

The fraction of interception decreases with increasing precipitation event amount and 180 can be described with an asymptotic decrease of interception with increasing precipitation, 181 similar to what we show in figure 2a) and equations (2) to (5) (Darryl E. Carlyle-Moses 182 and Gash, 2011; Maniak, 1997; McDowell et al., 2020). For small precipitation events 183 measuring throughfall becomes increasingly difficult, an issue which can be mitigated by 184 using more rain gauges or larger throughfall sampling areas (Cuartas et al., 2007; Price 185 and D. E. Carlyle-Moses, 2003). Literature values for canopy interception range from 186 9 % to 29 % of annual precipitation for beech forests (Bren, 2015; Krämer and Hölscher, 187 2009; Mindaš et al., 2018; Rowe, 1983) and from 21 % to 37 % for spruce forests (Holko 188 et al., 2009; Kofroňová et al., 2021; Mahendrappa, 1990; Ringgaard et al., 2014; Xiao 189 et al., 2000). For individual events Puncochar et al. (2012) reported interception values 190 of 44 % up to 65 % for a predominantly coniferous forest. Some studies show higher 191 interception at deciduous stands compared to coniferous stands, which is the opposite of 192 what we found in our data (Darryl E. Carlyle-Moses and Gash, 2011; Snakin et al., 2001; 193 Thimonier, Schmitt, Waldner, and Rihm, 2005). The generalising grouping into coniferous 194 and deciduous trees could be misleading, and more objective parameters such as leaf area, 195 canopy cover or stand density should be assessed for interception comparisons. 196

¹⁹⁷ Uncertainties in these measurements stem from the large variability of both precipita-¹⁹⁸ tion and throughfall, possibly enhanced by the proximity of our site to the forest edge, ¹⁹⁹ and the limited measurements under only one tree canopy for each species.

3.2 Seasonality of Canopy Cover and Interception

The seasonality of canopy cover and interception for the three plots beech, mature spruce 201 and young spruce are shown in figure 3. Example pictures of how canopy cover was as-202 sessed from pictures taken with a DCLR camera are shown in figures 1c to 1d. While 203 beech showed a clear, statistically significant seasonality with lower canopy cover in win-204 ter (DJF) and spring (MAM) and higher canopy cover in summer (JJA) and autumn 205 (SON), the canopy cover for the spruce trees was constantly high across the entire year. 206 At our study site, canopy cover under beech increased from day 115 of the year on (28^{th}) 207 of April) and decreases from day 285 on, which spans the typical growing season of beech 208 (Ahrends et al., 2008; Prislan et al., 2019; Yang et al., 2017). Canopy cover is an easily 209 measurable proxy for leaf area index (Chianucci and Cutini, 2013), which influences the 210 amount and the enrichment of throughfall and stemflow (Draaijers, Van Eak, et al., 1992; 211 McDowell et al., 2020). Interception at our site showed less distinct seasonal differences 212 (figure 3b)) than canopy cover. Some seasonality of interception was evident for beech, 213 however much less pronounced than the canopy-cover seasonality. Interception decreases 214 from summer (JJA) to winter (DJF) (56 % to 54 % for B, 88 % to 61 % for mS and 215 100 % to 64 % for yS). As changes in canopy cover cannot explain these changes, other 216 factors such as precipitation intensity may play a role. Mean precipitation intensities had 217 a strong seasonal variability (figure 3) with low intensity precipitation being dominant in 218



Figure 3: Canopy cover **(a)** % and interception **(b)** % in winter (DJF), spring (MAM), summer (JJA) and autumn (SON) below beech (orange), mature spruce (dark green) and young spruce (light green) as well as the maximum precipitation intensity **(c)** as a mean for each event in mm/h.

winter. We found median precipitation intensities of 0.24 mm/h in winter and 0.42 mm/h in summer, which is an indicator of more convective precipitation in summer and more stratiform precipitation in winter.

222

Higher canopy cover increases interception (Staelens, De Schrijver, Verheyen, and Ver-223 hoest, 2008). In our study throughfall was generally lower in the dormant season (figure 3) 224 under both beech and spruce, even though canopy cover was larger in summer for the beech 225 canopy. As spruce canopy cover was almost constant over the year, the lower interception 226 in spruce canopies in winter is the result of other factors, such as precipitation patterns 227 like precipitation intensity, which can be seen in figure 10a). The seasonal development 228 of the interception under spruce can be interpreted as solely a function of factors such 229 as precipitation intensity and amount, while beech seasonal interception development is 230 additionally affected by the seasonality of the canopy cover. 231

232 3.3 Enrichment processes

Nutrient enrichment processes in the forest are mainly affected by precipitation and its origin, but also by factors such as geographic location and surrounding geology, tree type, climate and weather, dry deposition, canopy exchange from leaves, needles and ²³⁶ branches, and uptake and release from epiphytic organisms such as lichens, mosses, and ²³⁷ algae (Akkoyunlu and Tayanç, 2003; McDowell et al., 2020; Novak et al., 2020; Polkowska ²³⁸ et al., 2005). In the following section we will show and qualitatively and quantitatively ²³⁹ discuss the enrichment processes below beech and spruce in section 3.3.1, after long dry ²⁴⁰ periods in section 3.3.2, as well as the seasonality on enrichment in section 3.4, and ²⁴¹ the seasonal enrichment of salt, nitrogen and geogenic ions specifically in sections 3.4.1 ²⁴² to 3.4.3. Further we will discuss potential forcing of seasonal enrichment in section 3.5.

