Biotic and abiotic controls of nitrogen and phosphorus cycling in Central European forests

Inauguraldissertation
der Philosophisch-naturwissenschaftlichen Fakultät
der Universität Bern

vorgelegt von

Martin Thilo Schwarz

von Deutschland

Leiter der Arbeit:

Prof. Dr. W. Wilcke
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Von der Philosophisch-naturwissenschaftlichen Fakultät angenommen.

Bern, 28.04.2015

Der Dekan:
Prof. Dr. G. Colangelo

To my grandfather.

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List of Abbreviations

μ_g	geometric mean
ϕ	estimated correlation among repeated observations
σ_g	geometric standard deviation
AEG	experimental grassland plot in the Schwäbische Alb
AEW	experimental forest plot in the Schwäbische Alb
AICc	Akaike's information criterion adjusted for small sample size
ALB	Schwäbische Alb
CB	canopy budget
CFA	continuous flow analyzer
dbh	diameter at breast height
DD	dry deposition
DON	dissolved organic nitrogen
DOP	dissolved organic phosphorus
EP	experimental plot
G	stand basal area
GS	growing season
HAI	Hainich-Dün
HEG	experimental grassland plot in Hainich-Dün
HEW	experimental forest plot in Hainich-Dün
LL	litter leachate
LME	linear mixed effects model
MAP	mean annual precipitation
MAT	mean annual temperature
mmol_c	charge-equivalent millimol per litre
N_{min}	inorganic/mineral nitrogen
n.i.	not included
n.s.	not significant
$\mathrm{NH_4}^+$-N	$\mathrm{NH_4}^+$ as mass of N only
$\mathrm{NO_3}^-$-N	$\mathrm{NO_3}^-$ as mass of N only
$\mathrm{PO_4}^{3-}$-P	$\mathrm{PO_4}^{3-}$ as mass of P only
RF	bulk wet deposition
SCH	Schorfheide-Chorin
SD	standard deviation
SEG	experimental grassland plot in Schorfheide-Chorin
SEW	experimental forest plot in Schorfheide-Chorin
SF	stemflow

TD	total deposition
TDN, TN	total dissolved nitrogen
TDP	total dissolved phosphorus
TF	throughfall
TF+SF	stand deposition
VIP	very intensively studied experimental plot

Abstract

The functioning and services of Central European forests are threatened by global change and a loss of biodiversity. Nutrient cycling as a key forest function is affected by biotic drivers (e.g., dominant tree species, understory plants, soil organisms) that interact with abiotic conditions (e.g., climate, soil properties). In contrast to grassland ecosystems, evidence for the relationship of nutrient cycles and biodiversity in forests is scarce because the structural complexity of forests limits experimental control of driving factors. Alternatively, observational studies along gradients in abiotic conditions and biotic properties may elucidate the role of biodiversity for forest nutrient cycles.

This thesis aims to improve the understanding of the functional importance of biodiversity for nutrient cycles in forests by analyzing water-bound fluxes of nitrogen (N) and phosphorus (P) along gradients in biodiversity in three regions of Germany. The tested hypotheses included: (1) temperate forest canopies retain atmospheric N and retention increases with increasing plant diversity, (2) N release from organic layers increases with resource availability and population size of decomposers but N leaching decreases along a gradient in plant diversity, (3) P leaching from forest canopies increases with improved P supply from recalcitrant P fractions by a more diverse ectomycorrhizal fungal community.

In the canopies of 27 forest stands from three regions, 16 % to 51 % of atmospheric N inputs were retained. Regional differences in N retention likely resulted from different in N availability in the soil. Canopy N retention was greater in coniferous than in beech forests, but this was not the case on loess-derived soils. Nitrogen retention increased with increasing tree and shrub diversity which suggested complementary aboveground N uptake. The strength of the diversity effect on canopy N uptake differed among regions and between coniferous and deciduous forests. The N processing in the canopy directly coupled back to N leaching from organic layers in beech forests because throughfall-derived N flushed almost completely through the mull-type organic layers at the 12 studied beech sites. The N release from organic layers increased with stand basal area but was rather low (< 10 % of annual aboveground litterfall) because of a potentially high microbial N immobilization and intensive incorporation of litter into the mineral soil by bioturbation. Soil fauna biomass stimulated N mineralization through trophic interactions with primary producers and soil microorganisms. Both gross and net leaching from organic layers decreased with increasing plant diversity. Especially the diversity but not the cover of herbs increased N uptake. In contrast to N, P was leached from the canopy. Throughfall-derived P was also flushed quickly through the mull-type organic layers and leached P was predominantly immobilized in non directly plant-available P fractions in the mineral soil. Concentrations of plant-available phosphate in mineral soil solution were low and P leaching from the canopy increased with increasing concentrations of the moderately labile P fraction in soil and increasing ectomycorrhiza diversity while leaf C:P ratios decreased. This suggested that tree P supply benefited from complementary mining of diverse mycorrhizal communities for recalcitrant P. Canopy P leaching increased in years with pronounced spring drought which could lead to a deterioration of P supply by an increasing frequency of drought events.

This thesis showed that N and P cycling in Central European forests is controlled by a complex interplay of abiotic site conditions with biological processes mediated by various groups of organisms, and that diverse plant communities contribute to tightening the N cycle in Central European forests and that diverse mycorrhizal communities improve the limited P availability. Maintaining forest biodiversity seems essential to ensure forest services in the light of environmental change.

Zusammenfassung

Die Funktionen und Dienstleistungen mitteleuropäischer Wälder sind durch die globale Umweltkrise und den Verlust an Biodiversität gefährdet. Nährstoffkreisläufe als eine Schlüsselfunktion von Wäldern werden durch biotische (z.B. Hauptbaumart, Unterwuchs, Bodenorganismen) und abiotischen Bedingungen (z.B. Klima, Bodeneigenschaften) beeinflusst, die miteinander interagieren. Im Gegensatz zu Grünlandökosystemen existieren bisher wenige Belege für einen Zusammenhang zwischen Biodiversität und Nährstoffkreisläufen in Wäldern, weil die strukturelle Komplexität von Wäldern die experimentelle Kontrolle von Steuergrössen einschränkt. Alternativ können Beobachtungsstudien entlang von Gradienten abiotischer Bedingungen und biotischer Eigenschaften Aufschluss über die Bedeutung der Biodiversität für Waldnährstoffkreisläufe geben.

Mit dieser Arbeit soll das Verständnis über die funktionelle Bedeutung der Biodiversität für Nährstoffkreisläufe in Wäldern verbessert werden, indem wassergebundene Flüsse von Stickstoff (N) und Phosphor (P) entlang von Biodiversitätsgradienten in drei Regionen in Deutschland untersucht werden. Die geprüften Hypothesen umfassten: (1) Waldkronen halten atmosphärische N-Einträge zurück und die Retention nimmt mit zunehmender Pflanzendiversität zu, (2) die N-Freisetzung aus Humusauflagen nimmt mit zunehmender Ressourcenverfügbarkeit und Zersetzerpopulationen zu, während die N-Auswaschung entlang eines Pflanzendiversitätsgradienten abnimmt, (3) die P-Auswaschung aus Waldkronen nimmt mit einer verbesserten P-Bereitstellung aus rekaliztranten P-Fraktionen durch diversere Ektomykorrhizengesellschaften zu.

Atmosphärische N-Einträge wurden zu 16 % bis 51 % in den 27 Waldkronen der drei Regionen zurückgehalten. Regionale Unterschiede der N-Rückhaltung resultierten vermutlich aus Unterschieden der N-Verfügbarkeit im Boden. Die Kronen-N-Retention war in Nadelwäldern grösser als in Buchenwäldern, dies galt jedoch nicht für Lössstandorte. Die N-Retention nahm mit zunehmender Baum- und Strauchdiversität zu, was auf komplementäre oberirdische N-Aufnahme hindeutete. Das Ausmass des Diversitätseffektes auf die N-Aufnahme in der Krone unterschied sich zwischen den Regionen sowie zwischen Nadel- und Laubwäldern. Die N-Umsetzung in der Krone wirkte sich auf die N-Auswaschung aus Mullauflagen aus, weil N aus dem Bestandesniederschlag fast vollständig durch die Mullauflagen der 12 untersuchten Buchenwälder gespült wurde. Die N-Freisetzung aus Mullauflagen nahm mit zunehmender Basalfläche zu, war aber aufgrund einer potentiell hohen mikrobiellen N-Immobilisierung und intensiver Streueinarbeitung durch Bioturbation in den Mineralboden gering (< 10 % des oberirdischen Streufalls). Die Biomasse der Bodenfauna stimulierte die N-Mineralisation durch trophische Interaktion mit Primärproduzenten und Bodenmikroorganismen. Sowohl die Brutto- als auch Netto-N-Auswaschung aus Mullauflagen nahm mit zunehmender Pflanzendiversität ab. Vor allem die Diversität von Kräutern, nicht aber der Bedeckungsgrad, erhöhte die N-Aufnahme. Phosphor wurde im Gegensatz zu N aus der Krone ausgewaschen. Bestandesniederschlagbürtiges P wurde ebenfalls rasch durch die Mullauflage gespült und wurde in nicht direkt pflanzenverfügbaren P-Fraktionen im Mineralboden gebunden. Konzentrationen pflanzenverfügbaren Phosphats in der Mineralbodenlösung waren gering. Die P-Auswaschung aus der Krone nahm mit steigender Konzentration der mittelfristig verfügbaren P-Fraktion im Mineralboden sowie steigender Ektomykorrhizendiversität zu, während das C:P-Verhältnis der Blätter abnahm. Dies deutete darauf hin, dass die P-Versorgung der Bäume von einer komplementären Erschliessung rekalzitranten Phosphors durch diverse Mykorrhizengesellschaften profitierte. Die P-Auswaschung aus der Krone stieg in Jahren mit ausgeprägter Frühjahrstrockenheit an, was angesichts zunehmender Trockenereignisse zu einer Verschärfung der P-Versorgung von Buchenwäldern führen könnte.

Diese Arbeit zeigte, dass N- und P-Kreisläufe in mitteleuropäischen Wäldern von einem komplexen Zusammenspiel abiotischer Standorteigenschaften und biologischer Prozesse, ausgeübt von verschiedenen Organismengruppen, gesteuert werden, dass diverse Pflanzengesellschaften dazu beitragen, den N-Kreislauf in mitteleuropäischen Wäldern zu straffen, und dass eine eingeschränkte P-Versorgung von Wäldern durch diverse Mykorrhizengesellschaften verbessert wird. Die Erhaltung der Waldbiodiversität scheint daher essentiell zu sein, um Walddienstleistungen im Hinblick auf gegenwärtige Umweltveränderungen zu sichern.

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Chapter 1

Summarizing overview

1.1 Introduction

The functioning of Central European forests is threatened by nitrogen (N) deposition, climate change, land use and a loss of biodiversity (Sala *et al.* 2000). This has led to a growing concern about the stability of ecosystem services (e.g., wood and water production, climate regulation, water purification, biogeochemical cycles, spiritual and recreational benefits) provided by forests to the society (Millennium Ecosystem Assessment 2005) and driven by abiotic and biotic conditions responding to the current environmental change. Deciduous forests are the native vegetation form in Central Europe which has been widely replaced by coniferous production forests, croplands and grasslands by humans (Ellenberg 1996) and only 3 % of the forests in Europe (excluding the Russian Federation) are classified as primary forests (FAO 2011). Today, the dominating tree species in Germany are Norway spruce (*Picea abies* (L.) H. Karst; 26 % cover), Scots pine (*Pinus sylvestris* L.; 23 % cover) and European beech (*Fagus sylvatica* L.; 16 % cover; BMELV 2011). The manipulation of the tree species composition and the management of forests has resulted in changes of biogeochemical cycles (Kristensen *et al.* 2004) and plant species composition, a loss of endangered plant species and associated plant traits (Boch *et al.* 2013; Mayfield *et al.* 2013), and potential feedbacks on the composition of other taxonomic groups like the soil fauna and bacteria (Hooper and Vitousek 1998; Knops *et al.* 2002; Nacke *et al.* 2011). The consequences of this change in biodiversity for forest functioning are poorly understood because the longevity and complexity of forest ecosystems limits the applicability of experimental manipulations of forest biodiversity (Scherer-Lorenzen *et al.* 2005). Long-term observational studies of biogeochemical fluxes along gradients in biodiversity and environmental conditions can contribute to investigate the functional importance of biodiversity in forests and to improve the understanding of the complex interplay of abiotic and biotic environmental controls of element cycling.

Element cycling comprises inputs, outputs, internal fluxes, and recycling processes. Nutrient inputs to forests occur via atmospheric deposition of solutes, gases and particles or via N fixation. Liming of acid acid soils or fertilizing (mainly during establishment of forests) can represent an additional anthropogenic input to forests of Central Europe. Outputs encompass mainly losses by leaching and harvest and to lesser extent by gaseous emissions. The greatest fraction of annual forest nutrient requirements is provided by internal recycling of organic matter (e.g., litter, necromass; Attiwill and Adams 1993) which include a cascade of processes mediated by different taxonomic organism groups that link aboveground and belowground processes (e.g., primary production, decomposition, mineralization, assimilation; Knops *et al.* 2002; Wardle *et al.* 2004; Fornara *et al.* 2009). Furthermore, nutrients can be transferred between ecosystem compartments (e.g., canopy, organic layer, mineral soil) with water. Water-bound nutrient fluxes are indicative of the nutritional status and the controls of biogeochemical cycling in structurally and functionally complex ecosystems like forests. Consequently, the variation of nutrient fluxes along gradients in abiotic conditions and biotic controls can help to forecast the impact of environmental change on forest functioning.

Temperate forests in Europe are most frequently limited in N and the vegetation and the soil can usually retain additional N inputs (Brumme and Khanna 2008). According to *Liebig's Law of the minimum* and observational studies, however, the capacity of ecosystems to retain N is limited and persistently high loads of atmospheric N inputs have pushed northern temperate forests towards what is described as 'nitrogen saturation' (Nihlgård 1985; Aber *et al.* 1998; Matson *et al.* 2002; Galloway *et al.* 2004). Direct consequences of N enrichment in forests comprise increased nitrification and denitrification rates, and hence increased nitrate (NO_3^-) leaching and nitrous oxide (N_2O) emissions, respectively (Dise and Wright 1995; MacDonald *et al.* 2002; van Breemen *et al.* 2002) and thus a malfunction of ecosystem services. As the quantitatively most important nutrient, N cycling plays a crucial role in ecosystem functioning. Nitrogen closely interacts with water, carbon (C) and phosphorus (P) cycling, as well as the plant and decomposer community composition and diversity, respectively (Schulze *et al.* 1994; De Vries *et al.* 2006; Gilliam 2006; Bobbink *et al.* 2010; Vitousek *et al.* 2010; Crowley *et al.* 2012; Verheyen *et al.* 2012; Frey *et al.* 2014). Nitrogen deposition is therefore regarded the greatest threat for forest functioning and biodiversity of northern temperate forests (Sala *et al.* 2000) and mitigating N deposition effects is an essential component of sustainable forest management (von Wilpert *et al.* 2000).

Phosphorus is the second most important nutrient for forest growth. Unlike N, inputs and outputs of P are negligible relative to the internal recycling (Attiwill and Adams 1993). While this might explain why P received less attention in forest biogeochemical research in the past, current N deposition rates raised doubts whether P supply rates are sufficient to meet the increasing demands to balance surplus N availability (Güsewell 2004; Elser *et al.* 2007; Vitousek *et al.* 2010; Marklein and Houlton 2012; Crowley *et al.* 2012). Little is known about the variability in time of controls of forest P cycling. Minerals are the ultimate P source of ecosystems which can only be rendered bio-available at slow rates (Walker and Syers 1976). Phosphorus availability decreases with time because of small but continuous exports, small atmospheric inputs, and the sequestration of inorganic P in sparingly available forms during pedogenesis (Walker and Syers 1976; Cross and Schlesinger 1995; De Schrijver *et al.* 2012). Low P availability is not only a feature of old acidic soils but also of young soils from calcareous bedrocks because of the low solubility of phosphate (PO_4^{3-}) and precipitation as secondary apatites at high pH and high Ca concentrations. It is well accepted that mycorrhizae can access P bound to minerals and organic matter (Colpaert and van Tichelen 1996; van Breemen *et al.* 2000; Wallander 2000; Blum *et al.* 2002; Taylor *et al.* 2009; Plassard and Dell 2010). Mycorrhizae are common in topsoils and colonize almost all root tips of temperate tree species (Lang *et al.* 2011) and mutualistic tree P nutrition seems to be ubiquitous in temperate forests (Plassard and Dell 2010; Cairney 2011). Because of the high mycorrhizal colonization rate, Baxter and Dighton (2001) proposed that the diversity of ectomycorrhizal fungi is more important than abundance for P transfer rates to the fungi's host.

