Impact of tree species diversity on throughfall deposition in young forest plantations

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Abstract

The chemical composition of throughfall water is a key determinant of forest nutrient cycling, affecting many ecosystem processes and biodiversity. Although throughfall deposition biochemistry has been well studied in forest ecosystems, less is known about how throughfall deposition is modified by tree species diversity. To disentangle the effects of tree species identity and diversity on throughfall deposition, we installed rain gauges in a 10-year-old tree diversity experiment. With these rain gauges, we monitored throughfall biweekly, and performed chemical analyses for all the major ions (Na^+, Cl^-, SO_4^{2-}-S, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}-P, NO_3^--N and NH_4^+-N) every 4 weeks, for a period of one year. Based on these data, we analysed species identity (i.e. whether throughfall deposition was tree species-specific), and diversity effects (i.e. whether tree species richness effects on throughfall deposition were present). We confirmed species identity effects on throughfall deposition. Presence of pine led to higher throughfall deposition of inorganic nitrogen, and lower amounts of phosphorus, calcium and magnesium reaching the forest floor. Additionally, species characteristics and stand structural traits, i.e. basal area and canopy cover, emerged as key factors driving throughfall deposition of sodium, chloride, nitrate, sulphate and potassium. Tree species diversity effects on throughfall deposition were also present, mostly via increased basal area and canopy cover, leading to increased throughfall deposition of inorganic nitrogen, sulphate, chloride, sodium and potassium. In addition, our data revealed an important pathway of phosphorus cycling in post-agricultural lands, from the soil via the foliage and throughfall back to the forest floor. In summary, our research shows that tree species diversity can enhance throughfall deposition for most of the ions, resulting in higher nutrient inputs to the soil and the below-canopy communities.

Key-words: biodiversity, throughfall deposition, forest, nitrogen, phosphorus, base cations

1. Introduction

Throughfall deposition is an important process via which particles, aerosols and gases can move from the atmosphere to the forest floor, the soil and, eventually, to the groundwater (Lindberg et al., 1986; Parker, 1983). Throughfall deposition, therefore, can have important impacts on forest biodiversity and functioning, directly influencing litter decomposition (Koopmans et al., 1998), soil nutrient cycling (Lindberg et al., 1986), and root growth and distribution (Leuschner et al., 2004).

Past studies have shown that ion fluxes to the forest floor by throughfall might be higher or lower than the above-canopy ion input by rainfall events, i.e. wet deposition (Staelens et al., 2007). This is because the chemical composition of throughfall water is altered when passing through a tree canopy, (1) via uptake and release of substances by the plant and associated microflora, i.e. canopy exchange and (2) via wash-off of particles and gases that were first deposited on leaves, branches and stems, i.e. dry deposition (Lovett & Lindberg, 1992). Therefore, differences in throughfall deposition are attributable to differences in leaf traits and canopy structure among tree species (Adriaenssens et al., 2012; De Schrijver et al., 2008; De Schrijver et al., 2007; Herrmann et al., 2006). Many studies have assessed the effects of tree species identity on throughfall deposition, mainly to address how throughfall deposition differs below contrasting tree species. De Schrijver et al. (2007), for example, conducted a review based on studies of throughfall deposition in temperate forests, and reported that conifers received higher throughfall deposition of N and S when compared to deciduous forests. As a result, forests that differ in species composition will likely differ in terms of the amounts of ions deposited and their ecological consequences (e.g. lower soil pH in coniferous stands). While the effects of individual tree species are well documented, studies on diversity effects of tree species on throughfall deposition are still lacking. We thus do not know to what extent throughfall deposition differs in monocultures compares to throughfall deposition in mixed species stands.

Tree species diversity can determine throughfall deposition via different mechanisms. First of all, individual trees planted in mixed stands may differ in physiology and morphology compared to their conspecifics planted in monocultures. Crown complementarity in mixed stands, for example, is expected to increase canopy closure and a stand's leaf area index (LAI) (Pretzsch, 2014; Williams et al., 2017). These factors have

been proven to promote the exchange of particles and gases from the atmosphere to the plant surface. This is because 'rough' forest canopies can exert a drag force on moving air masses and thus increase the amount of particles and gases deposited on a tree's surface (Erisman & Draaijers, 2003). Dry deposition increments, therefore, are to be expected when mixing tree species. More specifically, we expect that throughfall deposition of sulphate (SO_4^{2-}-S), which is generally not being exchanged by the canopy, will subsequently increase with tree species richness. Due to canopy exchange, which may contribute substantially to throughfall deposition depending on the ion under investigation, we do not expect this increase of deposition in mixed stands to hold for all ions. This is because canopy exchange is generally a passive process, which is strongly affected by the chemical concentration of the leaves, which may differ strongly between tree species (De Schrijver et al., 2007; Lovett et al., 1989). For example, part of the dry deposition of inorganic N is being assimilated by leaves of most deciduous species, while this assimilation was insignificant in conifers (De Schrijver et al., 2008). The relative abundances of different functional groups (e.g. coniferous *vs* deciduous species) in a mixed stand, therefore, determines to what extent the amount of deposited N can be depleted by this stand. As tree species diversity has been proposed to affect species biomass productivity (e.g. Van de Peer et al., 2018), the relative abundances of different functional groups may thus be altered. We therefore hypothesize that species diversity can determine throughfall deposition, not only via a more complex canopy structure, but also via changes in the relative abundances of different functional groups.