Enrichment in throughfall and stemflow will be displayed as the ion concentration measured in throughfall or stemflow minus the ion concentration measured in precipitation for the major ions Cl, Na, Mg, Ca, K, NH₄, NO₃ and NO₂.

3.3.1 Enrichment processes in beech and spruce canopies

Figure 4a) shows the enrichment in throughfall and stemflow relative to precipitation for 247 the major ions Cl, Na, Mg, Ca, K, NH₄, NO₃ and NO₂. We measured median enrichment 248 of up to 0.15 mmol/l in throughfall and 0.18 mmol/l in stemflow, whereas K enrichment 249 was strongest for both throughfall and stemflow. Differences in enrichment between stem-250 flow and throughfall were statistically significant for Ca, K and NH₄. In figure 4b) and c) 251 we show the enrichment for all ions for beech, mature and young spruce for throughfall 252 and stemflow, respectively. Enrichment was largest for Ca, K and NH₄ ions. Differences 253 in throughfall between beech and mature spruce were significant for all ion species except 254 for Ca and NO_2 . Differences in throughfall between beech and young spruce were signifi-255 cant for all ion species except for Ca and NO_2 . Differences in throughfall between mature 256 and young spruce were significant for Na only. Differences in stemflow between beech and 257 mature spruce were significant for all ion species except for NO_2 . 258

Enrichment in stemflow is significantly larger than in throughfall for only Ca, K and NH₄ 259 (figure 4). Understanding the processes that affect throughfall and stemflow differently 260 are difficult to distinguish, as water in both, throughfall and stemflow, may come in 261 contact with several layers of both leaves or needles, branches and stems (McDowell et 262 al., 2020; Parker, 1983). For a conceptual understanding, throughfall and stemflow should 263 possibly rather be viewed on a spectrum of longer or shorter contact with either leaves, 264 branches or the stem. More contact would lead to stronger enrichment but also greater 265 interception, which would explain both the larger beech stemflow amounts as well as the 266 higher concentrations of spruce stemflow. 267

Whereas throughfall affects a larger area of the forest floor and is volumetrically promi-268 nent, stemflow can affect the stand scale nutrient availability (Chang and Matzner, 2000; 269 Parker, 1983; Thimonier, Schmitt, Waldner, and Rihm, 2005). The contribution of stem-270 flow to the overall ion concentration a forest stand receives might therefore be higher 271 than its contribution to the hydrological fluxes (Neary and Gizyn, 1994). Some link 272 larger stemflow nutrient input to larger stemflow quantities, while others expect bark 273 ionic composition of affect the nutrient content of stemflow (Adriaenssens et al., 2012; 274 Parker, 1983). Nitrogen was found to be more enriched under spruce than under beech, 275 possibly due to dry deposition on the rough bark and branches of spruce compared to 276 beech (Berger, Inselsbacher, et al., 2009; De Schrijver et al., 2007). 277

The single effects of canopy shape, properties of leaves, branches and stem and tree interaction could not be separated in the scope of this study and remain to be looked at in further research. Overall, our results suggest that differentiating between beech



Figure 4: a) Enrichment in throughfall (blue boxplots) and stemflow (green boxplots) for all tree species together, **b)** enrichment in throughfall for beech (orange), mature spruce (dark green) and young spruce (light green), **c)** enrichment in stemflow for beech, major and young spruce.

and spruce increases the understanding of both volume (see section 3.1) as well as ion concentration in throughfall and stemflow. Both throughfall and stemflow get enriched in magnitudes larger than the concentrations found in precipitation (see figure 5a)).

284 3.3.2 Enrichment processes in relation to antecedent precipitation

We tested the hypothesis that fewer antecedent precipitation leads to stronger enrichment 285 signals in throughfall and stemflow (Berger, Untersteiner, et al., 2008; McDowell, 1998). 286 This would be the case when rainfall after a long dry period would flush dry deposition off 287 the canopy. Therefore, we divided the precipitation event data into four quartiles depend-288 ing on the amount of precipitation in the 10 days prior to the precipitation event, and 289 plotted the measured enrichment in figure 5. Plot a) shows the concentrations measured 290 in precipitation, **b**) shows the enrichment in throughfall and **c**) shows the enrichment in 291 stemflow for all measured ions. We performed a Mann-Kendall-test on the data ordered 292 by the amount of antecedent precipitation, to assess the significance of the trend that 293 drier antecedent conditions lead to larger enrichment. For precipitation, the trend was 294 negative and significant for Cl, K and NH₄. For throughfall the ion concentrations for an 295 increasing amount of antecedent precipitation showed a significant negative trend for the 296

following ions: $Cl>Mg>Ca>K>NH_4>Na>NO_3$ (in order of the magnitude of the trend). For stemflow, the ion concentrations for an increasing amount of antecedent precipitation showed a significant negative trend for the following ions: $Cl>Mg>NH_4>K>Ca>NO_3$ (in order of the magnitude of the trend).



Figure 5: Ion concentrations in **a**) precipitation, **b**) throughfall and **c**) stemflow for the four quartiles of antecedent precipitation in the 10-day periods prior sampling of our record for the major ions Cl, Na, Mg, Ca, K, NH_4 , NO_3 and NO_2 . The blue numbers indicate the absolute numbers of cases that shape the boxplots.