In grassland experiments, it was shown that ecosystem productivity and stability increases with plant diversity (Tilman *et al.* 1996; Isbell *et al.* 2011). Correspondingly, studies in experimental grasslands revealed an enhanced nitrogen use efficiency of more diverse plant assemblages (Tilman *et al.* 1996; Scherer-Lorenzen *et al.* 2003; Oelmann *et al.* 2007). This diversity effect was ascribed to the theory of complementarity that assumes niche partitioning among species through functional traits like rooting depths, seasonal absorption patterns and facilitation (Hooper 1998; Hooper *et al.* 2005; Kahmen *et al.* 2006; McKane *et al.* 2002). Others claimed the observed positive relationship between plant diversity and ecosystem functioning simply arises from a greater likelihood of the presence of highly productive or functional key-species and a greater functional redundancy in more diverse communities (Naeem 1998; Wardle 1999). Increasing evidence was gained in the past decade that biodiversity contributes to ecosystem functioning and that effects may be indirectly mediated or fostered by interactions and trade-offs among various taxa and the diversity thereof (Isbell *et al.* 2011; Allan *et al.* 2013). However, effects of interactions among taxonomic groups and their diversity are still unclear, especially in real-world ecosystems because of site-specific confounding environmental and land-use effects (Symstad *et al.* 2003). For instance, effects of plant diversity on the decomposer community were reported from an experimental grassland site in Germany (Scherber *et al.* 2010) while other studies reported that plant diversity effects on decomposition diminish after plant death (Wardle *et al.* 1997; Srivastava *et al.* 2009). Similar positive effects of biodiversity on ecosystem processes like in grasslands are expected for forest ecosystems (Scherer-Lorenzen *et al.* 2005; Gamfeldt *et al.* 2013) especially because effects of biodiversity increase over time (Symstad *et al.* 2003; Cardinale *et al.* 2007). The diversity-ecosystem functioning relationship can hardly be tested in forests by full-factorial sampling designs which would require the consideration of a too large number of factors to account for the complexity of forests and a too long time to be commensurate with the forest life cycle (Nadrowski *et al.* 2010). However, observational studies of tree species mixtures showed increasing wood (Vilà *et al.* 2007; Morin *et al.* 2011; Paquette and Messier 2011) and fine-root production (Brassard *et al.* 2013) and soil carbon storage (Schleuß *et al.* 2014) with increasing tree diversity. More recently, it was shown that multiple ecosystem services increase with increasing tree species diversity (Gamfeldt *et al.* 2013). To date, no study comprehensively addressed the influence of the diversity as well as the abundance of various taxonomic groups or the diversity of other functional plant groups than trees on nutrient fluxes in forests. For instance, plant diversity in Central European forests is greatest in the understory layers (Boch *et al.* 2013) and in spite of the well-accepted importance of the forest understory for nutrient cycling (Muller and Bormann 1976; Olsson and Falkengren-Grerup 2003), the functional role of herb and shrub diversity for nutrient cycling in forests has not been investigated. Similarly, evidences for beneficial effects of the diversity of mycorrhizal fungi for forest functioning at the stand level are scarce (e.g., Lang and Polle 2011) although mechanistic studies suggest a potentially great influence of mycorrhizal diversity on ecosystem processes (Buscot *et al.* 2000; Baxter and Dighton 2001; Jones *et al.* 2010).

The aim of this thesis is to improve our understanding of N and P cycling in temperate forests under different environmental conditions (abiotic drivers) and the functional importance of biodiversity (main biotic driver considered in this thesis) on nutrient cycling in Central European forests. By monitoring water-bound fluxes of N and P through forests under different environmental conditions in three regions of Germany, I tested the following hypotheses:

i. Central European forest canopies retain atmospheric N (Chapter 2).

ii. Atmospheric N inputs are more efficiently retained in more diverse forest canopies (Chapter 2).

iii. The release of N from organic layers increases with stand basal area and soil fauna biomass because of greater resources and facilitated mineralization (Chapter 3).

iv. The leaching of N from organic layers decreases along a gradient of vascular plant diversity (Chapter 3).

v. Canopy P leaching of P is greater in forests with greater P supply and the cycling of P is increased by a more diverse of ectomycorrhizal fungal community because of an improved access to recalcitrant P pools (Chapter 4).

vi. Canopy P leaching decreases under dry soil conditions because of impaired P uptake (Chapter 4).

1.2 Methods

This study was performed as part of the interdisciplinary research project 'Biodiversity Exploratories' which addresses feedbacks between land use, biodiversity and ecosystem processes (Fischer *et al.* 2010). To allow for conclusions which are representative of large areas in Central Europe, three large-scale research regions in Germany, so-called exploratories, were selected, namely the Schwäbische Alb, Hainich-Dün and Schorfheide-Chorin (Fig. 1.1) where observational and experimental studies are conducted in well-established ecosystems. The Biodiversity Exploratories use a hierarchical sampling design including at least 500 grassland and forest grid plots per area, respectively, which are used to assess spatial variation of soil types, land-use intensities and plant diversity. A subset of 50 grassland and forest grid plots per exploratory, respectively, was selected for more detailed biodiversity assessment, manipulative experiments and environmental monitoring (Experimental Plots; EPs). Very detailed studies of biodiversity and ecosystem processes and highly labor-intensive studies are conducted on a subset of the EPs, the Very Intensive Plots (VIPs), the forest sites of which are subject of this thesis. In each exploratory, 9 grassland sites and 9 forests sites were designated as VIPs (Fig. 1.2, Fig. 1.3, Fig. 1.4) covering triplicates of the three main land-use classes in grasslands (meadows, pastures, mown-pastures) and forests (managed coniferous, managed deciduous, and extensively managed deciduous forests; Tab. 1.1), respectively (see Fischer *et al.* 2010 and www.biodiversity-exploratories.de for more details on the Biodiversity Exploratories and plot selection).

Figure 1.1: Location of the three study regions and nearby cities in Germany.

1.2.1 Study site

Schwäbische Alb

The Schwäbische Alb is located in southern Germany (Fig. 1.1) and is part of the Southern German Escarpment Landscape. The area of the exploratory meets that of the UNESCO Biosphere Reserve Schwäbische Alb (Fig. 1.2). The bedrock is Jurassic limestone that was slightly tilted during the orogenesis of the Alps and falls by approximately 5 to 10° towards southeast. The topography of the area is characterized by smooth domes and depressions and typical karst formations. The altitude ranges from 700 – 850 m a.s.l. and annual mean temperature is 6°C and annual precipitation ranges from 850 – 1000 mm. Soils in Schwäbische Alb are Rendzic Leptosols and Cambisols (IUSS Working group WRB 2006) and are generally shallow, loamy, and slightly acidic. Because of the limestone porosity only few small rivers exist and water is leached mainly to groundwater that partially discharges to the Neckar and the Rhine in the north or to the Danube in the south. The area is sparsely populated and there are only few small industrial plants and no large cattle farms. Land use is distributed patchily and more than half of the area is under sylvicultural use and approximately 20 % is used as grassland.

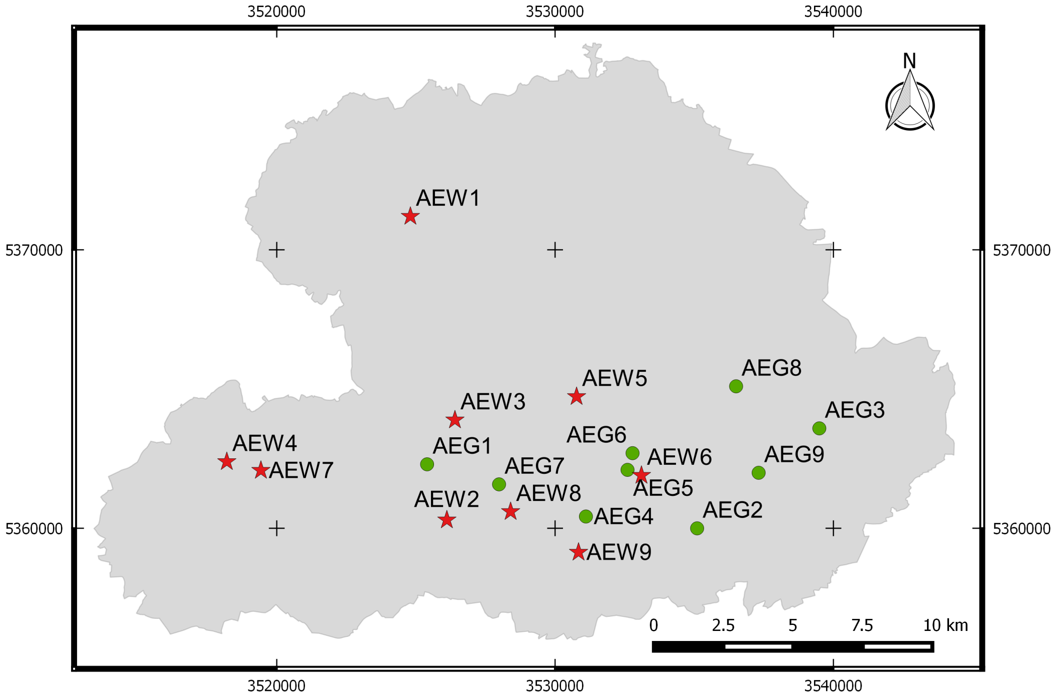

Figure 1.2: Map of the Schwäbische Alb exploratory and location of the studied plots. Grassland plots are indicated by green dots, forest plots are indicated by red stars. Coordinates refer to Gauss-Krüger zone 3.

Table 1.1: Altitude, soil type (IUSS Working group WRB 2006), stand properties and management of the studied forest plots. Age-class forests consist of one or more even-aged development stages which are harvested at 80 – 120 year intervals by clear cut or shelterwood logging and extensively managed forests are mature forests protected for at least 60 years. All trees with a diameter at breast height (dbh) > 7 cm were registered by a forest inventory of the whole plot area (100 m × 100 m). The stand basal area (G) of plot HEW4 was estimated because this forest is a thicket stand with only one tree exceeding the caliper limit. During the time of the study, stand property data have been revised resulting in differences to Tab. 2.2.

Region	Plot ID	Altitude [m a.s.l.]	Soil type	Main tree species	management	stand density [n ha^{-1}]	dbh [cm]	G [m^2 ha^{-1}]
Schwäbische Alb	AEW1	748	Cambisol	*Picea abies* (L.) H. Karst	age-class forest	816	24.5	41.4
	AEW2	737	Leptosol	*Picea abies* (L.) H. Karst	age-class forest	425	31.5	36
	AEW3	693	Cambisol	*Picea abies* (L.) H. Karst	age-class forest	632	28.7	44.5
	AEW4	765	Cambisol	*Fagus sylvatica* L.	age-class forest	2219	12.4	29.7
	AEW5	788	Cambisol	*Fagus sylvatica* L.	age-class forest	139	49.8	27.6
	AEW6	740	Cambisol	*Fagus sylvatica* L.	age-class forest	374	27.6	26.5
	AEW7	772	Leptosol	*Fagus sylvatica* L.	extensively managed forest	199	36	33.2
	AEW8	766	Cambisol	*Fagus sylvatica* L.	extensively managed forest	277	38.5	40.2
	AEW9	742	Leptosol	*Fagus sylvatica* L.	extensively managed forest	376	29.6	32.2
Hainich-Dün	HEW1	427	Stagnosol	*Picea abies* (L.) H. Karst	age-class forest	278	42.6	43.3
	HEW2	366	Stagnosol	*Picea abies* (L.) H. Karst	age-class forest	658	25.5	41.2
	HEW3	410	Luvisol	*Picea abies* (L.) H. Karst	age-class forest	651	27.7	42.6
	HEW4	491	Luvisol	*Fagus sylvatica* L.	age-class forest	1	31.2	7
	HEW5	416	Luvisol	*Fagus sylvatica* L.	age-class forest	487	23.6	25.6
	HEW6	435	Luvisol	*Fagus sylvatica* L.	age-class forest	283	38.3	35.3
	HEW10	378	Stagnosol	*Fagus sylvatica* L.	extensively managed forest	379	28.8	34.8
	HEW11	414	Luvisol	*Fagus sylvatica* L.	extensively managed forest	565	22.4	36.9
	HEW12	333	Luvisol	*Fagus sylvatica* L.	extensively managed forest	326	32.2	36.5
Schorfheide-Chorin	SEW1	54	Cambisol	*Pinus sylvestris* L.	age-class forest	1303	16.8	30.7
	SEW2	75	Cambisol	*Pinus sylvestris* L.	age-class forest	1097	20.1	37.5
	SEW3	66	Cambisol	*Pinus sylvestris* L.	age-class forest	384	32.4	32.7
	SEW4	56	Cambisol	*Pinus sylvestris* L. / *Fagus sylvatica* L.	age-class forest	712	24.7	41.6
	SEW5	64	Cambisol	*Fagus sylvatica* L.	age-class forest	103	46	24
	SEW6	55	Cambisol	*Fagus sylvatica* L.	age-class forest	138	32.2	17.3
	SEW7	78	Cambisol	*Fagus sylvatica* L.	extensively managed forest	152	53.1	36.4
	SEW8	98	Albeluvisol	*Fagus sylvatica* L.	extensively managed forest	150	50.9	37.4
	SEW9	79	Cambisol	*Fagus sylvatica* L.	extensively managed forest	257	43.5	43.1

Hainich-Dün

Hainich-Dün is located in Central Germany (Fig. 1.1). The exploratory area includes part of the Thuringian Basin in the east and the south, and side-horsts of the basin in the west and the north. Altitude ranges 280 – 550 m a.s.l.. The bedrock in Hainich-Dün is Triassic sandstone and limestone. Slopes are additionally covered with loess. Soil types are Luvisols and Cambisols in forests and Stagnosols and Cambisols (IUSS Working group WRB 2006) in grasslands. Mean annual temperature in Hainch-Dün is 6.5 – 8°C and mean annual precipitation ranges 500 – 800 mm. Water discharges from the Hainich-Dün via small tributaries to the Elbe and the Weser and to the North Sea. Land use in Hainich-Dün is linked to topography with grasslands dominating the basin and forests dominating the hilly area in the west and the north, however, grassland and forest VIPs are not spatially distant (Fig. 1.3). The western part encompasses the Hainich National Park which is part of the biggest connected deciduous forest area of Germany.