Here we investigate biodiversity effects on throughfall deposition based on data collected in a large-scale tree species diversity experiment in Belgium (Verheyen et al., 2013, 2016). Within the experimental site, we deployed 128 below-canopy rain gauges in both monocultures and mixtures and collected water samples every two weeks to monitor throughfall during one year. The chemical concentrations of air pollutants (SO_4^{2-}-S, NO_3^--N and NH_4^+-N) as well as other major ions (Na^+, Cl^-, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}-P) were measured for in total 12 collection moments, once every month. With these data we aim to investigate (1) whether throughfall deposition of these ions depends on the identity of the tree species present in the overstorey; (2) whether tree species richness affects throughfall deposition; and (3) whether tree species richness and/or presence

of coniferous species affects throughfall deposition either directly, and/or indirectly via basal area and/or canopy cover effects.

2. Materials and methods

2.1. Study area

We performed our study in Zedelgem (51°08'52.2"N, 3°07'12.0"E, 11–16m elevation, 9.5 ha), an experimental plantation belonging to a large-scale, multisite tree diversity experiment in Belgium (FORBIO), that includes five key European tree species (*Betula pendula* [birch], *Fagus sylvatica* [beech], *Pinus sylvestris* [pine], *Quercus robur* [oak] and *Tilia cordata* [lime]) (Verheyen et al., 2013, 2016). The site is former agricultural land, where, for instance, potatoes and maize were grown prior to afforestation in 2010. The site is located around 15 km from the North Sea and has a mild oceanic climate with a mean annual temperature of 10.8°C and a mean annual precipitation of 861 mm evenly distributed across the year (based on average 1991-2020 climate data, our experiment is conducted 5 km away from the weather station).

The experiment consists of 40 plots within two replicate blocks, including ten monoculture plots (one plot per species per block) and 30 mixture plots (ten for each tree species diversity level of 2, 3 and 4), each species occurring in the same frequency. In this study, only the monoculture plots and the 2- and 4-species mixtures were considered, so that 15 treatments were selected, including five monocultures, five two-species combinations (being a random selection of all possible two-species combinations), and five four-species combinations in each block, resulting in a selection of 30 plots in total. All trees were planted in 2010 as 2- or 3-year old saplings on a 1.5 m x 1.5 m grid (planting density of 4,444 trees/ha) and were thus 12-13 years old at the time of our measurements. For more details on the site's information see Figure 1 and supplementary information Table S1 and S2.

2.2. Throughfall collection, transport and storage

To collect throughfall water, we installed rain gauges in all selected plots, at locations representative for the plots' tree species composition (i.e. at the crossing point between 4 groups of 3 x 3 trees, with each group

representing another species in the four-species mixtures, Figure 1). In each location, we installed four rain gauges to account for spatial heterogeneity (Figure 1). We used rain gauges consisting of plastic bottles (2 litres) with a white plastic funnel on top (diameter of 14 cm). In each funnel, we placed a nylon wire mesh to prevent contaminations from large particles e.g. leaves, insects and small animals, etc. Besides the rain gauges below the trees, we also installed two sets of four rain gauges well away from trees (at least 50 m in all directions) to collect the open-field rainfall at the study site, which is then used to calculate wet deposition for each ion. This resulted in a total of 32 measurement locations (2 blocks x [5 monocultures + 5 two-species mixtures + 5 four-species mixtures + 1 reference]) and a total of 128 rain gauges (4 rain gauges at each location). Throughfall water was collected every two weeks, resulting in 25 collection moments from March 2019 to March 2020.

For each collection moment, throughfall water from 4 rain gauges of each plot was mixed thoroughly and at least 100 ml of this mixed sample stored in a plastic bottle. This resulted in a total of 800 water samples (32 plots × 25 collection dates) throughout a year. All parts of rain gauges (i.e. funnels, bottles and meshes) were cleaned after each collection using demineralized water. Rain samples were kept cool during transport, and stored in freezer at -5 °C in the laboratory, which were used for the next step chemical analysis.