We see significantly higher ion concentrations in throughfall and stemflow after longer 301 periods of no precipitation, which was also observed by Berger, Untersteiner, et al. (2008) 302 and McDowell (1998). The difference between precipitation and throughfall and stemflow 303 which we show in figure 5b) and c) can be seen as a measurement of dry deposition of nu-304 trients, if we assume no or negligible exchange processes by the tree (Berger, Untersteiner, 305 et al., 2008; Staelens, Schrijver, et al., 2005; Thimonier, Schmitt, Waldner, and Rihm, 306 2005). Dry deposition happens as aerosol particles settle on canopy leaves, branches or 307 stems, and is larger in forests is larger than in the open field, and stronger at the for-308 est edge than in its centre (Adriaenssens et al., 2012; Draaijers, Van Eak, et al., 1992; 309 McDowell et al., 2020; Thimonier, Schmitt, Waldner, and Rihm, 2005). 310

311 The observed dry deposition is most likely a relevant nutrient input into the forest, and

the observed magnitude shows the relevance of dry deposition at our study location.

313 3.4 Seasonal patterns of enrichment processes

We found seasonal patterns in ion concentration in precipitation, throughfall and stemflow, as shown in figure 6a), b) and c), respectively. The seasonal patterns were stronger in throughfall and stemflow than in precipitation. Enrichment was strongest in spring (MAM), followed by autumn (SON) and summer (JJA) with the weakest enrichment found in winter (DJF) when averaged across all measured ion species. Seasonality of the salt ions Cl and Na is further discussed in section 3.4.1, the seasonality of geogenic ions Ca, K, Mg in section 3.4.2 and the seasonality of nitrogen species NH₄, NO₃ and NO₂ in section 3.4.3.



Figure 6: Seasonal variation in ion concentrations of all ions for precipitation (dark blue) as well as throughfall (green) and stemflow (blue). The blue numbers indicate the total number of samples used to compile the boxplots.

321

Seasonality of ion enrichment is reported to be primarily a function of climate seasonality, being dependent on precipitation variance, presence or absence of canopy cover and differences in dry deposition, exchange or dew and fog (Akkoyunlu and Tayanç, 2003; Berger, Untersteiner, et al., 2008; Draaijers, Van Eak, et al., 1992; Groh, Slawitsch, et al., 2018; Klemm and Wrzesinsky, 2007; Levia and Frost, 2006; McDowell, 1998; Moffat et al., 2002).

328 **3.4.1 Salt**

Concentrations of Na and Cl and their difference in precipitation (figure 7a)) are low 329 for most of the year with a slight increase from February until April. For precipitation 330 there is no significance difference between the concentrations of Na and Cl. In throughfall 331 and stemflow the concentrations of both Na and Cl are enriched with peak enrichment 332 taking place from February until May for both Na and Cl as shown in figure 7b) and c). 333 respectively. Cl shows an additional peak in enrichment in November. Concentrations 334 reach their yearly low from June until August. The difference of the concentrations in Na 335 and Cl are plotted in all three panels of figure 7 to show disconnection of the concentrations 336 in Na and Cl. 337



Figure 7: Seasonal variability of the concentration of Cl (yellow) and Na (gray) as well as the difference in Cl and Na concentration (in cyan) in **a**) precipitation, **b**) throughfall and **c**) stemflow. The blue numbers indicate the total number of samples used to compile the boxplots.

As Na and Cl are relatively inert, they can be used as a proxy for dry deposition, 338 which in our case might be amplified by the forest edge (Draaijers, Van Eak, et al., 339 1992; McDowell et al., 2020). The high concentrations in spring and autumn point to 340 the impact of maritime sources of the low pressure systems crossing middle Europe in 341 spring and autumn from the west, (Moffat et al., 2002; Thimonier, Schmitt, Waldner, and 342 Schleppi, 2008). The molecular formula of sodium-chloride salt is NaCl, meaning that 343 if coming from the crystalline form, as would be expected in dry deposition, the Na:Cl 344 ratio should be 1:1. As evident from the large molar discrepancy seen in figure 7b) and 345 c) from October until January, there must be another source of Cl or a sink of Na which 346 leads to this disconnection of the concentrations. Na is often used as a tracer ion as it is 347 only deposited in particles and canopy exchange rates for Na are low (Macinnis-Ng et al., 348 2012; Staelens, De Schrijver, Verheyen, and Verhoest, 2008). 349

A possible explanation for higher Cl concentrations would be salt brime used to de-ice roads during the winter months. (Thimonier, Schmitt, Waldner, and Rihm, 2005). As no temporally resolved data on the salt use in the study area exists, we can only compare ³⁵³ our data to annual data: According to the salt use of the Canton of Zurich (Kanton ³⁵⁴ Zürich; Strassennetz; Winterdienst; Salzverbrauch 2022), responsible for the de-icing of ³⁵⁵ the closest road to the study site, in the winter of 2020/21 10 times more salt was used ³⁵⁶ than in the winter of 2021/22 and we observed 2-times higher salt concentrations in the ³⁵⁷ 2021/22 winter compared to the winter 2020/21.

358 **3.4.2 Geogenic ions**

The ion concentrations of Mg, Ca and K are shown in figure 8 for precipitation, throughfall and stemflow.

The concentrations in precipitation were low or below detection limit all year round. For throughfall and stemflow however, we observed an annual pattern of highest concentrations in November, high concentrations in spring and summer and lowest concentrations in December, January and February.