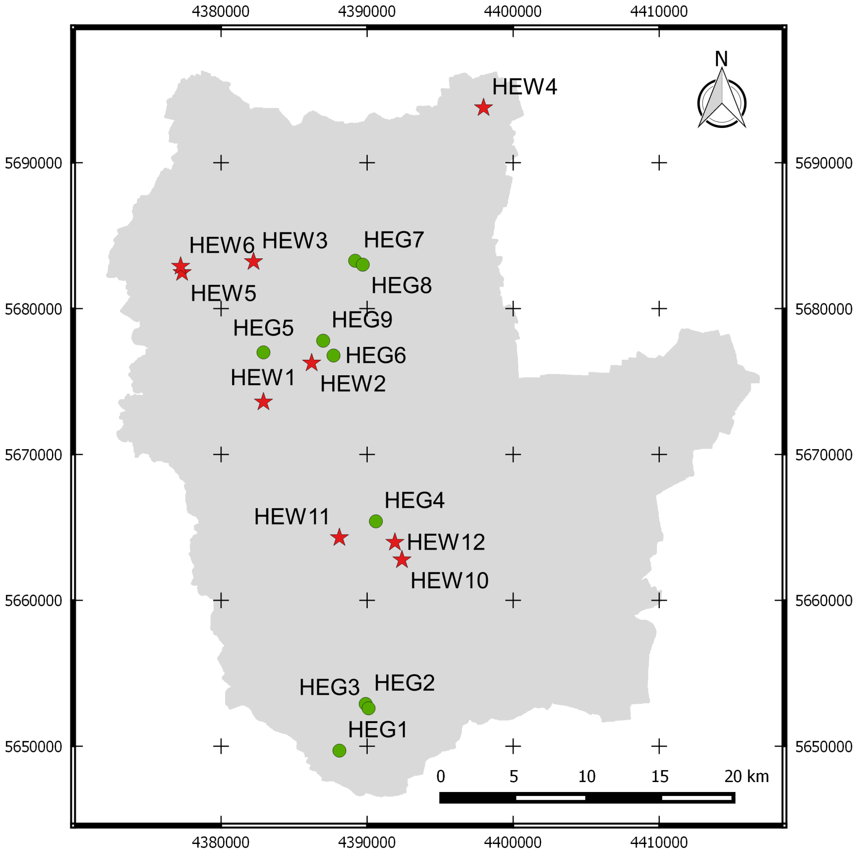

Figure 1.3: Map of the Hainich-Dün exploratory and location of the studied plots. Grassland plots are indicated by green dots, forest plots are indicated by red stars. Coordinates refer to Gauss-Krüger zone 4.

Schorfheide-Chorin

Schorfheide-Chorin is located in the North German Plain (Fig. 1.1) and the exploratory covers the area of the UNESCO Biosphere Reserve Schorfheide-Chorin (Fig. 1.4). The landscape was covered by an ice sheet for the last time during the Weichsel ice age and shaped during the ice retreat in the Holocene giving the typical ensemble of relief features of glacial landscapes. The bedrock consists of quarternary quartzitic sands and glacial till. In depressions, bogs have developed. Therefore, soil types in Schorfheide-Chorin range from Cambisols, Albeluvisols, Gleysols to Histosols (IUSS Working group WRB 2006). Altitude ranges from 3 – 140 m a.s.l.. Mean annual temperature ranges 8 – 8.5°C and mean annual precipitation is only 500 – 600 mm. Water in Schorfheide-Chorin discharges to groundwater or via the Oder to the Baltic Sea. Schorfheide-Chorin is mainly under agricultural use. Spatial patterns of land use in Schorfheide-Chorin are intimately linked to relief position depend on bedrock and soil type: grasslands and agricultural fields are located in depressions on drained Histosols and Gleysols while forests are located on moraines with acidic Cambisols and Albeluvisols.

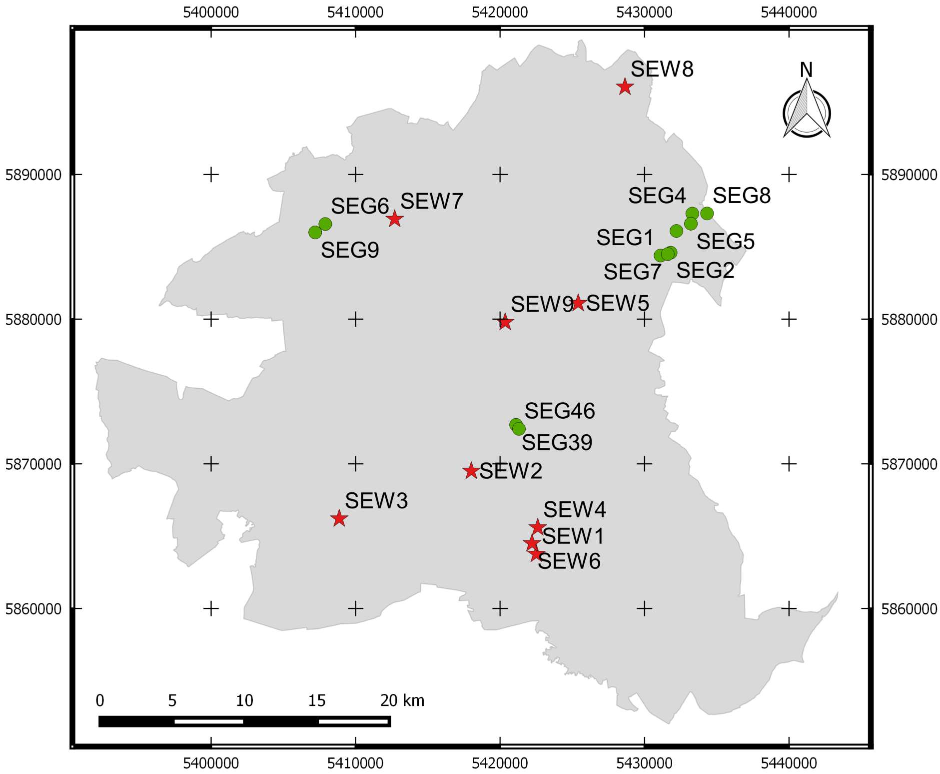

Figure 1.4: Map of the Schorfheide-Chorin exploratory and location of the studied plots. Grassland plots are indicated by green dots, forest plots are indicated by red stars. Coordinates refer to Gauss-Krüger zone 5.

1.2.2 Study design

Instrumentation

The sampling instrumentation to collect water-bound element fluxes through forest ecosystems (Fig. 1.5) was installed in summer and autumn 2009. At three forest sites in Hainich-Dün (HEW1, HEW2, HEW3), stemflow collectors were installed in spring 2010. The installations are depicted in Fig. 1.6.

Nine grassland study plots in the Schwäbische Alb and Hainich-Dün and 11 plots in Schorfheide-Chorin were equipped with 5 samplers for rainfall. The samplers consisted of 2-L polyethylene bottles with a polyethylene funnel ($d = 0.115$ m) attached to it. The samplers were continuously open and therefore collected bulk precipitation and deposition. The sampling bottles were wrapped with aluminum foil to prevent photochemical reactions. A polyester mesh (mesh size = 1.6 mm) was put at the bottom of the funnel to prevent sample contamination with coarse particulate matter. A table-tennis ball was placed into the funnel to reduce evaporation losses during sample collection. The 5 rainfall samplers were placed on the poles (height = 1.8 m) of a fence which protected climate monitoring devices.

In forests, throughfall was collected with 20 samplers constructed in similar manner to rainfall collectors. Throughfall collectors were placed into holes in the ground adjusted to a sampling height of 0.3 m and were spaced equidistantly along two diagonal transects (from NW to SE and from SW to NE) in a subplot of 20 m × 20 m. According to Thimonier (1998), the replicate number of samplers is sufficient to account for spatial heterogeneity of throughfall quantity in Central European forests. No efforts were made to periodically relocate samplers in order to restrict disturbance of other experiments by trampling because of frequent sampling. The subplot for throughfall sampling was chosen to be representative for forest structure and composition of the respective forest.

Stemflow was collected in each forest but HEW4 with 3 collar-type collectors that consisted of polyurethane hoses ($d = 40$ mm) connected around the stem with polyurethane glue and a plastic hose draining the water to polypropylene/polyethylene barrels (different sizes: 210 L, 60 L, 15 L, depending on tree species and diameter at breast height). Target trees for stemflow sampling were selected to reflect tree species composition and diameter classes of the respective stand. At the time of installation, however, no precise information on forest structure was available and decision was thus based on expert knowledge. Stemflow sampling was difficult because of animal

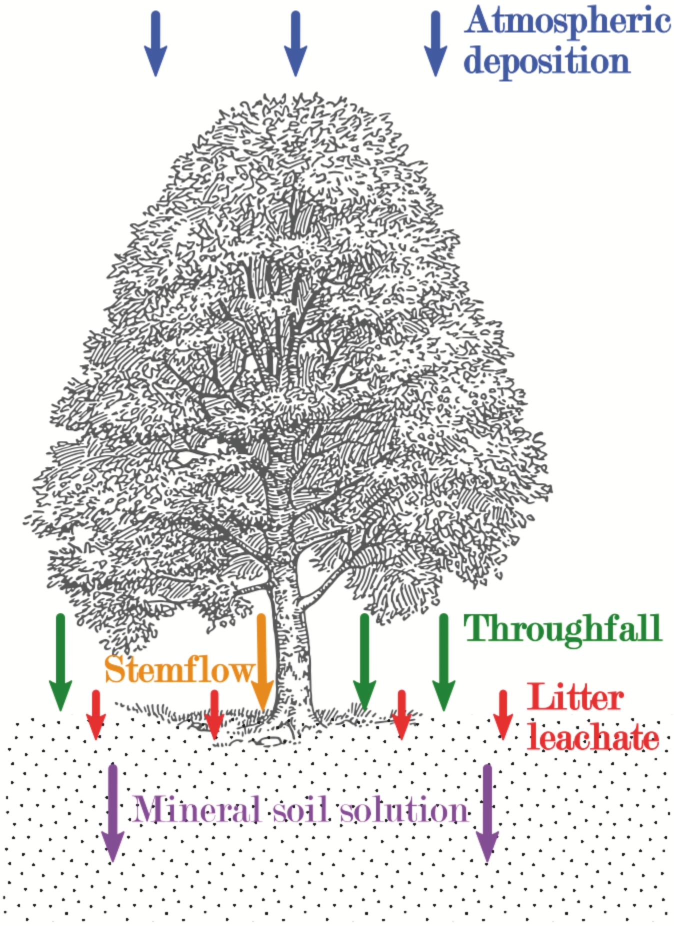

Figure 1.5: Schematic overview of water-bound element fluxes in forest ecosystems as considered in this thesis.

feces in the barrels and frequent leakage of the collar and no reliable data of stemflow was acquired in the years 2011 and 2012. Stemflow was not collected at the forest plot HEW4 because this stand is in thicket stage. In 2012, one stemflow sampling tree at AEW5 and AEW6, respectively, had to be replaced because the original one had been harvested.

Litter leachate was sampled with three circular zero-tension lysimeters (diameter of 0.2 m, polyvinyl chloride) per site which were installed horizontally below the soil organic layer in summer and autumn 2009. Polyethylene hoses attached to the lysimeter outlet drained the collected sample into 2-L polyethylene bottles stored in the dark below ground. The lysimeters were located in a fenced area that already harbored various experiments and instruments which are susceptible to damage by browsing. The organic layers were allowed to regenerate from disturbance over the following litterfall season prior to the beginning of sampling.

Figure 1.6: Sampling devices for forest throughfall (top left), litter leachate (top right), stemflow (center), arrangement of rainfall and throughfall samplers in grasslands (bottom right), and mineral soil solution (bottom left). The center picture was provided by Sebastian Bischoff.

Soil solution in forests was collected with 3 suction cups (polyethylene body with a nylon membrane, 0.45 μm pore width; ecoTech Umwelt-Messsysteme GmbH, Bonn, Germany) per site. Suction cups were installed at an angle of 45°. Sampling depths for mineral soil solution in Hainich-Dün were 0.08 – 0.15 m and 0.28 – 0.35 m, respectively. In Schorfheide-Chorin, mineral soil solution was sampled at the 0.03 – 0.1 m and the 0.63 – 0.7 m depth. Suction cups in Schorfheide-Chorin were replaced by glass suction cups in 2012 because the nylon cups never delivered soil solution. Because forest soils in the Schwäbische Alb were shallow soil solution sampling was restricted to the 0.13 – 0.2 m depth. Suction cups were connected with a 5 m-long polytetrafluorethane tubing to 1-L polypropylene sampling bottles which were stored in a metal box that was buried in the ground. Vacuum was set to ~ 500 mbar after sampling and dropped only little during the sampling interval.

In autumn 2013, the forest plots were equipped with 5 bucket-type litterfall collectors. Litterfall collectors consisted of a circular polyethylene frame and a polyester mesh and had a collection area of 0.25 m^2.

Sampling

Sampling was conducted fortnightly usually from March to November which roughly reflects the growing season. Sampling started in August 2009 and is still ongoing today. The growing seasons 2010, 2011 and 2012 were considered for this thesis. In response to meteorologic conditions, sampling start, end, and length varied by region and year. A sampling campaign usually required 2 – 3 days and was conducted simultaneously in the 3 study regions. Some sampling campaigns could not be realized because of plot inaccessibility, frost or staff illness and therefore refer to longer sampling intervals. Details on the considered sampling periods and treatment of prolonged sampling intervals are presented in the respective methods sections of Chapters 2, 3 and 4.

Water samples were collected cumulatively between sampling campaigns. The volume of each collector of rainfall, throughfall, litter leachate and mineral soil solution was measured manually with a graduated cylinder and registered. Depending on sample amount, stemflow volume was measured with a graduated cylinder or by employing a water-level function established for the barrel types in use. A volume weighted aliquot of each sample type was created in the field excluding obviously contaminated samples (e.g., bird feces in rainfall collectors). A 250 – 500 mL of the sample was brought refrigerated in cooling boxes to the field station.

Litterfall was sampled from 24 September 2013 to 03 June 2014 in the Schwäbische Alb and from 09 October 2013 to 17 June 2014 in Hainich-Dün in 2-week intervals in autumn, cumulatively over the winter season, and in 4-week intervals in spring and summer. Litterfall subsamples were combined per plot and date and dried in an oven at (60°C). The coarse woody litter fraction was removed prior to determination of litter mass. Litterfall was interpreted as an index of foliar biomass, however, due to resorption and leaching from senescing leaves, true foliar biomass was likely greater.

References containing method descriptions of explanatory variables provided by accompanying projects and external data sources are summarized in Tab. 1.2 and are briefly described in the method sections of the respective chapters.

1.2.3 Chemical analysis

Within 24 hours after water sampling, electric conductivity (TetraCon 325, WTW GmbH, Weilheim, Germany) and pH (Sentix 41, WTW GmbH) were measured in an unfiltered subsample. Samples of Rainfall, throughfall, stemflow, and litter leachate

Table 1.2: Explanatory external data used for analysis in Chapter 2, 3 and 4, respectively, and reference to the corresponding method description or data source.

Parameter	used in	Method/data reference
Radar precipitation (RADOLAN)	Chapter 2	DWD (2012)
Forest stand properties	Chapter 2, Chapter 3 Chapter 4	E.-D. Schulze, personal communication, Schall and Ammer (2013)
Vascular plant diversity	Chapter 2, Chapter 3	Boch *et al.* (2013)
Organic layer mass, C, N concentration	Chapter 3	E.F. Solly, M. Schrumpf and I. Schöning, personal communication
Soil fauna biomass	Chapter 3	Klarner *et al.* (2014)
Precipitation	Chapter 4	DWD (2014)
Phenology	Chapter 4	PEP725 (2014)
Soil phosphorus fractions	Chapter 4	Alt *et al.* (2011)
Leaf P concentration, leaf C:P ratio	Chapter 4	Gossner *et al.* (2014)
Ectomycorrhizal fungal diversity	Chapter 4	Wubet *et al.* (2012)
Soil moisture	Chapter 4	T. Nauss, personal communication

were split into an unfiltered subsample for the analysis of particulate organic C and particulate N content and and filtered subsamples for the analysis of dissolved compounds and dissolved organic matter properties. The latter were filtered through pre-rinsed (50 mL H_2O and 50 mL sample, except when sample amount was insufficient) folded paper filters (5 – 8 μm, 292, Munktell & Filtrak, Bärenstein, Germany, and Sartorius, Göttingen, Germany). Filtration was not necessary for mineral soil solution. Water samples were stored at –18°C until analysis or transport to the responsible laboratory. Samples were transported to the analyzing laboratories at the Universities of Berne, Bonn, Berlin, and Jena in polystyrene boxes and did not thaw completely during transport (< 2 days).