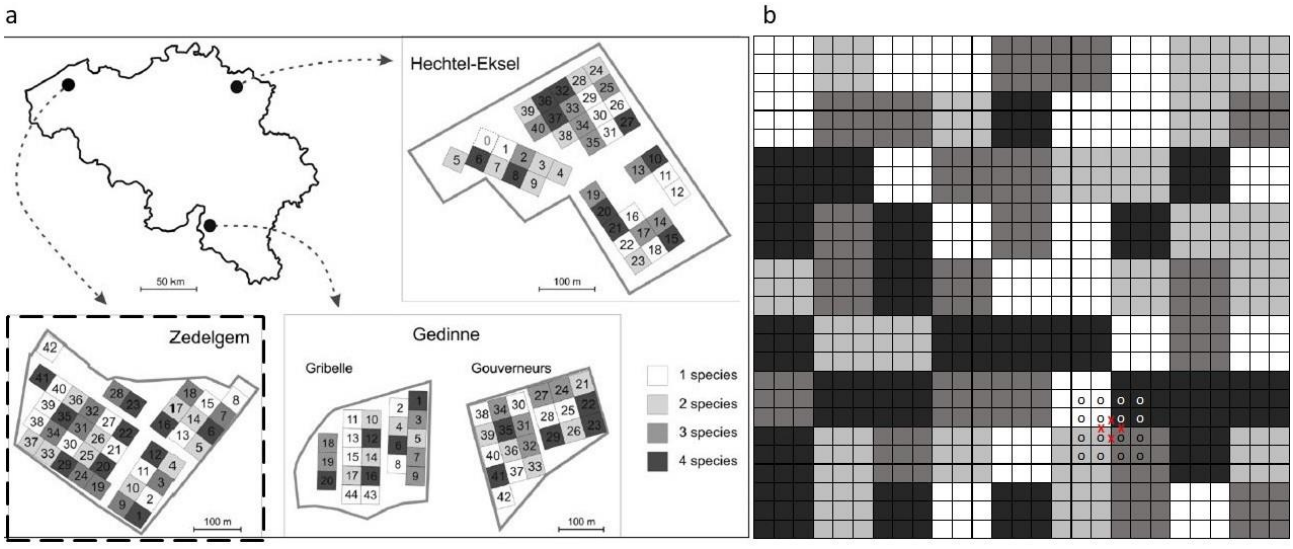


Figure 1 Schematic diagram of (a) the selected research site (Zedelgem) in Belgium and (b) one four-species plot with a randomly selected subplot. Trees were planted on a 1.5 m * 1.5 m grid in groups of 9 individuals per species in mixed plots. The subplots consist

of 4 groups of four trees (circled by O), each group representing a different species (grey scaling was used to differentiate between the four species). Four rain gauges were installed in between four trees (denoted by red "X").

2.3. Chemical analysis and data quality

For the chemical analysis, we selected 384 rain samples (12 collection dates evenly distributed across the year × 32 rain samples per collection date) from the 800 samples collected in total, which reduced the temporal resolution of our data to one month. This selection of rain samples was assumed to be representative to describe the yearly nutrient fluxes in all plots. Before each analysis, water samples were defrosted firstly and then filtered through 0.45 µm polypropylene membranes. After filtration, concentrations of K^+, Ca^{2+}, Na^+, Mg^{2+} were measured by flame atomic absorption spectrophotometry (AA240FS, Fast Sequential AAS), while NO_3^-, SO_4^{2-}, PO_4^{3-} and Cl^- were determined via ion chromatography (Dionex). NH_4^+ Concentrations were determined through colorimetric measurements according to ISO 14256-2:2005 on an auto-analyser (AA3, Bran Luebbbe, Germany). Finally, H^+ concentrations were derived from pH measurements. Determination limits (DL, umol l^{-1}) of ion-specific chemical analyses were: 5.3 (Na^+), 4.4 (K^+), 4.1 (Ca^{2+}), 0.4 (Mg^{2+}), 2.5 (Cl^-), 1.7 (NO_3^-), 0.6 (SO_4^{2-}), 0.5 (PO_4^{3-}) and 0.6 (NH_4^+). In total, we encountered 5 (NH_4^+), 94 (PO_4^{3-}) and 3 (NO_3^-) concentrations that were below the DL, out of in total 384 observations per element. Observations below the DL were set to half of the DL. The accuracy of the chemical analysis was checked by verifying whether the ion balance was close to zero (<0.2 mmol L^{-1}). This check revealed that most of the chemical analyses were of good quality (80 % of the ion balance are below 0.2 and 17 % of that in between 0.2-0.4). Finally, we also removed outliers that potentially originated from contaminations with bird droppings. As it has been shown that PO_4^{3-} can be seen as a tracer element to indicate bird dropping contamination (Erisman & Draaijers, 2003), we excluded observations with concentrations that exceed the third quartile [Q3] value by more than 1.5 times the interquartile range [IQR]. This procedure led to a selection of 26 samples that could be considered contaminated. As probably not only PO_4^{3-} concentrations were affected, we excluded all observations (for all elements) from these contaminated samples. In the end, compounds (PO_4^{3-}, NO_3^- and NH_4^+) were expressed as PO_4^{3-}-P, NO_3^--N and NH_4^+-N for the data analyses.

Forest structure

Tree height and diameter at breast height (DBH) were measured on 16 trees surrounding the installed rain collectors (Figure 1b). Tree height was measured with a vertex clinometer and DBH with a calliper at 1.30 m above the ground. Measurement of tree height and DBH occurred in March 2020. Subsequently, basal area (BA, m^2 ha^{-1}) of individual species was calculated based on these DBH measurements. Canopy cover was measured exactly in the middle of the four rain gauges with a spherical densiometer (Depauw et al., 2021; Lemmon, 1956).

2.4. Data analysis

We, firstly, calculated wet (water samples collected in the open field) and throughfall (based on below-canopy throughfall water) depositions for all the ions using the following formula:

$$D = (C * V)/(A * 100\,000)$$

Where D is deposition of a certain ion (kg ha^{-1}), A is the funnel area of the collectors (unit in m^2), C is concentration of a certain ion (mg L^{-1}) and V is the water volume in each month (ml per gauge). Next, we summarised our monthly dataset (unit in kg ha^{-1}) into yearly cumulative statistics for each ion by a summation of all values (kg ha^{-1} y^{-1}). Accordingly, we obtained a new dataset containing year-round deposition values for each ion, for 32 plots ([5 four-mixture + 5 two-mixture + 5 monoculture + 1 open-field] * 2 blocks).