Mg had its concentration peaks in throughfall and stemflow in April and May and had significantly higher concentrations after long dry periods (figure 5).

Ca concentrations in throughfall and stemflow were relatively homogeneous all year round with lowest concentrations during December and January and highest concentrations in November, where the median was two times higher than during the rest of the year. Ca showed high differences between beech and spruce for stemflow (figure 4c)), having significantly higher concentrations in stemflow than in throughfall. Events after long dry periods (figure 5) had significantly higher concentrations.

K had its highest concentration in throughfall and stemflow in November, followed by its lowest concentrations in December, January and February with an increase in concentration again in March and April and a decrease across the summer months. K concentrations were higher in spruce stemflow than in beech stemflow (figure 4c)) and they were significantly higher in stemflow than in throughfall. Longer dry periods had a significant effect on K concentration in both throughfall and stemflow (figure 5).

Mg, Ca and K mainly originate from rock weathering and are therefore highly dependent 379 on geographical location (Botter et al., 2019; Polkowska et al., 2005). Kumar Gautam 380 et al. (2017) reported enrichment in Ca and Mg stemming from dry deposition, with 381 Ca having the highest dry deposition and K the lowest, which stands in contrast to our 382 finding of much higher enrichment in K and Ca than in Mg. Reasons for that might be 383 differences in the surrounding bedrock. As our data does not show the same seasonality as 384 the biologically less active Na and Cl ions (figure 7), we assume that there are other sources 385 of Mg, Ca and K, such as leaching processes from the canopy. Thus, it is likely that peaks 386 in Mg, Ca and K at our site did not originate from dry deposition, but rather from canopy 387 leaching. Mg concentrations were similar in beech and in spruce in both throughfall and 388 stemflow (figure 4b) and c)), which is a further indicator that the Mg concentrations did 389 not originate from dry deposition, which generally affected concentrations under spruce 390 much more than under beech. According to D. W. Johnson and Steven E. Lindberg (1992) 391 and Parker (1983) Mg, Ca and K are getting leached from the canopy, which might be 392 increased by acid precipitation (Polkowska et al., 2005). Variations however are being 393 reported in the amount of leaching, whereas Rothe et al. (2002) reported higher leaching 394 in Mg than in Ca, which is not what we found at our study site. 395

Levia and Frost (2006) reported an increase in Ca concentration when the amount of throughfall decreased. This connection between decreasing amounts of throughfall and



Figure 8: Seasonal variability of the concentrations of calcium [Ca] (violet), magnesium [Mg] (green) and potassium [K] (beige) in **a**) precipitation, **b**) throughfall and **c**) stemflow. The blue numbers indicate the total number of samples used to compile the boxplots.

³⁹⁸ increasing Ca concentrations is also evident from our data figure 5b).

Concluding, the geogenic ions (Mg, Ca, K) showed a different seasonality than other ions, which suggests that leaching, in combination with dry deposition, played a more important role for these ions at our site. This could potentially explain peaks in November, when wind is more abundant at our site. If this is correct, the concentrations in stemflow should be larger than in throughfall, which is only true for K and not for Mg and Ca, so there might be some leaching or another process involved.

405 **3.4.3 Nitrogen**

Nitrogen was plotted in NH₄, NO₃ and NO₂ for precipitation, throughfall and stemflow in figure 9. The concentration in precipitation of NO₂ was just around detection limit for almost all measurements, and the enrichment compared to precipitation was zero for most months for both throughfall and stemflow, with the exception of an increase in NO₂ concentrations in April in both throughfall and stemflow.

 $_{411}$ Concentrations of NH_4 in precipitation and to a lesser extent also NO_3 only increased

⁴¹² in March and April (figure 9a)).

For throughfall and stemflow we found a strong seasonal pattern with strongest concentrations in spring, followed by autumn, summer and winter, with peaks in concentrations in March and September for both NH₄ and NO₃. NH₄ and NO₃ showed different enrichment patterns in throughfall and stemflow, the latter had two times the concentrations of throughfall from May until November for NH₄. Enrichment in stemflow was much more variable than in throughfall, especially for NH₄ and enrichment was strongest in summer.



Figure 9: Seasonal variability of the concentrations of ammonium $[NH_4]$ (light blue), nitrate $[NO_3]$ (teal) and nitrite $[NO_2]$ (navy) in **a**) precipitation, **b**) throughfall and **c**) stemflow. The blue numbers indicate the total number of samples used to compile the boxplots.

419

Nitrogen is one of the limiting factors of plant growth (Addiscott, 2005; Botter et al., 2019; Eugster and Haeni, 2013; Michel et al., 2013; Zhang, 2017). Both NH₄ and NO₃ are widely used as fertiliser, and affecting plant metabolism and biodiversity of forests they are the most important ion inputs to measure in forests ecosystems (Addiscott, 2005; Eugster and Haeni, 2013; Michel et al., 2013; Schulze, 2000). Nitrogen is thought to enter the forest mainly through dry deposition, however how much enters the forest is hard to determine since nitrogen is biologically active (Eugster and Haeni, 2013; McDowell