Water samples were analyzed for concentrations of total dissolved organic carbon and total dissolved nitrogen (TDN) with TOC Analyzers (device manufacturer and product type differ by source regions of samples and are given in Tab. 1.3). Depending on the origin of the sample, concentrations of K, Na and Ca were analyzed with atomic absorption spectrometry or inductively coupled optical emission spectrometry (Tab. 1.3). Concentrations of Cl^-, $NH_4{}^+$, $NO_3{}^-$, $PO_4{}^{3-}$ and total dissolved P (TDP) were analyzed in Berne with a continuous flow analyzer (Tab. 1.3). For Cl^- determination, the sample was automatically mixed with a background electrolyte solution ($NaNO_3$) and transferred to an ion-selective electrode. The concentrations of $NH_4{}^+$ were analyzed photometrically after a modfied Berthelot reaction using a buffer solution ($C_4H_4KNaO_6 \cdot 4\,H_2O$, $C_6H_5Na_3O_7 \cdot 2\,H_2O$, Brij-35®) adjusted to a pH of 5.2, a salycilic acid solution (NaOH, $NaC_7H_5O_3$, $Na_2[Fe(CN)_5NO] \cdot 2\,H_2O$) and a $Na[C_3N_3O_3Cl_2]$ solution. The concentrations of $NO_3{}^-$ were determined colorimet-

Table 1.3: Analytical devices used to determine concentrations of total dissolved nitrogen (TDN), NH_4^+-N, NO_3^--N, PO_4^{3-}-P, total dissolved phosphorus (TDP), Cl^-, K, Ca and Na in water samples from Schwäbische Alb, Hainich-Dün, and Schorfheide-Chorin, respectively. Manufacturers and addresses are given when first mentioned.

Parameter	Source region of sample	Analytical device	Device specifications
TDN	Schorfheide-Chorin	TOC Analyzer	VCPH, Shimadzu, Düsseldorf, Germany
	Hainich-Dün	TOC Analyzer	VCPN, Shimadzu
	Schwäbische Alb	TOC Analyzer	VarioTOC cube, Elementar Analysensysteme GmbH, Hanau, Germany
NH_4^+	all	Continuous Flow Analyzer (photometer)	AutoAnalyzer 3, Seal Analytical GmbH, Norderstedt, Germany
NO_3^-	all	Continuous Flow Analyzer (photometer)	AutoAnalyzer 3
PO_4^{3-}	all	Continuous Flow Analyzer (photometer)	AutoAnalyzer 3
TDP	all	Continuous Flow Analyzer (photometer)	AutoAnalyzer 3
Cl^-	all	Continuous Flow Analyzer (ion-selective electrode)	AutoAnalyzer 3; Orion 9417BN, Thermo Scientific, Nijkerk, The Netherlands
K, Ca, Na	Schorfheide-Chorin	Atomic absorption spectrometer	AAnalyst 300, PerkinElmer Inc., Norwalk, MA, USA
	Hainich-Dün	Inductively-coupled plasma optical emission spectrometer	Liberty 150, Varian, Mulgrave, Australia
	Schwäbische-Alb	Atomic absorption spectrometer	ZEEnit 700p, Jena Analytik GmbH, Jena, Germany

rically after Cd reduction and raction with a color reagent (H_3PO_4, $C_6H_8N_2O_2S$, $C_{12}H_{14}N_2 \cdot 2\,HCl$) in a buffer solution ($NH_4Cl$, NH_3, $CuSO_4$, Brij-35®). Concentrations of ${PO_4}^{3-}$ were analyzed as ${H_2PO_4}^{-}$ using the modified molybdenum blue method described in Murphy and Riley (1962). Denison *et al.* (1998) showed that inorganic P is overestimated by this method because of a ${PO_4}^{3-}$ release due to the hydrolysis of labile organic sugars in the acidic reaction environment when samples had been stored for > 72 hours. Since the sampling interval was beyond this critical storage time, I regard this fraction as reactive P comprising inorganic and labile organic P. Samples were acidified with a H_2SO_4 solution containing $C_{12}H_{25}NaO_4S$ and mixed with an ascorbic acid/antimony reagent ($C_6H_8O_6$, $K_2Sb_2C_8H_4O_{12} \cdot 3\,H_2O$) and an acidic molybdenum solution (Na_2MoO_4, H_2SO_4, $C_{12}H_{25}NaO_4S$) in a water bath at 40°C. Concentrations of TDP were analyzed with the same method after oxidation with $K_2S_2O_8$ and ultraviolet radiation. Concentrations of N and P forms were transformed to the elemental concentrations of N and P, respectively. Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were calculated as difference between TDN and ${NH_4}^{+}$-N + ${NO_3}^{-}$-N, and TDP and reactive P, respectively. Concentrations of DON and DOP were set to 0 when measured negative, and TDN and TDP were set to equal ${NH_4}^{+}$-N + ${NO_3}^{-}$-N, and reactive P, respectively, in such cases.

1.2.4 Calculations

Element fluxes were calculated by multiplying element concentration and water flux and summed for the growing seasons. Missing concentrations in throughfall and litter leachate because of insufficient sample amount for analysis were substituted by the volumetric mean concentration per sample type and plot.

In Chapter 2, bulk precipitation for each forest plot was assessed using RADOLAN data provided by the German Weather Service (DWD, Offenbach, Germany) gathered from radio detection and ranging methods that have a temporal, spatial, and quantitative resolution of 1 h, 1 km^2, and 0.1 mm, respectively, which were calibrated with biweekly volumetric precipitation measurements at the grassland study sites. However, in Chapter 4, I calculated bulk precipitation as the mean of data from two nearby stations of the DWD (Schwäbische Alb: Sonnenbühl-Genkingen, Münsingen-Apfelstetten; Hainich-Dün: Leinefelde, Mühlhausen-Windeberg). Throughfall water fluxes were calculated as mean of available volumetric measurements per plot. Stemflow water flux was calculated by scaling up the measured stemflow volume per basal area of the sampled trees to total basal area of the respective forest.

Water fluxes through organic layers could not be inferred directly from the collected water amount by lysimeters because of the so-called interface effect (i.e. the artificial barrier prevents water drainage until water saturation of the organic layer is reached). Thus, I used a two-step Cl^- balance approach to infer the water flux through the organic layer from throughfall precipitation for beech forests in the Schwäbische Alb and Hainich-Dün. Given sufficient water flow, Cl^- is regarded to be inert in soils (Beese and van der Ploeg 1979) and can therefore be used to calculate water flux according to Eq. 1.1.

$$q_{LL}[mm] = q_{TF}[mm] \times \frac{Cl^-_{TF}}{Cl^-_{LL}}, \tag{1.1}$$

where q_{LL} is the water flux through the organic layer, q_{TF} is the throughfall precipitation, Cl^-_{TF} and Cl^-_{LL} is the Cl^- concentration in throughfall and litter leachate, respectively. The coefficients for predicting water flux through organic layers from throughfall were estimated with a linear regression function using all available samples (Fig. 1.7). To reduce uncertainties and Cl^- imbalances due to transient retention and spontaneous release of Cl^- and insufficient drainage of the lysimeters, I excluded sampling periods with very low and very high throughfall (5 mm $(14\ \text{days})^{-1}$ < throughfall < 80 mm $(14\ \text{days})^{-1}$; 6 % of available cases). The coefficients of the linear regression revealed an interception loss of 1.03 mm and a fractional water loss of throughfall precipitation due to evapotranspiration in the organic layer of 27 % on a 14 days basis.

In Chapter 2, I calculated the canopy budget (Ulrich 1983) of TDN, ${NH_4}^+$-N, ${NO_3}^-$-N, and DON according to Eq. 1.2.

$$CB_i = TD_i - TF_i - SF_i, \tag{1.2}$$

where TD_i, TF_i, SF_i are total deposition, throughfall flux and stemflow flux of substance i, respectively. Total deposition was calculated as sum of bulk deposition and dry deposition. Since dry deposition cannot be measured directly, I modeled dry deposition using Cl^- as a tracer according to Eq. 1.3.

$$DD_i = BD_i \times \frac{Cl^-_{TF}}{Cl^-_{RF}} - BD_i, \tag{1.3}$$

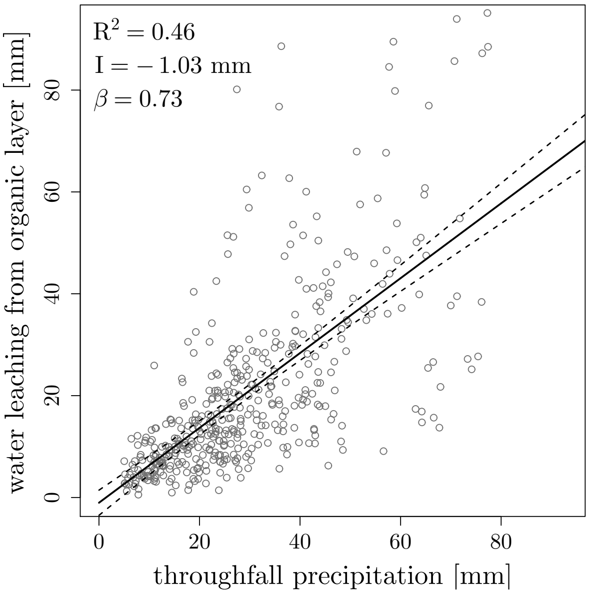

Figure 1.7: Relationship of throughfall precipitation and water flux through the organic layers as calculated by Eq. 1.1 for all plots and all sampling campaigns with 5 mm (14 days)$^{-1}$ < throughfall < 80 mm (14 days)$^{-1}$ (n = 443). The coefficients I and β of the linear regression (solid line) were used to infer water fluxes through organic layers from throughfall measurements. The dashed lines indicate the 0.95 confidence interval of the linear regression.

where DD_i and BD_i is the dry deposition and the bulk deposition of substance i, respectively, and Cl^-_{TF} and Cl^-_{RF} is the Cl^- concentration in throughfall and rainfall, respectively. For unknown reasons, total deposition exceeded below canopy flux of Cl^- at Schorfheide-Chorin from 15 September 2010 until 9 November 2010 and calculation of dry deposition was therefore based on Cl^- canopy budgets of the preceding period only (14 April 2010 to 14 September 2010). In Chapter 3, I further calculated net fluxes of TDN, $NH_4{}^+$-N and $NO_3{}^-$-N in the organic layer by subtracting throughfall fluxes of the respective N form from gross fluxes in litter leachate.

Because of inaccessibility of the plots or persisting frost at the beginning and end of the sampling periods, few fluxes of throughfall and litter leachate were missing and were substituted by the average throughfall flux in the respective region and sampling period (Schwäbische Alb: 1 %; Hainich-Dün: 4 %). To obtain an equally spaced time series for the analysis of seasonality in Chapter 4, fluxes with throughfall which referred to 28 days (Schwäbische Alb: n = 1 sampling campaign; Hainich-Dün: n = 8 sampling campaigns) were split into two 14-day intervals weighted by the corresponding regional precipitation.

1.2.5 Statistical analysis

All statistical analyses were performed with the statistical software environment R (R Development Core Team 2011). In Chapter 2, differences between paired samples were tested with the Wilcoxon matched-pairs test. Two-level and multiple level group comparisons were performed with a *t*-test and one-way ANOVA (*F*-Test) followed by Tukey's honest significant differences post-hoc test with Bonferroni correction, respectively. Nitrogen canopy budgets were analyzed with sequential ANCOVA (Type I, sum of squares). Model development was based on the principles of marginality, backward selection and single-term deletion of a beyond-optimal model based on *F*-statistics. For the analysis of N canopy budgets, plot HEW4 was identified as a highly influential observation (Cook's distance value of > 1) and plot HEW10 was identified as an outlier with respect to the canopy budget of TDN (–8.2 kg ha^{-1}) violating the homogeneity assumption and thus was excluded from the model development. Gaussian distribution of residuals and homogeneity of variances were inspected visually and verified with the Anderson-Darling and the Fligner-Killeen tests, respectively.

In Chapter 3, data represented repeated measures and were analyzed with general least squares models including a first-order auto-regressive correlation structure. Model development was based on principle of marginality and backward selection aiming at minimizing Aikaike's Information Criterion adjusted for small sample sizes (AICc) as an integrative criteria for goodness of fit and model complexity using maximum likelihood estimation. Gaussian distribution and homogeneity were inspected with the Shapiro-Wilk test, diagnostic plots and the Bartlett test (for factors), respectively. The model describing DON fluxes in the organic layer was only developed to a model without heterogeneity. The optimal models were refitted using restricted maximum likelihood estimation and tested with ANCOVA. Pearson's coefficient of correlation ($r_{Pearson}$) was used to test correlations among covariates. Annual differences of throughfall precipitation and deposition were tested for each region separately with an *F*-test and Tukey's honest significant difference *post hoc* test. Regional differences of water fluxes in the organic layer, throughfall precipitation and deposition were tested with a pairwise t-test grouped by growing season.

In Chapter 4, fluxes of P with throughfall and litter leachate were $\log_{10}$-transformed prior to statistical analysis. Figures and averages are presented in original scale and means and standard deviations thus refer to geometric means (μ_g) and geometric standard deviations (σ_g), respectively. Differences in throughfall and litter leachate P fluxes between regions and among growing seasons were investigated with linear mixed effects models (LME) from the package nlme (Pinheiro *et al.* 2014) with a random plot effect to account for repeated measures from the same forest. The significant differences were determined with sequential ANOVA (Type I; F-test). Differences among individual growing seasons were further investigated with general linear hypothesis testing using Tukey's contrasts of the LME with the package multcomp (Hothorn *et al.* 2008) to adjust P-values for multiple testing. Most environmental properties were collinear and were not repeatedly measured and were thus redundant to each other and to the random plot effect, respectively. Therefore, I used ordinary least squares regression analysis and parametric and non-parametric correlation analysis of potential environmental controls on log-transformed geometric plot means to describe reactive P flux response to environmental conditions instead of including the covariates in the LME. In some cases, however, I excluded dislocated growing season fluxes from correlation analysis to hold the assumptions of linear regression. I will present qualitative explanation for the deviation from the remaining sample in such cases. Generalized additive models (Wood 2006) were used as an exploratory method of the temporal course of throughfall reactive P fluxes using a smooth term for the day of the year. Cubic regression spline with shrinkage was used as smoothing technique and smoothing parameters were estimated with generalized cross-validation. To this end, I centered single-event log-scaled throughfall fluxes by plot to omit the offset induced by different scales of fluxes and set up individual models for each region × growing season combination because of different sampling periods (Tab. 4.2).

1.3 Results

1.3.1 More efficient aboveground nitrogen use in more diverse Central European forest canopies (Chapter 2)

Total N deposition in the growing seasons 2010 was 17.1 ± SD 4.3 kg ha^{-1} in the Schwäbische Alb, 13.8 ± SD 2.5 kg ha^{-1} in Hainich-Dün and 16.6 ± SD 3.4 kg ha^{-1} in Schorfheide-Chorin. I observed a wide-spread retention of deposited atmospheric N in the canopy of Central European forests ranging from an uptake of 15.6 kg ha^{-1} to a small release of 1.5 kg ha^{-1} in the growing season 2010 (Fig. 2.1). Canopy N retention averaged 29 %, 16 %, and 51 % of total TN deposition in the Schwäbische Alb, Hainich-Dün and Schorfheide-Chorin, respectively, and increased with

N deposition (Fig. 2.2). Canopy N retention was accompanied by an equivalent release in K^+ suggesting ion exchange was an important pathway of canopy N uptake. The canopy uptake of N forms differed by region: ${NH_4}^+$ was retained in all regions and ${NO_3}^-$ was efficiently retained in the Schwäbische Alb and in Schorfheide-Chorin (Fig. 2.1). Forest canopies in Schorfheide-Chorin even retained DON. The magnitude of canopy N retention differed between forest type (i.e. coniferous and deciduous) in the Schwäbische Alb and in Schorfheide-Chorin but not in Hainich-Dün (Fig. 2.1, Tab. 2.5). In coniferous forests of Hainich-Dün, ${NO_3}^-$ was released from the canopy which indicated that N scarcity is less prominent than in the other studied regions. Also dry and total deposition of N differed among the forest types and was greater in spruce than in beech forests in the Schwäbische Alb and in Hainich-Dün (Fig. 2.1). There was, however, no difference in deposition between pine and beech forests in Schorfheide-Chorin. The greater canopy N retention of spruce forests in the Schäbische Alb rendered the below canopy N flux similar to that in beech forests (Fig. 2.1). Canopy N retention correlated with the Shannon index of trees and shrubs, but only when accounting for effects of region, forest type and stand basal area (Tab. 2.5, Fig. 2.3). However, also interactions of the Shannon index of woody plants with region and forest type, respectively, correlated with the canopy N retention, suggesting that the extent of a biodiversity effect on canopy N retention can not be generalized across habitats.