After that, we applied linear mixed-effects models (LMMs) with 'species richness' as a fixed predictor and 'block' as a random term, to test for tree species richness effects on throughfall deposition in the forest. The lme function of the nlme-package was applied to fit our models (Zuur et al., 2007). Goodness-of-fit was determined by calculating marginal and conditional R^2 values using the r.squaredGLMM function in the MuMIn-package (Bartón, 2014).

Finally, piecewise structural equation models (pSEM) were applied to test the way tree species diversity affects throughfall deposition of each ion. We specifically test whether species mixing affects throughfall deposition directly, or indirectly via its effect on stand basal area (as mixing can increase stand productivity) and canopy cover (as mixing might lead to enhanced crown complementarity). As significant differences between coniferous and deciduous species in terms of throughfall deposition have already been reported,

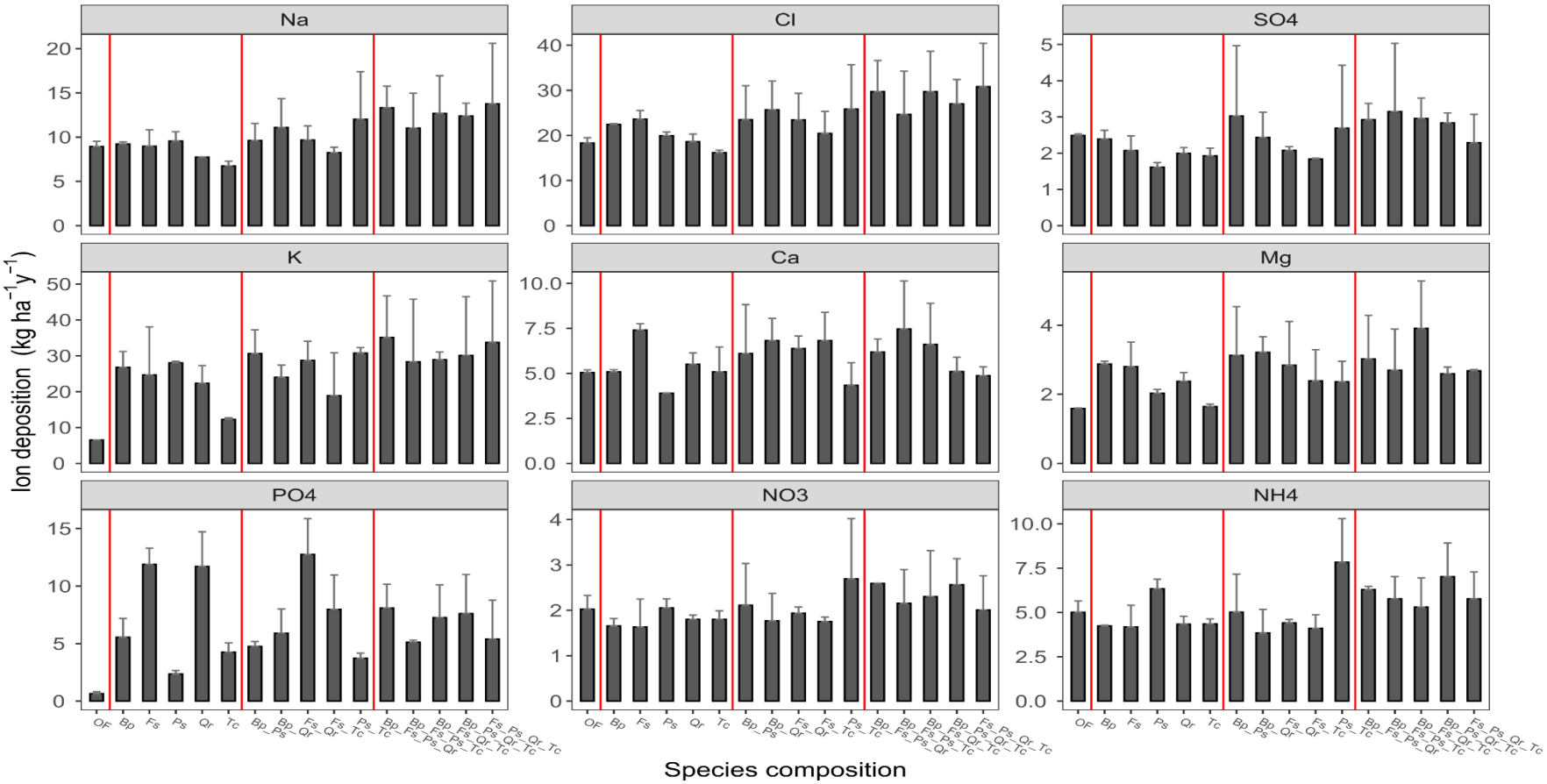
we additionally control for the relative abundance of conifers (i.e. pine in the experiment) in the model. For each path in the structural equation model, we fitted mixed-effect models with 'block' as random intercept. SEM models were fitted using the piecewiseSEM-package (Lefcheck, 2016). All analyses were performed in R version 4.1.1.