et al., 2020). Looking at the change in concentrations of NH_4 and NO_3 after longer dry 427 periods in figure 5b) and c) indicates that NH_4 is more influenced by dry deposition. 428 Canopy exchange of nitrogen can go both ways: nitrogen was found both leaching from 429 the canopy as well as taken up by the canopy (Fenn et al., 2013; D. W. Johnson and 430 Steven E. Lindberg, 1992; Kumar Gautam et al., 2017; Rothe et al., 2002). Whether 431 nitrogen uptake or leaching is taking place is a function of leaf or needle nitrogen content 432 (Moffat et al., 2002). Our study site lies close to both a city and agricultural areas, and 433 met the expectation of therefore having strong nitrogen enrichment (Michel et al., 2013). 434 The strong enrichment in spring and autumn underline the assumption that nitrogen 435 reaches the forest mainly through dry deposition, as these were the months where also 436 enrichment in the dry-deposition proxy Na and Cl was highest. The high concentrations in 437 NH₄ and NO₃ in figure 4b) and c) indicate that the high concentrations in throughfall and 438 stemflow mainly come from the measurements taken below spruce canopies. This could 439 either suggest that we had much higher dry deposition on the spruce as discussed in more 440 detail in section 3.5.1 due to the rougher bark structure, or a nitrogen uptake by beech, 441 if the nitrogen content of the leaves were lower relative to the stemflow concentration 442 (McDowell et al., 2020). Further research is needed to determine the nitrogen fluxes and 443 exchange along the trees and the impact thereof on the forest soil nutrient availability. 444

Measuring nitrogen in throughfall and stemflow increases our understanding of small 445 scale nitrogen inputs around the stems of trees (Thimonier, Schmitt, Waldner, and Rihm, 446 2005), which is supposed to increase chances of soil acidification (Michel et al., 2013). 447 Around spruce trees the large concentrations are met with often very small stemflow 448 amounts, or for small precipitation events no stemflow at all (figure 2). The high con-449 centrations of nitrogen could therefore origin from several precipitation events where the 450 amount of stemflow of the previous precipitation events was not large enough to reach the 451 forest soil. This would also explain the large variability of concentrations seen in stemflow 452 (e.g. figure 9c)).453

Interestingly we observed a rise in NO₂ in April, which we cannot explain. Nitrite usually gets produced by nitrificating bacteria in the soil, and we did not find comparable studies, as NO₂ rarely got reported in literature on throughfall and stemflow.

⁴⁵⁷ Overall seasonal patterns in the different ions across our site exist and it is still unclear ⁴⁵⁸ what drives these seasonal enrichment patterns. Therefore, in the following chapter we ⁴⁵⁹ will discuss potential forcing of enrichment patterns and their seasonality across our site.

3.5 Forcing of seasonal enrichment patterns

We found distinct seasonal differences in enrichment patterns for different ions (figure 6), 461 however it is yet unclear to which extent these differences can be attributed to dry deposi-462 tion and accumulation, canopy exchange, and dew and fog deposition, which are deemed 463 the major enrichment sources in a forest (Lovett and S. E. Lindberg, 1984). Thus, in 464 figure 10 we show the potential climatic forcing of enrichment seasonality across our study 465 site. Higher precipitation intensities (figure 10a)) lead to less interception as discussed in 466 section 3.1, which means that the concentrations measured in throughfall and stemflow 467 will be relatively lower. Higher temperatures (figure 10b)) will increase enrichment mea-468 sured in concentrations in summer due to higher evaporation, and stronger winds during 469 spring and autumn (figure 10d)) may amplify evaporation as well as lead to more dry 470

deposition, or input from maritime sources with low pressure systems arriving from the west during those periods. Large temperature variations around 0 °C (figure 10c)) lead to ion inputs from dew and fog along the canopies and stems. Large vapour pressure deficit such as observed during the summer months figure 10e) leads to increased transpiration by the trees and more evaporation losses. Long periods without rain (figure 10f)) might increase dry deposition, which has already been discussed in section 3.3.2.



Figure 10: Potential forcing of seasonal patterns of enrichment as boxplots throughout the different months of the year. a) Maximum precipitation rate in mm/h, b) mean daily temperature in $^{\circ}$ C, c) minimum (blue) and maximum (yellow) daily temperature as well as the difference between maximum and minimum daily temperature (grey) in $^{\circ}$ C, d) mean daily wind speed if larger than 1 m/s, e) mean daily vapour pressure deficit (VPD) in kPa, f) consecutive days without rainfall.

At our site we measured ion enrichment by collecting samples after each precipita-477 tion event > 3 mm, thus signals of dry and wet deposition were mixed within the same 478 sample, as dry deposited ions are washed out with precipitation and finally ending up 479 in our throughfall and stemflow measuring gauges (Thimonier, Schmitt, Waldner, and 480 Rihm, 2005). The ion concentrations in precipitation samples resemble wet deposition 481 only, therfore the difference between the concentration in precipitation and throughfall or 482 stemflow respectively, as shown in figures 7 to 8 can be assumed to be a measurement of 483 dry deposition and canopy exchange. 484

485 **3.5.1 Dry deposition**

⁴⁸⁶ Dry deposition affects nutrient input into forest ecosystems by deposition of aerosols in
⁴⁸⁷ the canopy without involvement of precipitation and fog (Andersen and Hovmand, 1999;

Lovett and S. E. Lindberg, 1984; McDowell, 1998) and is measured in our data set by the 488 subsequent washing out of the ions from tree surfaces by precipitation. For the aerosols to 489 settle on the tree surface, turbulence of air flow at the top of the canopy or at the forest 490 edge are prerequisites (Adriaenssens et al., 2012; Draaijers, Van Eak, et al., 1992). Due to 491 its high variability turbulence is hard to measure (Kumar Gautam et al., 2017), and it is 492 further difficult to distinguish between wet and dry deposition fluxes (Staelens, Schrijver, 493 et al., 2005) and to measure either of them separately (Macinnis-Ng et al., 2012). Thus, 494 for dry deposition longer dry periods are beneficial (Berger, Untersteiner, et al., 2008). 495 Due to the rougher bark structure and the accompanying larger surface area of spruce, 496 dry deposition should be larger on spruce than on beech (Rothe et al., 2002). 497