1.3.2 Drivers of nitrogen leaching from organic layers in Central European beech forests (Chapter 3)

Throughfall fluxes of TDN during the growing seasons 2010, 2011 and 2012 in beech forests were 14.62 ± SD 3.37 kg ha^{-1} in the Schwäbische Alb and 9.37 ± SD 1.93 kg ha^{-1} in Hainich-Dün (cf. Fig. 3.1). The throughfall composition was similar in both regions (52 – 57 % ${NO_3}^-$-N, 23 – 26 % ${NH_4}^+$-N, 20 % DON). Gross fluxes of TDN with litter leachate were 14.05 ± SD 7.9 kg ha^{-1} in the Schwäbische Alb and 14.35 ± SD 5.95 kg ha^{-1} in Hainich-Dün (cf. Fig. 3.1). Litter leachate was enriched in ${NO_3}^-$-N (Schwäbische Alb: 61 ± SD 12 %; Hainich-Dün: 71 ± SD 9 %) and depleted in ${NH_4}^+$-N (Schwäbische Alb: 8 ± SD 3 %; Hainich-Dün: 6 ± SD 4 %) relative to throughfall. Net fluxes (i.e. throughfall – litter leachate) of TDN with litter leachate in beech forests during the growing seasons 2010 – 2012 varied widely in both the Schwäbische Alb (–2.3 ± 4.3 kg ha^{-1}) and Hainich-Dün (5.9 ± 5.4 kg ha^{-1}) reflecting both apparent retention of throughfall N and release of N from organic layers (Fig. 3.3). Net fluxes with litter leachate also varied among

N species: NH_4^+-N was generally retained in organic layers, while NO_3^--N was released from organic layers in Hainich-Dün but was apparently reatained in organic layers in some studied forests in the Schwäbische Alb (Fig. 3.3). In both regions, net fluxes of TDN with litter leachate were greater in 2010 than in 2011 and 2012 (Fig. 3.3).

Gross fluxes fluxes of TDN and NO_3^--N with litter leachate correlated with respective throughfall deposition and therefore indicated a partial throughflow of deposited NO_3^- through the mull-type organic layers (Fig. 3.2a). Net and gross fluxes of TDN, NO_3^--N and DON were influenced by various controls while gross and net fluxes of NH_4^+-N were only subject to temporal and regional variation (Tab. 3.2). Gross and net fluxes of TDN, NO_3^--N and DON (only gross flux) with litter leachate increased with stand basal area (Tab. 3.2, Fig. 3.2c, d). Stand basal area was positively correlated with litterfall ($r_{Pearson} = 0.82$, $P = 0.001$) and with C and N stocks of the organic layers ($r_{Pearson} = 0.70$ and $r_{Pearson} = 0.65$, respectively, $P < 0.05$) and thus indicated that basal area also reflects C and N resources in the organic layer. However, including C and N stocks of the organic layer did not improve the explanatory power of the models presented in Tab. 3.2. The C:N ratio of the organic layer was not significantly correlated with gross and net fluxes of N forms with litter leachate and was dropped from the models during model development. Furthermore, microbial biomass was not correlated with gross and net fluxes of dissolved N with litter leachate. The soil macrofauna biomass correlated with the net flux of TDN, NO_3^--N and DON with litter leachate (Tab. 3.2, Fig. 3.2b). The soil mesofauna biomass increased net and gross fluxes of TDN and NO_3^--N, but only after accounting for the effects of covariates, suggesting an indirect relationship to N release (Fig. 3.3, Fig. 3.2g, h).

The gross and net fluxes of TDN and NO_3^--N, but not of NH_4^+-N and DON, correlated negatively with the Shannon index of vascular plants suggesting an increased N uptake or a decrease in N release during decomposition in more diverse forest plant communities (Tab. 3.2, Fig. 3.2e, f). Among functional plant groups (i.e. trees, shrubs, herbs), the Shannon index of herbs was most closely correlated with the gross and net fluxes of TDN and NO_3^--N (Tab. 3.3). However, the cover value of both herbs and shrubs (as a surrogate for understory biomass), was not significantly correlated with the gross and net fluxes of TDN and NO_3^--N (Tab. 3.4).

1.3.3 Abiotic and biotic controls of the dissolved P cycle in Central European beech forests (Chapter 4)

Bulk deposition of reactive P (i.e. ${PO_4}^{3-}$-P + easily hydrolyzed organic P) during the growing seasons 2010, 2011 and 2012 was 0.027 ± 0.005 kg ha^{-1} in the Schwäbische Alb and 0.016 ± 0.004 kg ha^{-1} in Hainich-Dün. Growing season fluxes of reactive P with throughfall were an order of magnitude greater than bulk deposition, and varied widely within regions and were 0.55 kg ha^{-1} ($\sigma_g = 2.01$) in the Schwäbische Alb and 0.36 kg ha^{-1} ($\sigma_g = 1.91$) in Hainich-Dün (Fig. 4.1, Fig. 4.3). Fluxes of reactive P with litter leachate were similar in the Schwäbische Alb (0.51 kg ha^{-1}, $\sigma_g = 2.91$) and in Hainich-Dün (0.55 kg ha^{-1}, $\sigma_g = 2.71$) and were also highly variable within regions (Fig. 4.1, Fig. 4.3). The concentration of reactive P in mineral soil solution was only 4.5 ± SD 2.5 μg L^{-1} in the Schwäbische Alb and 7.5 ± SD 5.4 μg L^{-1} in Hainich-Dün indicating limited plant P availability. Phosphorus deficiency was further suggested by the foliar P concentrations for all forest stands but AEW4 (Tab. 4.1).

Throughfall in the growing seasons 2010 – 2012 was greater in the Schwäbische Alb (539 ± SD 41 mm) than in Hainich-Dün (357 ± SD 47 mm). In both regions, the year 2011 was drier than 2010 and 2012. Especially the period from February to May 2011 was characterized by a remarkable deficit in precipitation compared to the normal period (1961 – 1990; Fig. 4.2). In both regions, cumulative canopy P leaching revealed a strong seasonality (Fig. 4.4), was greater in 2011 and 2012 than in 2010 ($P < 0.001$) but fluxes of reactive P with litter leachate were only greater in 2012 than in 2010 ($P = 0.018$; Fig. 4.3). Fluxes of reactive P with throughfall increased after leaf unfolding, peaked in the mid of the growing season and decreased before leaf coloring (Fig. 4.4). While the peaking of canopy P leaching in summer coincided with high precipitation, the increase during leaf unfolding occurred irrespective of precipitation amount (Fig. 4.4). Moreover, a sharp increase of throughfall reactive P fluxes occurred simultaneously to a drop in soil moisture in spring 2011 in the Schäbische Alb (Fig. 4.5). However, the response of throughfall P fluxes in Hainich-Dün was limited by the very low precipitation during this period. Additionally, P was leached from the canopy during heavy rainfall (Fig. 4.4). In most studied forests, the flux of reactive P with litter leachate resembled that of throughfall (Fig. 4.1) and also seasonal patterns were similar to throughfall. However, at the forest sites AEW7 and HEW10, reactive P was apparently released from organic layers.

The greatest fluxes of reactive P was observed at the forest stand AEW4 (Fig. 4.1), which was characterized by the highest total P concentration in the A horizon, the lowest foliar C:P ratio (Tab. 4.1), and a remarkably different seasonal pattern of throughfall reactive P fluxes (Fig. 4.5), suggesting different P cycling at this site. Hence, the forest stand AEW4 was excluded from further data analysis. Throughfall fluxes of reactive P were correlated with the P stock in foliage ($r_{Pearson} = 0.83$, $P = 0.002$; Fig. 4.7a) suggesting that foliar leaching was a predominant control of P release from the canopy. Furthermore, throughfall fluxes of reactive P correlated with the Shannon index of ectomycorrhizal fungal diversity ($r_{Pearson} = 0.73$, $P = 0.01$; Fig. 4.7b), and the NaOH-extractable inorganic P concentration in the A horizon ($r_{Spearman} = 0.67$, $P = 0.041$). Furthermore, the NaOH-extractable P concentration in soil correlated with the Shannon index of ectomycorrhizal fungal diversity ($r_{Spearman} = 0.595$, $P = 0.041$). The Shannon index correlated closely with the foliar C:P ratio when the thicket stand HEW4 was excluded from the data set ($r_{Spearman} = –0.78$, $P = 0.004$). Stand development at this site (approximately 15 years) was probably too short to result in a comparable functional relationship of fungal community and tree P nutrition. The reactive P flux with litter leachate correlated with the NaOH-extractable P concentration in the A horizon ($r_{Pearson} = 0.75$, $P = 0.007$; Fig. 4.7c) but not with the Shannon index of ectomycorrhizae ($r_{Pearson} = 0.36$, $P = 0.277$).

1.4 Discussion

1.4.1 Nitrogen cycling in Central European forests

In almost all studied forests, the canopy budget of TDN was negative indicating canopy N retention (Fig. 2.1). In line with findings of Lovett and Lindberg (1993) for North American forests, canopy N retention increased with N deposition (Fig. 2.2) suggesting that Central European forest canopies can partly buffer additional N input before it reaches the soil. Canopy N retention differed among regions and ranked Hainich-Dün < Schwäbische Alb < Schorfheide-Chorin (Fig. 2.1). Nitrogen availability in soils of Schorfheide-Chorin may have been limited by water shortage resulting from the sandy soil texture, and in the Schwäbische Alb by soil shallowness. The lower canopy uptake of N in Hainich-Dün instead may have resulted from greater nutrient supply and water holding capacity in loess-derived soils.

Sinks for deposited N in the canopy encompass foliar uptake, assimilation by microbes, epiphytes and lichens, and adsorption to canopy surfaces (Eilers *et al.* 1992; Papen *et al.* 2002; Lockwood *et al.* 2008; Dail *et al.* 2009; Adriaenssens *et al.* 2012). Sinks and also sources for N in the canopy are predominantly related to canopy surface properties which are different among the dominant tree species. The effect of the forest type interacted with region (Tab. 2.5) and thus indicated a response of tree species-related canopy N retention to site-specific environmental conditions. The greater canopy surface area and roughness of spruce compared to deciduous trees (Augusto *et al.* 2002) resulted in a greater dry deposition of N in the Schwäbische Alb and in Hainich-Dün (Fig. 2.1). Greater N retention due to a larger assimilating canopy surface area in spruce forests compensated for the surplus N deposition in spruce forests in the Schwäbische Alb. In Hainich-Dün, however, canopy N retention was similar in spruce and beech forests, resulting in a two-times greater N input to the soil under spruce. The lower canopy N uptake in spruce forests in Hainich-Dün was likely attributable to the combination of higher soil fertility and the lower N demand of spruce forests (Neary and Gizyn 1994; Rothe *et al.* 2002; De Schrijver *et al.* 2007). Despite the lower canopy surface area, beech forests were also efficient in taking up N in the canopy (Fig. 2.1) which probably resulted from the great N demand of beech and deciduous understorey plants and the thinner cuticle of deciduous leaves compared to needles (Harrison *et al.* 2000).

Dissolved N that passed the canopy of beech forests in the Schwäbische Alb and in Hainich-Dün partly flushed through the organic layers during the growing seasons 2010 – 2012 (Fig. 3.2a) and canopy processing of deposited N coupled back to fluxes of N in soils. NH_4^+ was strongly retained in the organic layer (Fig. 3.3) layer suggesting nitrification, immobilization and plant uptake. Similar to canopy N transformation, the greater NO_3^--N release from organic layers in Hainich-Dün suggested a greater N availability in the soil than in the Schwäbische Alb where throughfall-derived NO_3^--N was retained in some organic layers in 2011 and 2012 (Fig. 3.3). The apparent N release from organic layers was still low compared with the typical annual N input by litterfall in Central European beech forests (63 – 75 kg N ha^{-1} $year^{-1}$; Khanna *et al.* 2009), probably because the C:N ratio of the organic layers was above the threshold value of 25 at which significant net N mineralization and leaching is expected (MacDonald *et al.* 2002). High gross mineralization is partly out-competed by great microbial N uptake in calcareous beech forest soils (Kooijman *et al.* 2008). Furthermore, beech litter decomposes slowly and usually acts as a sink for N during early stages of decomposition (Vesterdal *et al.* 2008;

Berg 2000; Gebauer *et al.* 2000) and might therefore have contributed to the small apparent net N release.

The leaching of TDN, NO_3^--N and DON from organic layers increased with stand basal area which reflected a positive response of N leaching to greater resource availability (i.e. greater litterfall and greater C and N stocks in the organic layer) in more mature forests. The effect of the stand basal area on dissolved N fluxes in litter leachate might have been mediated by the soil detritivores (Tab. 3.2; Scheu 1987). The biomass of the soil macrofauna (mainly earthworms) was positively correlated with the net fluxes of TDN, NO_3^--N and DON (Fig. 3.2b). The burrowing activity of earthworms may have also led to a higher throughflow rate of throughfall N and to a greater nitrification in beech litter because of the abundance of macropores resulting from burrowing (Scheu 1997). In general, earthworms initiate and fasten decomposition by increasing surface area, improving micro-environmental conditions, and by mixing of soil organic matter and mineral soil (Curry and Schmidt 2007; Xiong *et al.* 2014). The subsequent decomposition of litter and soil organic matter by the soil mesofauna further increases N mineralization by increasing bacterial colonization (Verhoef and Brussaard 1990; Chamberlain *et al.* 2006) and thereby contributes to plant N supply (Bardgett and Chan 1999). In the studied forest soils, the soil mesofauna biomass increased TDN and NO_3^--N leaching conditional on covariates included in the model (Tab. 3.2, Fig. 3.2g, h). Most likely, the conditional correlation of the mesofauna biomass with gross and net N fluxes in litter leachate reflected trophic interactions with the macrofauna or the microbial community. In the studied forests, the soil fauna appeared to be an important driver of plant N availability by linking aboveground and belowground processes and counteracting the low net mineralization in slightly acidic topsoils under beech.

Plant diversity tightened the cycling of N in Central European forest ecosystems by increasing canopy N retention (Tab. 2.5, Fig. 2.3) and decreasing TDN and NO_3^--N leaching from organic layers (Tab. 3.2, Fig. 3.2e, f). Both suggested complementary and facilitative aboveground and belowground N use in more diverse plant assemblages in Central European forests. With respect to the canopy N budget, however, the Shannon index of woody plants interacted with region and forest type (Tab. 2.5), respectively, which reflected that the extent of the biodiversity-effect on canopy N retention depended on the region and forest type-related species pool and was thus co-determined by site-specific environmental conditions. I tested the significance of the Shannon indexes of various growth forms on gross and net fluxes of TDN and NO_3^--N with litter leachate and found that especially herb diversity contributed to a reduction of N fluxes with litter leachate (Tab. 3.3). To explain the canopy N budget, only tree and shrub (i.e. perennial woody species) diversity was used because the herbs did not exceed the collector height. However, canopy N retention was likely predominantly increased by the diversity in understory because shrub diversity and thus functional diversity exceeded tree diversity (Grime 1998; Boch *et al.* 2013).

Complementary N use among plant species can in general be related to functional niche partitioning among species and plant functional groups due to different N use strategies and preference for specific N forms (Scherer-Lorenzen *et al.* 2003; Hooper *et al.* 2005; Kahmen *et al.* 2006). Functional niche complementarity was probably the most important mechanism for greater canopy N retention in more diverse canopies. For instance, gymnosperms have a limited ability to use ${NO_3}^-$ (Harrison *et al.* 2000) and canopy uptake of ${NO_3}^-$ by angiosperms (e.g., deciduous trees and shrubs) might have supplemented canopy N retention in pine and spruce stands in the Schwäbische Alb and Schorfheide-Chorin because nitrate reductase activity was shown to be high in understorey plants (Olsson and Falkengren-Grerup 2003). Furthermore, the preferential uptake of ${NH_4}^+$ in tree canopies might have coupled back to understorey composition by favoring species specialized on ${NO_3}^-$ use (McKane *et al.* 2002). Spatial and temporal niche partitioning was likely important for complementary N use between overstory and understory as well as among understory plant species. Increased fine-root productivity and space-filling in more diverse forests (Brassard *et al.* 2013) because of different rooting traits may have decreased N leaching losses from organic layers and different growing heights and leaf traits may have complemented canopy N uptake. Some abundant understory plant species in Central European beech forests (e.g., *Allium ursinum* L.) have a great N uptake capacity and have greatest N demands at the end of the dormant season when tree N demand is still low and nitrification rates are high (Muller and Bormann 1976; Gebauer *et al.* 2000; Schulze *et al.* 2009). Different phenology of understory and overstory plant species may thus have temporally complemented N uptake.