3. Results

Yearly wet deposition, measured in open-field plots, found to be 2.0 ± 0.3 (NO_3^--N; Mean ± SD), 5.0 ± 0.6 (NH_4^+-N) and 2.5 ± 0.04 (SO_4^{2-}-S) kg ha^{-1} y^{-1} (Table S3). Throughfall deposition of these air pollutants were highly dependent on the tree species present in the overstorey. High throughfall deposition of inorganic N was detected below canopies of pine (*P. sylvestris*) in both monocultures and mixtures. The highest throughfall deposition occurred within mixtures of pine and lime (*T. cordata)* for both NH_4^+-N (7.8 ± 2.5 kg ha^{-1} y^{-1}) and NO_3^--N (2.7 ± 1.3 kg ha^{-1} y^{-1}). Stands composed of birch (*B. pendula*) and pine were always positively associated with throughfall deposition of SO_4^{2-}-S, which was highest within mixtures of beech (*F. sylvestris*), birch, lime and pine (3.2 ± 1.9 kg ha^{-1} y^{-1}), followed by mixtures of birch and pine (3.0 ± 1.9 kg ha^{-1} y^{-1}). Throughfall deposition of Na^+ and Cl^- was found to be in line with that of SO_4^{2-}-S, being higher in stands composed of birch and pine.

Furthermore, we obtained mean wet deposition of 6.5 ± 0.01, 5.1 ± 0.1 and 1.6 ± 0.01 kg ha^{-1} y^{-1} for K^+, Ca^{2+} and Mg^{2+}, respectively. Strong identity effects were detected for these elements as well. The lowest throughfall deposition of K^+ was found below canopies of lime (12.2 ± 0.5 kg ha^{-1} y^{-1}), while the highest value found in the mixtures of beech, birch, oak and pine (35.1 ± 11.6 kg ha^{-1} y^{-1}). In addition, the presence of pine was always negatively associated with depositions of Ca^{2+} and Mg^{2+}. The lowest deposition of Ca^{2+} was found in monocultures of pine (3.9 ± 0.02 kg ha^{-1} y^{-1}), followed by mixtures of pine and lime (4.3 ± 1.3 kg ha^{-1} y^{-1}).

Throughfall deposition of PO_4^{3-}-P was found to be much higher than its wet deposition (0.6 ± 0.2 kg ha^{-1} y^{-1}), ranging between 2.4 (the monoculture of pine) and 11.9 kg ha^{-1} y^{-1} (the monoculture of beech) in forests. Strong identity effects for PO_4^{3-}-P were also detected, with presence of pine generally leading to lower throughfall deposition of P.



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223 **Figure 2** Wet (open field) and throughfall (in the forest stands) depositions in a complete year. Black bars indicated year-round ion deposition and error bars displayed standard deviation [SD] within

224 each species composition. Abbreviation displayed in the x axis represents open field [OF] and the tree species composition, *Betula pendula* [Bp], *Fagus sylvatica* [Fs], *Pinus sylvestris* [Ps], *Quercus*

225 *robur* [Qr] *and Tilia cordata* [Tc].

We found that throughfall deposition of Na^+, Cl^-, SO_4^{2-}-S, K^+, NO_3^--N and NH_4^+-N significantly ($p < 0.05$) increased with tree species richness (Figure 3). Throughfall deposition increases with 1.38 (Na^+), 2.68 (Cl^-), 0.27 (SO_4^{2-}-S), 2.74 (K^+), 0.17 (NO_3^--N) and 0.45 (NH_4^+-N) kg ha^{-1} y^{-1} per species added to the mixture.