During our study period, the longest periods without precipitation were recorded in in 498 March and April, suggesting that these months are likely to experience more dry depo-499 sition enrichment. Further, the windiest periods were from February until May and in 500 October and November, which are also periods where we observed a lot of enrichment 501 most likely attributed to dry deposition section 3.4.1. Thus, peaks of Cl, Na, NH₄ and 502 NO₃ in March and April and of Cl, Mg, Ca, K and NH₄ in November were potentially 503 linked to dry deposition. However, inconsistencies exist as for example, Cl concentrations 504 were high in November, but Na not, but they are both quoted as biologically inert. Mg, 505 Ca and K are high in November, but not in October and December. NH_4 and NO_3 con-506 centrations are high in March, but not so in April and also do not peak in October or 507 November. 508

3.5.2 Canopy Exchange

⁵¹⁰ Canopy exchange is the process of uptake or release of nutrients by trees and epiphytic
⁵¹¹ vegetation over passive ion diffusion as well as gas uptake over stomata (Clark et al.,
⁵¹² 1998; Draaijers, Erisman, et al., 1997; McDowell et al., 2020; Staelens, De Schrijver, and
⁵¹³ Verheyen, 2007).

The magnitude of canopy exchange is dependent on the precipitation amount, foliage density and seasonality (Berger, Untersteiner, et al., 2008; Kumar Gautam et al., 2017; Levia and Frost, 2006). For example, nutrient values in needles of conifers are higher at the beginning and end of the growing season, suggesting that canopy leaching is small during these periods or that the leaves take up nutrients from the throughfall and stemflow (Levia and Frost, 2006; Moffat et al., 2002).

Canopy exchange is often reported for geogenic ions such as K, Mg and Ca, the direction 520 of the exchange and relative quantities vary in literature (Adriaenssens et al., 2012; Clark 521 et al., 1998; Macinnis-Ng et al., 2012; Parker, 1983). The nutrient content of the needles 522 determines whether uptake or release of nutrients take place (Levia and Frost, 2006). 523 Canopy exchange is expected to be larger on larger surface areas, therefore at beech 524 during the growing season and at spruce all year round (Kumar Gautam et al., 2017). 525 Also, canopy exchange via stomata is higher during high photosynthetic activity, thus 526 when vapour pressure deficits are high (figure 10e)). 527

⁵²⁸ During our study period, highest solar radiation and VPD were recorded during the ⁵²⁹ summer months, suggesting that these months are likely to experience more enrichment ⁵³⁰ from canopy exchange, as this is also the most active vegetative season, especially for ⁵³¹ beech. Thus, the enrichment of Ca and K in May until September as well as NH₄ and ⁵³² NO₃ in July until September were potentially linked to canopy exchange. However, inconsistencies exist as for example, NH₄ and NO₃ concentrations were low in May and June and only increased towards the end of summer. What is still to be further researched here is the possibility of canopy uptake in the beginning of the growing season in April and May, and then possible release towards the end of it in September and October. We also found little enrichment in Ca and K in December until February, potentially indicating the smaller canopy exchange rates outside the growing season.

3.5.3 Dew and fog accumulation

High ion concentrations in dew and fog might be the reason for the peak concentrations 540 in spring and autumn Groh, Pütz, et al. (2019), Hůnová et al. (2018), and Klemm and 541 Wrzesinsky (2007). Being a rather overlooked water flux in mid-latitudes so far, dew 542 might be a relevant but local and short term water input (Groh, Pütz, et al., 2019; Groh, 543 Slawitsch, et al., 2018). Concentrations of NO_3 and NH_4 are over 10 times as large in fog 544 compared to precipitation. Especially local effects such as local emissions may influence 545 fog ion concentrations stronger than rain ion concentrations (Klemm and Wrzesinsky, 546 2007). 547

Dew and fog accumulation are heavily linked to relative humidity, ambient SO_2 and 548 NO_x concentrations, air temperature and seasonality (Hůnová et al., 2018). As SO_2 549 concentrations were consistently small during out study, we omitted this data. However, 550 during our study period, these periods of small VPD (figure 10e)), were recorded from 551 October until February, low temperatures and large change in temperature (figure 10b) 552 and c)) being recorded from March until October. This is suggesting that the months 553 where the two overlap are likely to experience more enrichment dew and fog deposition. 554 Thus, enrichment of NH4 and NO3 in February and March and in October and were 555 potentially linked to dew and fog formation. However, we did not measure dew or fog 556 throughout our study period and can therefore only make generalised assumptions, as both 557 dew and fog are very small scale phenomena and neither their water flux contribution nor 558 their ion contents can be determined from our data. 559