Instead of increasing N uptake from the organic layer, plant diversity might have also reduced the release of N from organic layers. However, plant diversity was reported to have no or positive effects on mineralization (Blair *et al.* 1990; Wardle *et al.* 1997; Fornara *et al.* 2009; Rosenkranz *et al.* 2012). Understory herbs that reduced leaching in spring will provide N-rich litter (Schulze *et al.* 2009) that could increase N leaching during the growing season (Jandl *et al.* 1997). The associated N release may have been compensated for by uptake of species with different phenologic traits.

Additionally, N transfer from herb litter to N-poor litter (e.g., beech litter) may have reduced N leaching (Scheu 1997). Lower N leaching in more diverse forests could also have resulted from the positive relationship of plant diversity and productivity (Morin *et al.* 2011; Paquette and Messier 2011) and the associated greater N demand. Stand basal area, which serves as surrogate for tree biomass, however, had a positive effect on N leaching from organic layers in my study (Fig. 3.2c, d). I analyzed the gross and net fluxes of TDN and NO_3^--N with litter leachate using cover values of the vegetation strata as an estimate of biomass instead of the Shannon indexes and found only marginal effects of plant cover (Tab. 3.4). This supported the conclusion that synergistic biodiversity effects like complementarity and facilitation were more important for the reduction in N leaching from the organic layer than the associated greater productivity of more diverse forests.

1.4.2 Phosphorus cycling in Central European forests

In contrast to N, atmospheric inputs of P were small and P was released from the canopy. The low concentrations of P in mineral soil solution indicated that losses of P by leaching are also small, plant availability of P in mineral soil was low, and that P cycled internally in beech forests on calcareous soils. The P availability in mineral soils was impaired by the low pH of the A horizons (Tab. 4.1) resulting in precipitation of Al phosphates, the high pH (6.7 – 8.1) and Ca concentrations (4 – 47.2 mg L^{-1}) in mineral soil solution collected below the A horizon resulting in secondary apatite formation, and rapid recycling of P between soil organic matter and microbes (Wood *et al.* 1984; Walbridge *et al.* 1991; Yanai 1992).

Reactive P in throughfall (Fig. 4.3) represented the greatest flux of dissolved P and cumulative growing season fluxes of reactive P with throughfall ranged 5 – 50 % of the P stock in beech foliage. Therefore, canopy P leaching was a significant P loss for trees. In line with Qualls *et al.* (1991), the similar size of reactive P fluxes with throughfall and with litter leachate (Fig. 4.3) suggested a low net mineralization in organic layers and that throughfall-derived P contributed a substantial amount of P leached from the organic layer. As described above, bioturbation may have increased throughflow rate in shallow mull-type organic layers. In addition and similar to N, P accumulates in decomposing beech litter (Colpaert and van Tichelen 1996). At two of studied forests sites (AEW7, HEW10; Fig. 4.1), great P release from organic layers suggested net P mineralization; the reasons for this, however, remained unresolved. The low P concentrations in mineral soil solution and the correlation of reactive P flux with litter leachate and the NaOH-extractable inorganic P fraction in soil (Fig. 4.7c) suggested that P leached from canopy (and subsequently through the organic layer) and P released from the organic layer escaped the rapid recycling and was partly trapped in the moderately labile P pool (Negassa and Leinweber 2009). The moderately labile P pool is loosely defined by its extractant NaOH and Alt *et al.* (2013) suggested that this pool consists of poorly-crystalline Ca phosphates and hydroxylapatite in the Schwäbische Alb. Phosphorus trapped in the NaOH-extractable P fraction is only accessible to plants by rhizosphere acidification, extracellular enzymes and mycorrhizal associations (Wallander 2000; Blum *et al.* 2002; Lambers *et al.* 2008; Alt *et al.* 2013).

Reactive P fluxes with throughfall varied widely among the studied forests (Fig. 4.1) supporting the previous findings in Central European beech forests (Talkner *et al.* 2010). An especially large canopy P leaching was consistently detected at the forest stand AEW4 (Fig. 4.1). This site was characterized by an outstandingly high total P concentration in soil and was the only forest site were leaf P concentration did not indicate P deficiency (Tab. 4.1; Stefan *et al.* 1997) resulting in different P dynamics at this site. For instance, 50 % of the foliar P stock in the forest stand AEW4 was leached from the canopy each growing season with the majority of P leaching occurring in autumn (Fig. 4.5). This suggested that trees at the site AEW4 reduced P resorption in response to better P availability (Vergutz *et al.* 2012). The different P dynamics required excluding this site from the data. Throughfall fluxes of reactive P at the other forests but AEW4 were correlated with the soil NaOH-extractable P concentrations in the A horizon and the Shannon index of ectomycorrhizae suggesting an improved P recycling between soil and trees through recalcitrant P sources by a diverse mycorrhiza community. Ectomycorrhiza dominated P nutrition is supported by the almost complete colonization of European beech root tips (Lang *et al.* 2011) and higher ectomycorrhizal fungal diversity could improve P mining by functionally and spatially complementing foraging strategies (Buscot *et al.* 2000; Agerer 2001; van Schöll *et al.* 2008; Jones *et al.* 2010). Conclusively, a high diversity of ectomycorrhizae can potentially counteract the progressive plant P loss because of canopy leaching and P immobilization in the mineral soil.

In spite of a 50 % greater throughfall volume in the Schwäbische Alb than in Hainich-Dün, throughfall reactive P fluxes were only 20 % greater, suggesting a limited pool of leachable reactive P in the canopy. Moreover, the cumulative growing season throughfall fluxes of reactive P (Fig. 4.3) ranked inversely to annual precipitation and thus contradicted my hypothesis that canopy P leaching increases with precipitation amount. The years 2011 and 2012 were characterized by a deficit precipitation between February and May which coupled back to soil moisture (Fig. 4.2) and suggested that canopy P leaching was susceptible to spring drought. Further evidence for a response to water availability was provided by a change of the seasonality of canopy P leaching in the driest year 2011 (Fig. 4.4, Fig. 4.5). Generally, throughfall fluxes of reactive P increased irrespective of precipitation amount after leaf unfolding indicating that P is predominantly leached from foliage, peaked in the mid of the growing season coinciding with thunderstorms, and decreased before leaf coloring because of P resorption (Aerts 1996). In 2011, canopy P leaching peaked earlier. The meteorologic conditions 2011 led to the most intense fructification and crown transparency ever observed in beech forests in Germany (BMELV 2011). Thus part of the greater throughfall reactive P fluxes might have resulted from leaching of pollen. Leaf unfolding coincided with a drop in soil moisture in 2011 and 2012 in response to transpiration which is the driving force of P allocation to leaves. Thus, canopy P leaching might have been facilitated by greater stomatal aperture during high transpiration rates in dry periods. This was especially apparent in spring 2011 in the Schwäbische Alb (Fig. 4.4, Fig. 4.5). In Hainich-Dün however, spring drought was more exacerbated in 2011, potentially already impairing stomatal conductance and nutrient uptake (Bréda *et al.* 2006; Gessler *et al.* 2004). Peuke and Rennenberg (2004) observed a 16 % decrease in phosphate concentrations in beech seedling leaves prone to experimental drought relative to control treatments and attributed this to lower exchangeable orthophosphate concentrations in soil. The authors, however, did not investigate leaching losses from leaves. Trees can partly buffer a reduced P availability in soil by P mobilization from internal storage pools. Tree biomass P in a Mediterranean *Quercus ilex* L. forest decreased by 30 % under experimental drought because of continuous P transfer from woody plant parts to foliage followed by litterfall (Sardans and Peñuelas 2007). In face of the predicted increasing drought frequency (IPCC 2014), a similar response in the studied beech forests to increasing drought frequency may have long-term detrimental effects on P nutrition because the associated plant P losses will be immobilized in the calcareous soil.

1.4.3 Perspectives of N and P cycling in Central European forests

I could show that N cycling in temperate forests of Central Europe is influenced by plant diversity (Chapters 2 and 3) and that P cycling is influenced by ectomycorrhizal fungal diversity (Chapter 4). Although the two biodiversity effects had different directions with plant diversity tightening N cycling and ectomycorrhizal diversity accelerating P cycling, both improved forest functioning. However, N and P cycling were not solely affected by biodiversity but by interactions with abiotic conditions and the interplay of different taxonomic groups living in forests. Consequently, biogeochemical cycling in Central European forest ecosystems comprised a complex array of drivers and functions mediated by the biota in response to variations in the abiotic environment. A loss of functions and services provided by specific groups of organisms as well as changing environmental conditions may thus have negative consequences for forest functioning. In the following, I will discuss the possible impact of N deposition, the most important current threat for the functioning of temperate forests (Sala *et al.* 2000), on the cycling of N and P and their respective controls, and the interaction of the N and P cycling in the studied forests.

Total N deposition (Fig. 2.1) may support forest N demands which approximates ~ 98 kg ha^{-1} $year^{-1}$ in beech forests in Germany (Rademacher *et al.* 2009) by up to 20 %. The fact that forest canopies directly took up deposited N and the uptake increased with deposition strongly suggested that the capacity of the studied forests to store N was not yet reached and that canopy N uptake supports biomass production. Because the studied forests are either managed or currently regenerating wood extraction in the past, part of N retention is attributable to the aggrading state of the forests. Nitrogen deposition was estimated to contribute 10 % of C sequestration in biomass and soil of European forests and thus helps to mitigate climate change (De Vries *et al.* 2006; Pretzsch *et al.* 2014). Johnson (2006) even claimed that the current N deposition rates are a prerequisite to maintain forest growth of N-limited forests under elevated CO_2. However, N can only be beneficial for C sequestration in forests as long it is stored without negative feedbacks on forest functioning beyond N cycling (Janssens and Luyssaert 2009). Continuous N retention will cause enrichment and increased availability of N in the long-run which may couple back negatively to some of the identified controls of N cycling.

The cumulative growing season N deposition exceeded the empirical critical N load of 10 – 15 kg ha^{-1} $year^{-1}$ at which negative effects on herb species composition, parasite resistance, and mycorrhizal infection, respectively, and invasion of nitrophilous species are expected (Gilliam 2006; Bobbink *et al.* 2010). Although changes in herb species composition attributable to N deposition have partly already occurred during the 20th century in Central Europe (Gilliam 2006), the plant community composition is likely still adapting to the present N deposition rate. It is therefore possible that N cycling in the studied forests was affected by invaded N-tolerant species. Still, my results showed that under the present species composition, a greater diversity of vascular plants tightens N cycling (Chapters 2 and 3) and a further loss of plant diversity in response to N deposition will negatively affect forest functioning and associated services (Sala *et al.* 2000). Sylvicultural practices aiming at sustainable forest functioning should therefore try to maintain a diverse understory plant community. Nitrogen enrichment in tree litter will result in reduced decomposition rates (Frey *et al.* 2014). Furthermore, a disturbance of the decomposer community because of elevated N deposition was observed in past studies (Wolters *et al.* 2000). Chapter 3 suggested that the soil fauna is an important taxonomic group for the recycling of organic matter that counteracted plant–microbial competition for N in organic layers by facilitating N mineralization. Hence, the soil fauna likely contributes to maintain an enhanced biomass production in Central European forests under elevated CO_2. A change of the decomposer community composition by N enrichment will not have straightforward consequences on forest N cycling because of the antagonism of the functional redundancy among soil animals and the manifold interactions among soil faunal species and microorganisms (Wolters 2001). Lower decomposition rates because of declining soil fauna biomass resulting from the acidifying effect of N deposition would be accompanied by soil organic matter accumulation in the soil. However, greater organic matter resources may in turn lead to higher net N mineralization and greater N leaching (Chapter 3).

Furthermore, negative feedbacks of N deposition on the cycling of other elements such as Ca (Perakis *et al.* 2006), Mg (Fernandez *et al.* 2003), and P (Vitousek *et al.* 2010; Marklein and Houlton 2012) are threatening forest functioning. The decreasing trends in foliar N:P ratios in European beech forests highlight an impaired P supply of trees resulting from the current N enrichment (Duquesnay *et al.* 2000). Chapter 4 showed that P was a potentially limiting resource in studied beech forests and that plant P stress may be enhanced by increasing drought frequency in the future. Consequently, the capacity of plants in the studied forests to retain N and sequester C will become increasingly constrained by P. Phosphorus nutrition was dominated by mutualistic associations with ectomycorrhizal fungi and a diverse ectomycorrhizal fungal community improved the P status of beech trees (Chapter 4). Furthermore, a diverse ectomycorrhiza community but also admixed tree species can improve water availability of beech (Smith and Read 2008; Pretzsch *et al.* 2013). Management strategies that promote diverse ectomycorrhizal networks and tree communities could thus support P nutrition and efficient N use of the vegetation by increasing the elasticity of Central European beech forests to water stress and impaired P availability. While ectomycorrhizal infection was shown to decrease with an increase in N deposition from 27 to 43 kg ha^{-1} $year^{-1}$ (Kjøller *et al.* 2012), the consequences of N deposition on the diversity of ectomycorrhizae, however, are still unclear (Wallenda and Kottke 1998). In managed forests of Germany, P losses through harvest range 0.5 – 1 kg ha^{-1} $year^{-1}$ (Ilg *et al.* 2009). It is currently unknown if P supply by biological weathering and mobilization from organic P pools is sufficient to counterbalance the harvest-associated P loss. Additionally, the higher fructification frequency in Central European beech forest (BMELV 2011) will result in a greater tree P demand because of associated P losses through nut and pollen production and canopy leaching (Chapter 4). Both the response of the ectomycorrhizal community structure to N enrichment and the P mobilization rate in soil seem to have a critical relevance for the long-term stability of nutrient cycling in the studied forests and should thus receive specific attention in future studies.

1.4.4 Error discussion

The presented data and interpretations include some uncertainties. I used radio detection and ranging-derived precipitation for the analysis of canopy N retention in Chapter 2 because precipitation at the grassland study sites were not representative for all studied forest sites. However, radar detection and ranging-derived precipitation volumes are quantified by reflection from hydrometeors and therefore overestimates precipitation because not all raindrops reach the ground. To account for that, I calibrated the RADOLAN data with the precipitation measurements at grassland study sites. Radio detection and ranging-derived precipitation data were not available for the years 2011 and 2012. Therefore, spatial variation of precipitation was not represented in Chapter 4. I calculated instead a mean regional precipitation from two meteorologic stations of the DWD that surrounded each the Schwäbische Alb and Hainich-Dün to minimize the bias due to the spatial separation of grassland and forest study sites (cf. Fig. 1.2, Fig. 1.3).

I did not include stemflow deposition of N and P in Chapters 3 and 4, respectively, because of frequent leakage of sampling devices and thus may underestimate stand deposition. However, stemflow TDN and reactive P fluxes in the growing season 2010 were only 0.27 ± SD 0.15 kg ha^{-1} and 0.03 ± SD 0.05 kg ha^{-1} in the Schwäbische Alb and 0.71 ± SD 0.28 kg ha^{-1} and 0.002 ± SD 0.002 kg ha^{-1} in Hainich-Dün, respectively, reflecting a small contribution of stemflow to element input into the soil. Stemflow is furthermore concentrated around the base of trunks (Levia and Frost

2003) and thus has limited spatial relevance for the organic layer at the stand scale, although its importance for tree nutrition is be substantial. Additional lysimeters placed close to the trunks' bases would be required to investigate into the processing of stemflow-derived N and P in organic layers.