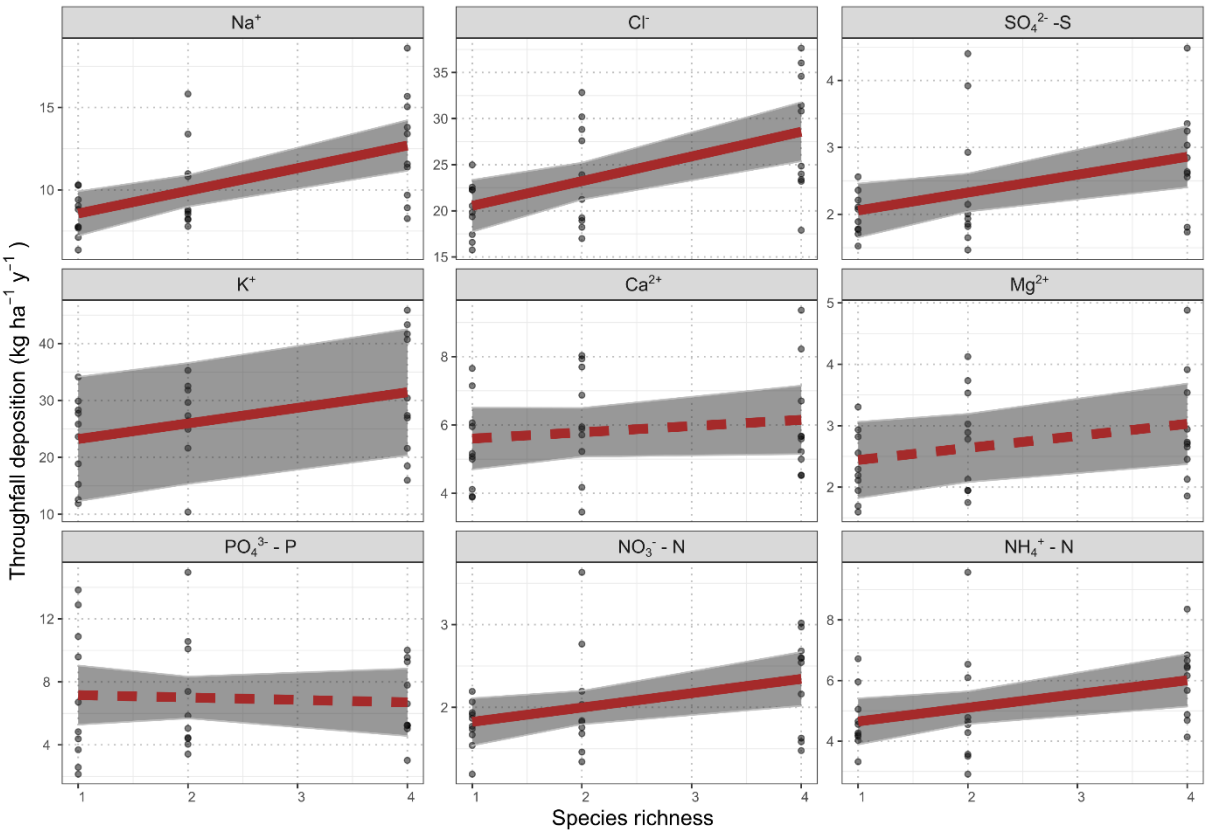

Figure 3 The relationship between tree species richness and throughfall deposition. Linear mixed models with random term "1 | *block*" were applied to test the relationship between tree species richness and throughfall deposition. Red solid lines indicate significant effects while red dashed lines represent non-significant effects. Grey areas display 95% confidence intervals.

Based on the pieceswise SEM model, a direct species richness effect was only found for Na^+ deposition (Figure 4). In addition, indirect positive effects of species richness, via increased basal area, were detected for Na^+, Cl^-, SO_4^--S, Mg^{2+} and NO_3^--N. Another indirect positive effect, via canopy cover, was detected for K^+. Besides these indirect species richness effects, we also detected strong identity effects. Presence of pine decreases throughfall deposition of Ca^{2+}, Mg^{2+} and PO_4^{3-}-P, and increases throughfall deposition of NH_4^+-N.

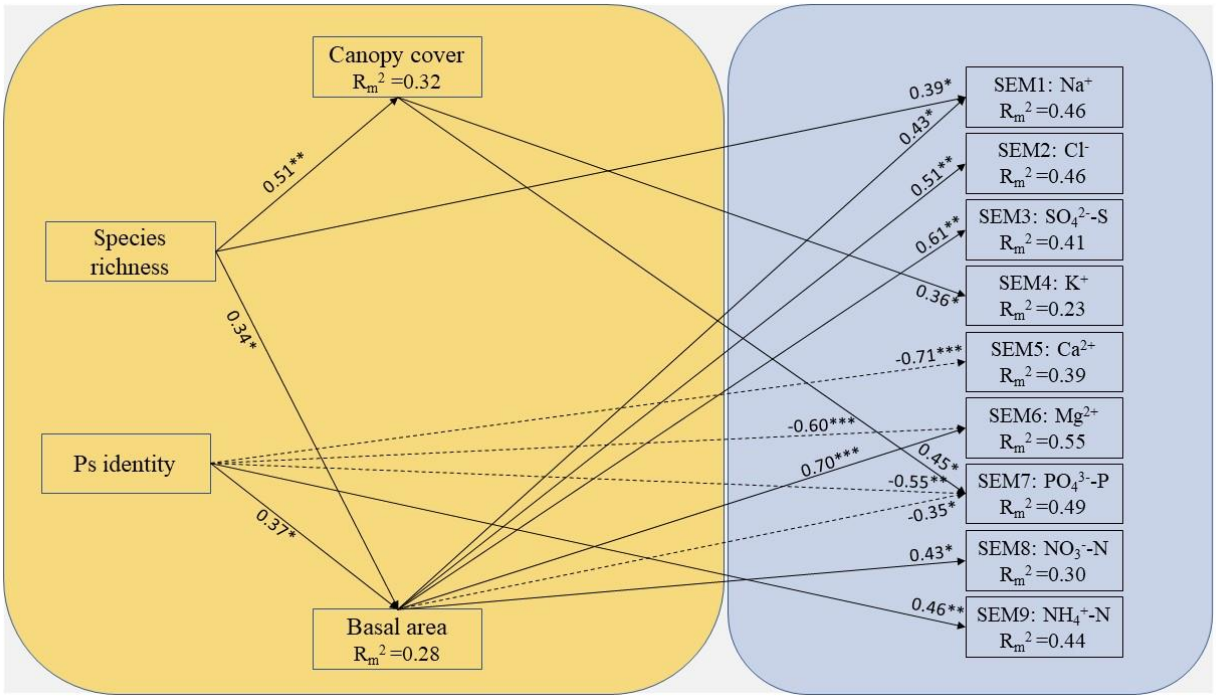

Figure 4 Direct and indirect effects of species richness, species identity, basal area and canopy cover on throughfall deposition, using piecewise structural equation models (SEMs). We fitted a SEM for each ion independently, but show these nine SEMS in one composite graph. The yellow part displays the common terms used in all nine SEMs while the blue part contains all ion-specific responses which were unique for each fitted SEM. Marginal (r^2m) R^2 values for all fitted linear regression models are shown below each response variable. Only significant effects were present, positive effects were denoted by solid arrows in the graph, while negative relationships were depicted by dashed arrows. All the models had a p close to 1, indicating no potentially significant missing paths were excluded and reliable structures were constructed. The numbers associated to each arrow indicate the standardised estimates of the fitted models. Labels *, **, *** indicate significance at the $P < 0.05$, $P < 0.01$ and $P < 0.001$ levels, respectively.