3.6 Conceptualisation of canopy enrichment processes

The annual enrichment pattern in the mixed temperate forest observed in this study 561 shows distinct seasonality, which we conceptualised in figure 11. Winter (DJF) shows the 562 lowest nutrient fluxes with no clearly distinguishable driver of the enrichment measured. 563 Enrichment in March and April is mostly driven by dry deposition due to increased wind 564 speeds, longer dry periods and warmer conditions. In addition to that, dew and fog 565 deposition may lead to nutrient rich water on plant surfaces. During the summer months 566 from May through October enrichment from dry deposition decreased while evaporative 567 enrichment increased due to higher temperatures. Also canopy exchange processes might 568 have played a larger role in enrichment. In November we found evidence of larger dry 569 deposition enrichment again, combined with canopy leaching and dew and fog deposition. 570 The contribution of each driver separately is only a qualitative estimation. Our study 571 highlights that seasonal variability in nutrient availability in forest ecosystems is still not 572 well understood, thus it is of major importance to continue studies of the spatial and 573 temporal variability of throughfall and stemflow enrichment and their forcing to assess 574 nutrient availability in forests. 575



Figure 11: Conceptualisation of the annual enrichment pattern and the relative influences of the forcing dry deposition, evaporation, canopy exchange and fog inputs. We estimated the relative influence of four forcing on the annual enrichment patterns found in throughfall and stemflow in a mixed beech and spruce forest. The general annual enrichment pattern was deduced from the total annual enrichment as previously shown in figure 6. The annual evaporation pattern is based on the annual temperature as shown in figure 10b), the effect of wind was neglected. The dry deposition pattern was based on the annual pattern of Cl as shown in figure 7. The seasonality of fog was based on Hůnová et al. (2018) due to lack of sufficient data from our site. However, their study site shows a very similar climatology compared to our site.

Please note, that the effect of evaporation in the conceptual scheme might be overestimated to the loss of dry deposition.

576 3.7 Discussion of Uncertainties

We acknowledge that our study has obvious limitations. The findings presented above 577 are derived from plot-scale observations within a single small forest site with only one 578 replicate per tree species. Measurements of throughfall are challenging as there is large 579 spatial variation, and long data series to understand temporal variability are often lacking 580 (Brooks et al., 2012). Both of these factors may lead to large uncertainties in throughfall 581 measurements. Longer measuring periods may mitigate the latter problem, the lack of 582 spatial distributed information however can only be mitigated by the use of more rain 583 gauges, an endeavour which becomes increasingly difficult if also small precipitation events 584 are to be sampled (Levia and Frost, 2006). There are studies which mention the decrease 585 of ion concentrations with increasing distance from the stem (Adriaenssens et al., 2012), 586 a property of throughfall which makes studies performed with single rain gauges highly 587 sensitive to the placement of the rain gauge. Thus, in our study, rather than using multiple 588 gauges across the site, we focused on integrated measurement of throughfall (with gutters) 589 directly below the canopies of three stands, however we could collect a reasonably high 590 resolved and long time series i.e., each precipitation event > 3 mm for almost three years. 591 For inter study comparison, reporting of nutrient fluxes in either mg/l and mmol/l is 592 common. While the former is easier for mass flux calculations, we chose the latter for this 593 study to be able to conduct stochastic comparisons such as performed in section 3.4.1, 594 which makes it hard to determine the absolute nutrient influx from throughfall or stemflow. 595 Thus, although many of our results are suggestive rather than definitive, they point to 596

the need for further research on the water and nutrient inputs below different tree species canopies to better understand water and nutrient dynamics in forest soils.

599 4 Conclusions

The water and nutrient availability for a forest ecosystem mainly depend on the tree 600 species composition and precipitation intensity which determine the amount and concen-601 tration of throughfall and stemflow. Interception patterns are different across seasons 602 and for tree species (i.e., spruce and beech) and not purely related to canopy cover but 603 also seasonal differences in precipitation intensities. While interception under coniferous, 604 evergreen tree species is mainly affected by precipitation patterns, interception below de-605 ciduous tree species is also affected by the seasonality of canopy cover. In percentage of 606 total annual precipitation, stemflow is negligible, however it might be a relevant water 607 input on small scales i.e., around the stem and to the root system. 608

Likewise, ion enrichment in throughfall and stemflow has seasonal variation, that can 609 not solely be explained by dry deposition. Although concentrations were mostly higher 610 after drier antecedent periods, dry deposition is not the only driver of ion enrichment 611 in throughfall and stemflow. However, evaporative enrichment, canopy exchange, and 612 dew and fog deposition yield major effects on the seasonality of iron enrichment. While 613 dry deposition is increased by longer dry periods and stronger winds and is therefore 614 prevalent in spring and autumn, evaporative enrichment is important during the summer 615 months. Canopy leaching is an important driver during the growing season, however it is 616 dependent on tree type and on the seasonal activity of nutrient uptake of the tree. Dew 617 and fog deposition may lead to peaks in ion enrichment in spring and autumn. Also, 618 enrichment in throughfall and stemflow is not statistically different for most ions. 619

Overall, our study highlights the complex interactions between tree species and climate forcing that affect the seasonal variability in water and nutrient supply to forest ecosystems.