Water fluxes through organic layers were calculated using a Cl^- balance approach. While the the use of Cl^- as tracer for water fluxes has been used frequently (e.g., Beese and van der Ploeg 1979), recent studies showed that Cl^- is not always conservative in terrestrial ecosystems (Lovett *et al.* 2005). However, as shown by Brumme *et al.* (2009), replacing the water column of organic layers two times is sufficient to remove the stored Cl^-. For the calculation of water leaching through the organic layer, I used a lower limit for throughfall volume of 5 mm $(14 \text{ days})^{-1}$ to approximate the complete replacement of stored Cl^-. I cannot rule out that Cl^- was leached from the soil organic matter which would have resulted in underestimation of the water flux through organic layers. The most serious limitation of my approach to calculate water fluxes through organic layers is that I did not apply plot-specific regressions of throughfall and litter leachate Cl^- fluxes. The underlying assumption for this approach was that physical and thus hydrological properties are similar among the studied organic layers because all are of the mull type. Although this is a rigorous simplification of soil heterogeneity, the calculated evapotranspiration and interception rates (Fig. 1.7) agreed well with the rates observed in other studies in European beech forests (Gerrits and Savenije 2011).

All water samples were cumulatively collected over a period of 14 – 28 days. Microbial transformations of N and P forms within the collectors during the collection time can not be ruled out because I did not treat the collectors with toxic substances. Michalzik *et al.* (1997) showed that the majority of N transformations only occurs after longer storage times than two weeks in the field. Thus, only the sampling campaigns with a period of 28 days might be seriously affected by N transformations (see Chapters 2, 3 and 4 for site and growing season specific cases). Dissolved organic P is usually quickly transformed to phosphate in rainfall collectors (Tipping *et al.* 2014) and easily hydrolyzable organic P is identified as inorganic phosphate with the molybdenium blue method (Denison *et al.* 1998). This might have resulted in an underestimation of DOP fluxes in Chapter 4. Photochemical reactions as well evaporative losses from collectors were probably negligible due to the construction of the collectors and storage in the dark.

To minimize measurement errors during chemical analysis, I consistently performed a quality assurance protocol that included the measurement of internal standards as a quality control after a set of 12 – 15 samples. Whenever the analytical result of the internal standard differed by more than ± 10 % from the theoretical concentration, the measurement of preceding samples was repeated after a recalibration of the analytical device. I measured the different sample types in random order to keep analytical precision similar for all considered sample types. Thus, the accepted analytical precision was unlikely to result in changes of the observed patterns of flux through ecosystem compartments. The concentrations of DON and DOP were calculated as difference of total and inorganic N and P concentrations, respectively. Whenever the calculated DON and DOP concentrations were negative (< 10 % of available cases), I adjusted TDN and TDP concentrations to equal $NH_4{}^+$-N + $NO_3{}^-$-N and $PO_4{}^{3-}$-P concentrations, respectively. Hence, organic concentrations of N and P were underestimated while inorganic N and P forms were overestimated in these cases. Missing concentrations were substituted by volume-weighted mean concentrations to account for dilution effects. Data validation and outlier removal was performed with all necessary precaution. Whenever possible, I repeated analytical measurements prior to eliminating data. However, since the samples were collected in the field, sample contamination can never be fully impeded and the contamination level of some samples might have been to small to be differentiated from natural variation.

I used Cl^- as a tracer for dry deposition. Ulrich (1983) originally developed the canopy budget model to quantify deposition of base metals which have, unlike to N, primarily marine sources in the atmosphere. A major drawback of the application of Ulrich's canopy budget model is that it does not account for gaseous N deposition. Various extensions of the canopy budget model were developed to include canopy exchange and gaseous deposition of N (reviewed in Staelens *et al.* 2008). Some of these methods strictly assume that $NO_3{}^-$ is not taken up by the canopy which seems not to be true according to existing studies (Eilers *et al.* 1992; Peuke *et al.* 1998; Lockwood *et al.* 2008). Additionally, the iterative approximation of the charge of dissolved organic carbon (Staelens *et al.* 2008) is arguable. However, I was not able to apply extended canopy budget models because acquisition of the necessary data (e.g., $HCO_3{}^-$) would have required different sampling methods. Furthermore, application of micro-meteorological methods to quantify gaseous N deposition was not possibly due to a lack of data on gaseous air concentrations and air turbidity.

A general limitation of derived conclusions about fluxes or budgets of ecosystem compartments arises from excluding winter months from the observation. This resulted in an underestimated annual deposition and available N and P for leaching through organic layers because matter that has been deposited in winter might have been temporally stored. In coniferous forests, canopy uptake is reduced during winter dormancy but the particle interception capacity remains stable (Harrison *et al.* 2000). Thus, the canopy N budget of coniferous forests presented in Chapter 2 might have been biased by exclusion of the winter period and neglecting a carry-over of winter deposition into the growing season. Coniferous forest were not considered in Chapter 3 and 4. The canopy N uptake/release in deciduous forests during the dormant season was likely negligible because of the lack of foliage (Harrison *et al.* 2000; Augusto *et al.* 2002) and throughfall was likely similar to bulk deposition. Nitrogen and P that has been deposited in winter accumulated with the snow-pack on the forest floor and was likely leached quickly during snow-melt. I therefore assume that the error arising from excluding the winter season was small for the results presented in Chapter 3 and 4.

1.5 General conclusions

This thesis described the controls and variability in N and P fluxes in Central European forests and allows to test the hypotheses derived from the state of knowledge:

i. Central European forest canopies retain 16 - 51 % of atmospheric N deposition (Chapter 2) and foliar N uptake supports forest nutrition, especially in environments where soil N availability is limited.

ii. A high plant diversity increases efficiency of canopy N retention likely through complementary aboveground N uptake and therefore contributes to buffering the negative impact of N deposition on soil conditions and forest services (Chapter 2).

iii. Nitrogen leaching from organic layers increases with available litter resources provided by plants and with the biomass of detritivorous soil fauna (Chapter 3). Both groups depend on the service provided by the other, i.e. plants provide C to heterotrophic soil organisms and the soil fauna stimulate and facilitate mineralization providing the basis of plant N nutrition in environments where plants have to compete strongly with microorganisms for N.

iv. Vascular plant diversity decreases leaching losses of N from organic layers by complementary N uptake (Chapter 3). Especially the diverse understory plant community filled functional, spatial, and temporal niches that were unoccupied by the species-poor tree layer.

v. Phosphorus recycling via canopy P leaching in beech forests increased with not directly plant-available P resources in soil. The access to these P pools was improved by a more diverse ectomycorrhizal fungal community (Chapter 4). Forest P nutrition on calcareous soils likely depends on the efficiency-raising service of diverse ectomycorrhizal associations because of the abiotic constraints of P availability. Consequently, ectomycorrhiza diversity may couple back to ecosystem services beyond P cycling (e.g., N retention) and the maintenance of ecosystem functioning of Central European beech forests under global change.

vi. In contrast to my hypothesis, canopy P leaching increased in response to potential water stress (Chapter 4) which is likely to lead to a further enhanced P stress in the studied beech forest because of the geochemical P sequestration in the mineral soil. In view of the progressive N enrichment, the predicted increasing water stress and the drought sensitivity of the beech physiology in general, this raises further concern about the stability of nutrient cycling in Central European beech forest under global climate change.

1.6 Author contributions

I designed the experimental setup in collaboration with Wolfgang Wilcke, Beate Michalzik and Jan Siemens. I developed the hypotheses of Chapters 2, 3 and 4 together with Wolfgang Wilcke. I installed and maintained field equipment and performed sampling at the Schwäbische Alb, measured concentrations of TDN, K, Ca, Na (Schwäbische Alb), and NH_4^+, NO_3^-, PO_4^{3-}, TDP, Cl^- (all regions), performed all calculations and statistical analysis and wrote all manuscripts (Chapters 2, 3 and 4). I furthermore determined litterfall mass in collaboration with Sophie Mösch (Chapter 4).

Sebastian Bischoff and Beate Michalzik performed sampling and maintained field equipment in Hainich-Dün and supplied TDN, K, Ca and Na concentrations for samples from Hainich-Dün (Chapters 2, 3 and 4). Jan Siemens and Lisa Thieme performed sampling and maintained field equipment in Schorfheide-Chorin and supplied TOC, TDN, K, and Na concentrations for samples from the Schorfheide-Chorin region (Chapter 2). Data on forest structure was provided by Christian Ammer, Jörg Hailer, Peter Schall, and Ernst-Detlef Schulze (Chapters 2 and 3). Ernst-Detlef Schulze further suggested to include cation exchange in Chapter 2. Vascular plant diversty was assessed and contributed by Stefan Blaser, Steffen Boch, Markus Fischer, Fabrice Grassein, and Barbara Schmitt (Chapters 2 and 3). Soil description, density and soil C and N concentration were supplied by Ingo Schöning, Marion Schrumpf and Emily F. Solly (Chapter 3). Soil fauna composition, abundance and biomass was assessed and supplied by Bernhard Klarner, Stefan Scheu (with contributions of Christoph Digel, Roswitha B. Ehnes, Bernhard Eitzinger, Georgia Erdmann, Melanie M. Maraun, and David Ott; Chapter 3). Stefan Scheu suggested to separate soil fauna by functional group in Chapter 3. Concentrations of soil P fractions of the A horizon were contributed by Fabian Alt and Yvonne Oelmann (Chapter 4). The diversity of ectomycorrhizae was contributed by François Buscot and Tesfaye Wubet (Chapter 4). The nutrient concentration of beech leaves was contributed by Martin Gossner and Wolfgang W. Weisser (Chapter 4). Soil moisture data (Chapter 4) was supplied by the central infrastructure project instrumentation and remote sensing of the Biodiversity Exploratories under supervision of Thomas Nauss. Radar precipitation data (RADOLAN) for the year 2010 were kindly supplied by the German Weather Service (DWD, Chapter 2). Additionally, open-access climate data of nearby weather stations of the DWD was used in Chapter 4. Phenology data were provided by the members of the PEP725 project (PEP725, Chapter 4). All authors listed in Chapters 2, 3 and 4 contributed to the respective manuscripts. Additionally, two anonymous reviewers helped to improve Chapter 2.

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Chapter 2

More efficient aboveground nitrogen use in more diverse Central European forest canopies

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2.1 Abstract

We hypothesized that biodiversity improves ecosystem functioning and services such as nutrient cycling because of increased complementarity. We examined N canopy budgets of 27 Central European forests of varying dominant tree species, stand density, and tree and shrub species diversity (Shannon index) in three study regions by quantifying bulk and fine particulate dry deposition and dissolved below canopy N fluxes. Average regional canopy N retention ranged from 16 % to 51 %, because of differences in the N status of the ecosystems. Canopy N budgets of coniferous forests differed from deciduous forest which we attribute to differences in biogeochemical N cycling, tree functional traits and canopy surface area. The canopy budgets of N were related to the Shannon index which explained 14 % of the variance of the canopy budgets of N, suggesting complementary aboveground N use of trees and diverse understory vegetation. The relationship between plant diversity and canopy N retention varied among regional site conditions and forest types. Our results suggest that the traditional view of belowground complementarity of nutrient uptake by roots in diverse plant communities can be transferred to foliar uptake in forest canopies.

2.2 Introduction

Ecosystem functioning comprises processes, services, and stability (Millennium Ecosystem Assessment 2005). Pools and fluxes of water, carbon and nutrients such as nitrogen (N) within and between ecosystems are provisioning, regulating and supporting ecosystem services, respectively, because they feed back to food production and non-food resource supply such as timber (Millennium Ecosystem Assessment 2005). A number of studies in experimental grasslands revealed the significant influence of species richness on the cycling of N by more exhaustive belowground N use through complementarity (Tilman *et al.* 1996; Hooper and Vitousek 1998; Scherer-Lorenzen *et al.* 2003; Kahmen *et al.* 2006). However, the relationships of biodiversity and ecosystem functioning are far from being understood in forests. Furthermore, the small-scale experimental results have not yet been linked with replicated large-scale observations and generalized across landscapes and different land-use systems (Symstad *et al.* 2003; Scherer-Lorenzen *et al.* 2005; Fischer *et al.* 2010). The latter is necessary to adequately address spatial and functional variability of biogeochemical cycles at different scales and among various management regimes (ranging from coniferous plantations to near-native deciduous forests).

Since the beginning of industrialization, the amount of N cycling in terrestrial ecosystems has increased and N from anthropogenic sources has become an important component of the N cycle in terrestrial ecosystems (Aber *et al.* 1998; Galloway *et al.* 2004). Anthropogenic N is transported and processed in the atmosphere and ultimately deposited mainly as reactive N. Forests receive high N deposition because of the large canopy surface area and its aerosol and gas scavenging capacity (Horn *et al.* 1989; Lovett and Lindberg 1993; Rothe *et al.* 2002). The consequences of N deposition on the stability and ecosystem services of northern temperate forests have been intensively debated in the context of N saturation (Aber *et al.* 1998).

Central European forests are likely under use by humans since several centuries which has resulted in changes of vegetation composition and forest structure (Sala *et al.* 2000; FAO 2011) and modified plant species richness among forest types (Boch *et al.* 2013). Especially the introduction and the preferred cultivation of conifers has impacted biogeochemical N cycling compared to native deciduous forests in Europe through feedbacks on the light and water passing the canopy, changes in litter quality and composition, and nutrient leaching (Augusto *et al.* 2002; Rothe *et al.* 2002; De Schrijver *et al.* 2007). The cultivation of conifers in areas where deciduous trees would naturally dominate represents an intensified forest management, because coniferous forests evolved from human planting and are usually managed in shorter rotation periods resulting in greater resource exploitation through harvest than in deciduous forests of Germany on the long run (Schmitz *et al.* 2004). The response of biogeochemical cycles to forest management may vary substantially depending on regional site conditions, resources and ecosystem resilience.

Many findings mainly derived from isotope experiments highlight retention, stomatal and microbial uptake, and transformation of dissolved and gaseous N species (e.g., NH_4^+, NO_3^-, NO_2^-, NO_x, peroxy-acetyl-nitrate, organic N) in forest canopies (e.g., Garten Jr. and Hanson 1990; Sparks *et al.* 2003; Gaige *et al.* 2007). However, the physiological capability of using the various atmospheric N species and thus canopy N uptake potential depends on plant functional traits like thinner cuticles, more-pronounced leaf-wettability, higher nitrate reductase activity in deciduous than in coniferous trees. Furthermore, canopy N retention may also be governed by differences in canopy surface area and seasonality of foliage between coniferous and deciduous trees (Harrison *et al.* 2000; Augusto *et al.* 2002) or feedbacks to soil N supply (Rennenberg *et al.* 1998). Canopy N uptake of a Norway spruce forest in

Germany was estimated to range from 15 % to 42 % of the annual tree N demand (Harrison *et al.* 2000) with the majority taken up as dissolved N (Horn *et al.* 1989). Therefore, canopy N retention contributes to plant nutrition and thus potentially increases productivity and carbon sequestration in N-limited forests (Sievering *et al.* 2007). Moreover, canopy N retention buffers negative effects of inorganic N deposition through immobilization, thus, increasing ecosystem stability and supporting ecosystem services like fresh-water supply. Canopy uptake of NH_4^+ and HNO_3 by foliage and bark is accompanied by base cation leaching (mainly K^+) to maintain a balanced charge in plant cells. Thus, excessive canopy N uptake may induce base cation leaching from foliage resulting in nutrient imbalances in trees (Horn *et al.* 1989).

Both, positive and negative biodiversity-ecosystem functioning relationships were reported from observational forest studies (Vilà *et al.* 2003; 2007; Morin *et al.* 2011; Paquette and Messier 2011), but these studies focused solely on the relationship between mature tree diversity and productivity. Hence, the existence of a complementarity effect in forests is still under debate because it can only be proven using strict experimental sampling designs to overcome the 'sampling-effect' (Wardle 1999). Such a degree of experimental control of driving factors can hardly be reached in structurally complex ecosystems like forests because the understory species composition in forests is not fully independent of the regional species pool, the dominant tree species, and forest management, respectively (Boch *et al.* 2013). Nevertheless, the assumption that species-rich plant assemblages improve N-use efficiency through complementary use of N should also hold true for forests (Scherer-Lorenzen *et al.* 2005). To our knowledge, a biodiversity effect has never been evaluated with respect to aboveground nutrient use in forests via plant surfaces. Several comparative studies addressed the influence of single and admixed tree species on nutrient-use efficiency in terms of N leaching (Norden 1991; Kelty 2006; Berger *et al.* 2009) but, to our knowledge, no study investigated the functional role of vascular plant diversity on canopy N retention including the forest understory although the diversity of woody canopy-forming understory plants usually exceeds tree species diversity in managed Central European forests and the understory vegetation competes for N resources with overstory trees (Gebauer *et al.* 2000).