4. Discussion

The obtained values of mean wet deposition of 2.0 ± 0.3 (Mean ± SD), 5.0 ± 0.6 and 2.5 ± 0.04 kg ha^{-1} y^{-1} for NO_3^--N, NH_4^+-N and SO_4^{2-}-S are in agreement – albeit a bit smaller – with wet deposition values of these ions reported by other studies. Zimmermann et al. (2003), for example, reported that wet deposition of NO_3^--N, NH_4^+-N and SO_4^{2-}-S ranges, respectively, between 5 and 6, 6 and 8 and 5 and 7 kg ha^{-1} y^{-1} in central Europe. In another experimental study, conducted in the same region as our study (Flanders), De Schrijver et al. (2008) estimated a mean wet deposition of 6.6 ± 0.3 (Mean ± SD), 11.6 ± 0.9 and 3.8 ± 0.3 kg ha^{-1} y^{-1} for NO_3^--N,

NH_4^+-N and SO_4^{2-}-S, respectively. The lower wet deposition of these ions might be due to differences in meteorological variables (e.g. the proximity and strength of emission sources, proximity to the sea), but also because overall emissions of both acidifying and eutrophying compounds have decreased in western Europe (e.g. via stricter emission norm for vehicles, reported by Waldner et al., (2014)). Furthermore, we also measured the mean wet deposition of other major ions, amounting up to 18.3 ± 1.2 (Cl^-), 8.9 ± 0.3 (Na^+), 6.5 ± 0.01 (K^+), 5.1 ± 0.1 (Ca^{2+}), 1.6 ± 0.01 (Mg^{2+}) kg ha^{-1} y^{-1}. These estimates were found to be higher than those reported in another study in central Europe (e.g. Zimmermann et al., 2003). Our finding, which is in agreement with Erisman et al. (1997) and Hedin et al. (1994), likely points at the influence of marine air trajectories, e.g. prevailing southerly to westerly winds in our case, which may influence the deposition of this set of ions. Higher inputs of these ions reported in our research, therefore, can be attributed to the proximity to the sea (15km). Finally, wet deposition of PO_4^{3-}-P was estimated to amount up to 0.6 ± 0.2 kg ha^{-1} y^{-1} on average. This value is more or less equal to P wet deposition (around 0.4 kg P ha^{-1} y^{-1}) based on global temperate P datasets, reported by Sohrt et al. (2017), suggesting that no pollen nor dust contaminated our samples.

Throughfall deposition of air pollutants differed dramatically among tree species, indicating strong species identity effects. We found, for example, that the presence of pine was always positively associated with increased deposition of inorganic N (Figure 2). This finding can be partially attributed to the species' fast-growing nature (see also Table S5), as we also found that stand structural attributes significantly affect NO_3^--N deposition (Figure 4), with increased throughfall deposition of NO_3^--N in stands with a higher basal area. This basal area effect has been found to affect throughfall deposition of NO_3^--N in other studies as well, mostly via its positive effect on dry deposition being investigated (De Schrijver et al., 2008; Erisman & Draaijers, 2003). On the other hand, NH_4^+-N seems being taken up by deciduous species only, being reflected in throughfall deposition values in deciduous stands that are obviously lower than wet deposition values, which is in line with findings reported by De Schrijver et al. (2008). Additionally, stands composed of birch and pine, were generally associated with higher throughfall deposition of SO_4^{2-}-S. This is because sulphur behaves conservatively within the canopy with negligible impacts from canopy exchange processes to overall throughfall deposition (Draaijers et al., 1997; Lindberg & Lovett, 1992). The factor favoring dry deposition,

i.e. basal area effect (Figure 4), became the strong determinant in SO_4^{2-}-S deposition, which is in line with the literature as well (De Schrijver et al., 2008; Erisman & Draaijers, 2003). Given that Na^+ and Cl^- are also known as inert ions in terms of canopy exchange (Ulrich, 1983), parallel results are thereby detected in our experiment – basal area effect comes out to be the key driver in throughfall deposition for this set of ions (Figure 4).