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A Supplement

A.1 Canopy Cover - Threshold function

```
"autoThreshold" <- ### function from the former package tiff which
    is discontinued for R4.0.0 or later, therefore implemented
    here
    function(d.m, est=0.5) {
      est.old <- 0
      while (est.old != est) {
         est.old <- est
         t1 <- mean(d.m[d.m < est], na.rm=TRUE)
         t2 <- mean(d.m[d.m > est], na.rm=TRUE)
         est <- mean(c(t1, t2), na.rm=TRUE)
         }
      return(c(t1, mean(c(t1, est)), est, mean(c(t2,est)), t2))
    }
```

A.2 Equations

$$IC_{all} = 77.7 - 4.6 \cdot \log(\text{PR})$$
 (2)

$$IC_B = 67.6 - 4.6 \cdot \log(\text{PR})$$
 (3)

$$IC_{mS} = 78.8 - 4.8 \cdot \log(\text{PR})$$
 (4)

$$IC_{yS} = 85.0 - 3.9 \cdot \log(\text{PR})$$
 (5)

$DC_{B, Hemery}$	$J = 15.23 \cdot DBH + 1.13312$	(6)
$DC_{B, Sharm}$	$_{na} = 15.0 \cdot DBH + 1.4$	(7)
\mathbf{D}		

$$DC_{S, Sharma} = 8.7 \cdot DBH + 1.4 \tag{8}$$

A.3 Tables

Table 1: P-values of paired Wilcox tests comparing the difference in the amounts of throughfall and stemflow. The difference between all 5 datasets are significant with p-values < 0.05.

	TF1	TF2	TF3	SF1	SF2
TF1	1	2.70E-03	5.94E-08	2.03E-25	1.54E-25
TF2	-	1	5.75E-03	8.81E-21	6.00E-24
TF3	-	-	1	3.05E-12	2.00E-13
SF1	-	-	-	1	6.73E-15
SF2	-	-	-	-	1

Table 2: Significance of trend analysis for a decreasing trend in concentration values for higher antecedent precipitation, performed with a Mann-Kendall-test on data from precipitation, throughfall and stemflow water samples sorted by the amount of 10 day antecedent precipitation.

water samples	name	p.value	significance
	Ca	1.24 E-01	-
	Cl	2.08 E-03	< 0.05
	Κ	2.78 E-02	< 0.05
•••, ,•	Mg	7.15 E-04	< 0.05
precipitation	Na	3.48 E-01	-
	NH4	2.80 E-02	< 0.05
	NO2	1.28 E-01	-
	NO3	5.21 E-02	-
	Ca	1.85 E-16	< 0.05
	Cl	5.46 E-21	< 0.05
	Κ	1.71 E-13	< 0.05
throughfall	Mg	2.89 E-19	< 0.05
unouginan	Na	3.81 E-06	< 0.05
	NH4	2.07 E-13	< 0.05
	NO2	1.13 E-01	-
	NO3	1.15 E-05	< 0.05
	Ca	1.76 E-03	< 0.05
	Cl	6.39 E-12	< 0.05
	Κ	1.40 E-04	< 0.05
stomflow	Mg	1.40 E-07	< 0.05
SUCHIIIOW	Na	5.28 E-02	-
	NH4	1.78 E-05	< 0.05
	NO2	1.41 E-01	-
	NO3	2.20 E-02	< 0.05

Table 3: Significance of differences between concentrations in throughfall and stemflow for the ions calculated with a paired Wilcox test.

datasets	name	p-value	significance
TF/SF	Ca	5.6E-05	< 0.05
TF/SF	Cl	9.5E-01	-
TF/SF	Κ	8.9E-05	< 0.05
TF/SF	Mg	9.5E-01	-
TF/SF	Na	2.2E-01	-
TF/SF	NH4	3.6E-05	< 0.05
TF/SF	NO2	1.9E-01	-
TF/SF	NO3	6.5E-01	-

water samples	comparison	ions	p-value	significance
	B/mS	Ca	9.3E-11	< 0.05
	B/mS	Cl	7.8E-10	< 0.05
	B/mS	Κ	1.7E-22	< 0.05
	B/mS	Mg	1.9E-06	< 0.05
SF	B/mS	Na	4.1E-19	< 0.05
	B/mS	NH4	1.0E-17	< 0.05
	B/mS	NO2	1.7E-01	-
	B/mS	NO3	1.0E-06	< 0.05
	B/mS	Ca	6.0E-02	-
	B/mS	Cl	1.9E-08	< 0.05
	B/mS	Κ	5.3E-09	< 0.05
	B/mS	Mg	3.0E-02	< 0.05
1F	B/mS	Na	2.9E-06	< 0.05
	B/mS	NH4	3.2E-10	< 0.05
	B/mS	NO2	1.9E-01	-
	B/mS	NO3	2.5E-07	< 0.05
	$\rm B/yS$	Ca	8.0E-01	-
	B/yS	Cl	2.9E-08	< 0.05
	B/yS	Κ	8.2E-12	< 0.05
	B/yS	Mg	5.5E-03	< 0.05
1F	B/yS	Na	1.1E-02	< 0.05
	$\rm B/yS$	NH4	1.1E-07	< 0.05
	$\rm B/yS$	NO2	4.7E-01	-
	B/yS	NO3	2.6E-07	< 0.05
	mS/yS	Ca	1.1E-01	-
	$\mathrm{mS/yS}$	Cl	8.6E-01	-
	m mS/yS	Κ	3.1E-01	-
ΤĿ	mS/yS	Mg	6.0E-01	-
ΤĻ	m mS/yS	Na	2.5E-02	< 0.05
	m mS/yS	NH4	6.3E-01	-
	$\mathrm{mS/yS}$	NO2	5.5E-01	-
	$\mathrm{mS/yS}$	NO3	5.7E-01	-

Table 4: Significance of differences between ion concentrations in stemflow and throughfall when comparing the concentration measured under different trees (beech B, mature spruce mS and young spruce yS).

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