Corroborating (Adriaenssens et al., 2012; G. M. Lovett & Lindberg, 1984; Tukey, 1970), for base cations, such as K^+, Ca^{2+} and Mg^{2+}, canopy tissue generally acts as a source, leading to a higher throughfall deposition than their wet deposition (see Figure 2). Throughfall deposition of K^+ increased on average 4.1 times compared to wet deposition, while for Ca^{2+} and Mg^{2+} the factor was 1.2 and 1.7, respectively (Table S3). This is in accordance with past studies (Adriaenssens et al., 2012; Staelens et al., 2007) and can be explained by the fact that K^+ forms only weak complexes in cells being readily exchangeable (Marschner, 1995), while Ca^{2+} and Mg^{2+} are bound stronger within the cell walls, structural tissues or enzyme complexes and are therefore basically immobile (Tukey, 1970). We found that throughfall deposition of Ca^{2+} and Mg^{2+} were negatively associated with stands composed of pine species (Figure 2 and 4). This negative pine effect can be explained by differences in leaf traits between needles and broadleaves, for instance, leaf wettability (Adriaenssens et al., 2012; Klamerus-Iwan & Błońska, 2018). Another explanation for this can be lower Ca^{2+} and Mg^{2+} concentrations of needles compared to broadleaves (Table S4).These leaf traits have been found to affect the amount of Ca^{2+} and Mg^{2+} leaching from the leaves significantly (Adriaenssens et al. 2012). Throughfall deposition of Ca^{2+} and Mg^{2+}, therefore, varied dramatically with the relative abundances of pine species, suggesting a strong identity effect of pine (Figure 4). In addition, we detected that stands composed of lime were always negatively associated with throughfall deposition of K^+ (Figure 2). This, mainly indirect (Fig. 4), stand effect can be explained by lime's low growth rate compared to the other species in terms of the build-up of the canopy crown (illustrated by the lowest canopy cover; Table S5). In the end, a strong identity effect was also found for throughfall deposition of PO_4^{3-}-P. Presence of pine was always negatively associated with P throughfall deposition (Figure 2 and 4), again attributable to lower wettability and P concentrations of needles compared to broadleaves (Table S4). Additionally, we found that throughfall deposition of P increased on average 10.9 times compared to wet deposition in the open field (Table S3). The higher P

311 deposition detected in our forests, is most likely due to canopy P leaching, and can be attributed to higher
312 leaf P concentrations in post-agricultural lands. Indeed, former agricultural lands have significantly higher soil
313 P concentrations, resulting in more P uptake and higher P concentrations in the aboveground biomass. Our
314 finding revealed an important pathway of P cycling in post-agricultural lands, from the soil via the foliage and
315 throughfall back to the forest floor. As a result, soluble phosphate enriched the forest floor. Our research
316 thus has important implications for below-canopy biodiversity (e.g. P can strongly affect growth of
317 contrasting understorey herbs differently) and functioning (e.g. enhanced eutrophication, negatively
318 affecting surface water quality).

319 Besides tree species identity effects on throughfall deposition being investigated in our experiment, species
320 richness effects were detected as well. We found, for example, that throughfall deposition of Na^+, Cl^-, SO_4^{2-}-
321 S, K^+, NO_3^--N and NH_4^+-N increased with tree species richness (Figure 3). These species richness effects,
322 however, were mainly indirect, mostly via increased basal area and canopy cover (Figure 4). Firstly, we
323 detected a higher basal area in stands with a higher tree species richness (Figure 4). The richness effect we
324 found can be attributed to overyielding of trees when grown in mixtures, as also found in previous studies
325 (e.g. Van de Peer et al., 2018). This overyielding might be attributable to crown complementarity in mixed
326 stands, reflected in increased canopy cover with tree species richness (Figure 4), which in turn, improves the
327 efficiency of light use and thereby increases the overall growth rate in mixtures. Given that stand structural
328 attributes (i.e. basal area and canopy closure) have been found to affect the amount of these ions deposited
329 significantly (Figure 4), with higher throughfall deposition of these ions with higher stand structural attributes.
330 This set of ions increased with tree species richness accordingly. In addition, we detected that throughfall
331 deposition of NH_4^+-N increased with tree species richness (Figure 3). This species richness effect might be
332 explained by the overall increased occupation (BA-based) of pine species being achieved in forest mixed
333 stands, which might be attributable to its fast-growing nature (Table S5). Given that throughfall deposition
334 of NH_4^+-N positively associated with the relative abundances of pine species (Figure 4), enhanced throughfall
335 deposition of NH_4^+-N with higher tree species richness is therefore in expectation (Figure 3).

336

5. Conclusion

In sum, we show that throughfall deposition highly depended on species identity, but that diversity effects were present as well. Species characteristics and stand structural traits, such as basal area and canopy cover, emerge as key factors driving throughfall deposition, and can also help to explain differences among forest stands with different diversity levels. Tree species diversity effects were indeed present, indicating that adding tree species explicitly increased the amount of throughfall deposition for the ions of Na^+, Cl^-, SO_4^{2-}-S, K^+, NO_3^--N and NH_4^+-N reaching the forest floor. These species richness effects were mainly indirect, mostly via increased basal area and canopy cover. In addition, our study highlighted an important P cycling pathway in post-agricultural lands, from the soil via the foliage and throughfall back to the forest floor. As a result, soluble phosphate enriched the forest floor. In summary, our research shows that tree species diversity can increase throughfall deposition for most of the ions, giving rise to higher nutrient inputs to the soil and the below-canopy communities.

Authors' contribution statement

SZ, PDF, DL and KV conceived and designed research. SZ led the data collection, data analysis and writing.

Data accessibility

Data and code will be made available on figshare.

Conflict of interest

The authors have no conflicts of interest to declare.

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