Our objective was to quantify the canopy budget of N in a range of central European forests to determine drivers of this budget. We hypothesized that canopy N budgets are driven by (1) the type of forest system determined by tree species and management intensity (reflected by the basal area) and (2) richness and diversity of trees and shrubs forming the forest canopy.

2.3 Materials and methods

2.3.1 Study site

This study was conducted as part of the ‘Biodiversity Exploratories’ project (www.biodiversity-exploratories.de) in three regions in Germany, Schorfheide-Chorin, Hainich-Dün, and Schwäbische Alb, where the assessments are conducted in established and actively managed forests (for details see Fischer *et al.* 2010). The three research regions differ in climate, geological setting and prevalent soils that are representative for large parts of Central Europe (Tab. 2.1). In each region, we investigated 9 forest plots (100 m × 100 m) comprising age-class forests (i.e. forests consisting of one or more even-aged development stages which are harvested at 80 – 120 year intervals by clear cut or shelterwood logging) dominated by European beech (*Fagus sylvatica* L.), Norway spruce (*Picea abies* (L.) H. Karst.), and Scots pine (*Pinus sylvestris* L.), respectively, and extensively managed forests (mature forests protected for at least 60 years) dominated by European beech (Fischer *et al.* 2010). The dominating tree species of the studied forests (Tab. 2.2) are representative for large parts of the respective region (Fischer *et al.* 2010).

Table 2.1: Main environmental properties of the three study regions partially taken from Fischer *et al.* (2010). Soil classification according to IUSS Working group WRB (2006).

	Schorfheide-Chorin	Hainich-Dün	Schwäbische Alb
Location	NE Germany (53° 2′ N, 13° 51′ E)	Central Germany (51° 10′ N, 10° 23′ E)	SW Germany (48° 24′ N, 9° 24′ E)
Altitude	3 – 140 m a.s.l.	285 – 550 m a.s.l.	460 – 860 m a.s.l.
Population density	23 km^{-2}	116 km^{-2}	258 km^{-2}
Mean annual temperature	8 – 8.5°C	6.5 – 8° C	6 – 7°C
Mean annual precipitation	500 – 600 mm	500 – 800 mm	700 – 1000 mm
Bedrock	Quarternary quartzitic sand (glacial till)	lacustrine limestone / Triassic sandstone / loess	Jurassic limestone
Soils	Cambisols Albeluvisols	Luvisols Stagnosols	Leptosols Cambisols
Common tree species	*Fagus sylvatica* L. *Pinus sylvestris* L. *Quercus spp.*	*Fagus sylvatica* L. *Picea abies* (L.) H. Karst. *Carpinus betulus* L.	*Fagus sylvatica* L. *Picea abies* (L.) H. Karst.

Table 2.2: Stand properties, management and plant species richness of the study plots. Age-class forests consist of one or more even-aged development stages which are harvested at 80 – 120 year intervals by clear cut or shelterwood logging and extensively managed forests are mature forests protected for at least 60 years. All trees with a diameter at breast height (dbh) > 7 cm were registered by a forest inventory of the whole plot area (100 m × 100 m). Plant species diversity of the study plots was based on a vegetation relevé of a 20 m × 20 m subplot.

Region	Plot ID	Main tree species	Management	Stand density [n ha^{-1}]	Mean dbh [cm]	Basal area [m^2 ha^{-1}]	Tree species [n]	Shrub species [n]	Species richness trees and shrubs [n]	Shannon index trees and shrubs
Schwäbische Alb	AEW1	spruce	age class forest	817	28.0	41.6	4	5	8	0.64
	AEW2	spruce	age-class forest	424	36.6	35.9	1	8	8	1.17
	AEW3	spruce	age-class forest	630	33.6	44.4	1	10	10	0.68
	AEW4	beech	age-class forest	2219	13.1	29.7	3	1	3	0.59
	AEW5	beech	age-class forest	137	51.9	27.4	1	8	9	0.50
	AEW6	beech	age-class forest	377	36.4	26.7	2	7	7	1.02
	AEW7	beech	extensively managed forest	200	85.2	33.3	2	3	3	0.80
	AEW8	beech	extensively managed forest	276	56.9	40.0	1	8	8	0.71
	AEW9	beech	extensively managed forest	376	42.5	31.7	2	15	16	0.88
Hainich-Dün	HEW1	spruce	age-class forest	276	49.4	43.0	5	13	14	1.68
	HEW2	spruce	age-class forest	660	35.9	41.3	5	11	13	1.51
	HEW3	spruce	age-class forest	651	32.2	42.7	4	14	16	1.53
	HEW4	beech	age-class forest	1	31.4	0.08	3	6	6	1.43
	HEW5	beech	age-class forest	489	32.2	25.8	3	6	6	1.27
	HEW6	beech	age-class forest	282	43.7	35.3	2	4	4	0.56
	HEW10	beech	extensively managed forest	377	50.3	34.3	3	8	8	1.19
	HEW11	beech	extensively managed forest	568	51.1	36.7	2	6	6	1.10
	HEW12	beech	extensively managed forest	326	54.9	36.5	1	4	4	0.73
Schorfheide-Chorin	SEW1	pine	age-class forest	1312	19.0	31.1	2	11	11	1.66
	SEW2	pine	age-class forest	1113	23.0	38.0	2	6	7	1.07
	SEW3	pine	age-class forest	391	34.6	33.4	2	6	7	1.17
	SEW4	beech	age-class forest	705	34.7	41.2	2	0	7	0.69
	SEW5	beech	age-class forest	103	73.3	23.8	2	4	4	0.32
	SEW6	beech	age-class forest	143	32.4	18.1	2	5	5	1.54
	SEW7	beech	extensively managed forest	155	61.2	36.9	1	2	2	0.13
	SEW8	beech	extensively managed forest	154	68.0	38.3	2	2	2	0.40
	SEW9	beech	extensively managed forest	259	52.5	43.6	2	1	2	0.09

2.3.2 Sampling and chemical analysis

Fluxes of Cl^-, K, Na, total dissolved N (TN), NO_3^--N, NH_4^+-N, dissolved organic N (DON), and total dissolved phosphorus with bulk deposition, throughfall, stemflow, and litter leachate were determined at intervals of 14 days for the growing season of 2010 (30 March to 9 November 2010 for Schwäbische Alb and Hainich-Dün, respectively, 14 April to 9 November 2010 for Schorfheide-Chorin). During some sampling campaigns, forest plots in Hainich-Dün ($n = 1$) and Schorfheide-Chorin ($n = 8$) were inaccessible because of hunting or harvest, therefore some samples of throughfall and stemflow refer to sampling periods of 28 days.

Rainfall was sampled at grassland sites distributed throughout the study regions (9 to 11 sampling sites) with 5 collectors per site placed at 1.8 m height. Obviously contaminated samples of rainfall were discarded in the field (Schwäbische Alb: 27 %, Hainich-Dün: 17 %, Schorfheide-Chorin: 24 %). Throughfall was sampled with 20 collectors per forest site in a subplot (20 m × 20 m) at 0.3 m above the soil surface to include the influence of overstorys and understorys of the canopy. Collectors for rainfall and throughfall consisted of 2-L polyethylene bottles equipped with a polyethylene funnel (diameter = 0.12 m). To prevent photochemical reactions, the sampling bottle was wrapped with aluminum foil. Funnels were equipped with a polyester mesh (1.6 mm mesh width) and a table-tennis ball to prevent contamination with coarse particulate matter and to minimize evaporation, respectively. Collectors for rainfall and throughfall were continuously open and therefore collected bulk deposition. However, the aerosol capturing capacity of collectors is negligible compared to that of forest canopies. Stemflow was collected from 3 trees per site using bisected polyurethane hoses (diameter = 0.04 m) as a collar fixed to the bark with a polyurethane-based sealing, and connected to a polyethylene tubing as drain outlet to a polyethylene or polypropylene trough (15 to 220 L). Litter leachate was sampled with 3 zero-tension lysimeters (diameter = 0.2 m, polyvinyl chloride) per site which were installed horizontally below the organic layer and collected the sample in polyethylene bottles stored belowground.

Bulk precipitation for each forest plot was assessed using RADOLAN data provided by German Weather Service (DWD, Offenbach, Germany) gathered from radio detection and ranging methods that have a temporal, spatial, and intensity resolution of 1 h, 1 km^2, and 0.1 mm, respectively, and were calibrated with biweekly volumetric precipitation measurements at ground level. During each sampling campaign,

Table 2.3: Analytical devices used to determine concentrations of total dissolved nitrogen (TN), NH_4^+-N, NO_3^--N, Cl^-, K, Na, and total dissolved phosphorus (TDP) in samples of rainfall, throughfall, stemflow, and litter leachate from Schwäbische Alb, Hainich-Dün, and Schorfheide-Chorin, respectively. Manufacturers and addresses are given when first mentioned.

Parameter	Source region of sample	Analytical device	Device specifications
TN	Schorfheide-Chorin	TOC Analyzer	VCPH, Shimadzu, Düsseldorf, Germany
	Hainich-Dün	TOC Analyzer	VCPN, Shimadzu
	Schwäbische Alb	TOC Analyzer	VarioTOC cube, Elementar Analysensysteme GmbH, Hanau, Germany
NH_4^+	all	Continuous Flow Analyzer (photometer)	AutoAnalyzer 3, Seal Analytical GmbH, Norderstedt, Germany
NO_3^-	all	Continuous Flow Analyzer (photometer)	AutoAnalyzer 3
Cl^-	all	Continuous Flow Analyzer (ion-selective electrode)	AutoAnalyzer 3; Orion 9417BN, Thermo Scientific, Nijkerk, The Netherlands
K, Na	Schorfheide-Chorin	Atomic absorption spectrometer	AAnalyst 300, PerkinElmer Inc., Norwalk, MA, USA
	Hainich-Dün	Inductively-coupled plasma optical emission spectrometer	Liberty 150, Varian, Mulgrave, Australia
	Schwäbische-Alb	Atomic absorption spectrometer	ZEEnit 700p, Jena Analytik GmbH, Jena, Germany
TDP	all	Continuous Flow Analyzer (photometer)	AutoAnalyzer 3

the volume of water intercepted by each collector was measured and a volume-weighted aliquot of each sample type per plot was created in the field that was filtered through pre-rinsed (at least 0.05 L distilled water and 0.05 L sample) folded paper filters (low N concentration, 5 – 8 μm, 292, Munktell & Filtrak GmbH, Bärenstein, Germany, and Sartorius AG, Göttingen, Germany) and were stored at -18°C until chemical analysis. Analytical devices used to determine concentrations of TN, NH_4^+-N, NO_3^--N, Cl^-, K, Na and total dissolved phosphorus are summarized in Tab. 2.3. DON concentrations were calculated as TN *minus* NO_3^--N *minus* NH_4^+-N. Concentrations of TN were adjusted to equal NO_3^--N *plus* NH_4^+-N if calculated DON concentrations were negative (Schwäbische Alb: 6 % of samples; Hainich-Dün: 12 %; Schorfheide-Chorin: 9 %).

2.3.3 Forest and vegetation properties

In each plot, diameter at breast height of all trees was measured between 2008 and 2012. Basal area of trees was calculated and summed for each plot to give total basal area. Richness of woody plant species was determined in each forest stand in a 20 m × 20 m subplot for shrubs ($<$ 5 m height) and trees ($>$ 5 m height) in summer 2010. For each plot, the Shannon index of woody plant species was calculated according to the equation

$$Shannon\ index = -\sum_{i=1}^{S} p_i \times ln(p_i)\ ,$$

where S denotes the total number of tree and shrub species present, i identifies an individual species, and p_i is the species-specific cover value of species i.

Management intensity was approximated by forest type and total basal area. The forest type component is factorial and distinguishes between coniferous (intensively managed) and deciduous forests (extensively managed). The basal area component reflects short-term human disturbances through thinning, planting and harvest (i.e. management reduces total basal area) but also natural disturbances.

2.3.4 Calculations and statistics

Calculations

Bulk deposition for each forest plot was calculated by multiplying site-specific bulk precipitation (RADOLAN data) and volume-weighted element concentration of rainfall for the growing season. Element concentrations in rainfall that referred to a sampling period > 14 days were excluded *a priori* from the analysis (Schwäbische Alb: 0 %, Hainich-Dün: 2 %, Schorfheide-Chorin: 17 %). Because of frequent contamination of rainfall samples, we excluded outliers that were outside of the 1.5 × interquartile range for (1) total dissolved phosphorus deposition (bird droppings), (2) electrical conductivity and (3) TN concentration (both fertilizer input), (4) of $0.5 <$ Na to Cl ratio < 1.5 (plausibility), and (5) Cl^- concentration (human contamination because of sample handling). Outlier identification was performed sequentially and for each exploratory separately and steps (2),(3), and (5) were based on single sampling events because of apparent seasonal patterns. In total, $n = 86$, $n = 94$, and $n = 65$ samples of rainfall from Schwäbische Alb, Hainich-Dün, and Schorfheide-Chorin, respectively, were used for the quantification of bulk deposition.

Throughfall water flux was calculated as mean of all samplers per plot. At one plot in Hainich-Dün (HEW4), sampling started 4 weeks later and ended 2 weeks earlier than at the other plots in Hainich-Dün and the throughfall water flux for these sampling periods was substituted using linear regression of precipitation and throughfall ($r^2 = 0.82$). Throughfall collectors at one plot in Schorfheide-Chorin

(SEW2) had to be removed between 8 June 2010 and 22 June 2010, however, precipitation was ~2 mm for this period and we therefore set throughfall water flux to 0. Stemflow water flux was calculated by scaling up the measured stemflow volume per basal area of the sampled trees to total basal area of the respective forest. We did not substitute missing stemflow water fluxes (Schwäbische Alb: 2 %; Hainich-Dün: 21 %; Schorfheide-Chorin: 1 %) because stemflow can poorly be inferred from rainfall volume and we therefore underestimate stemflow fluxes at some sites.

Element fluxes with throughfall and stemflow were calculated for each plot by multiplying volume and element concentration for each sampling campaign which were then summed up over the growing season. No samples of throughfall, stemflow, and litter leachate were removed from the dataset, except Cl^- concentration in throughfall of one plot in Hainich-Dün (HEW4) between September 14th and 28th because of obvious contamination. In contrast to rainfall, throughfall samples that refer to a sampling period of 28 days were not excluded from the analysis because the ratio of NH_4^+-N to NO_3^--N did not differ between throughfall samples with sampling periods of 14 days and 28 days (P = 0.385, *t*-test) indicating negligible N transformations in the samples. Missing element concentrations for throughfall and stemflow because of sample exhaustion by chemical analysis or plot inaccessibility were substituted by volume-weighted mean concentrations. We used the volume-weighted mean of NH_4^+-N *plus* NO_3^--N (N_{min}) concentration in litter leachate to describe N availability in soil.

Element fluxes with throughfall *plus* stemflow were considered as below canopy flux. Total deposition was calculated as bulk deposition *plus* dry deposition. Since dry deposition cannot be measured directly, total deposition was estimated according to the canopy budget model of Ulrich (1983) using Cl^- as a tracer for dry deposition. The model is based on the assumption that Cl^- is inert during the canopy passage, hence, Cl^- enrichment from bulk deposition to below canopy flux results solely from dry deposition. We did not determine gaseous dry deposition and therefore underestimate total deposition to the studied forests. Finally, the canopy budget was calculated as below canopy flux *minus* total deposition. A negative budget indicates uptake or retention of N in the canopy. For unknown reasons, total deposition exceeded below canopy flux of Cl^- at Schorfheide-Chorin from 15 September 2010 until 9 November 2010 and calculation of dry deposition was therefore based on Cl^- canopy budgets of the preceding period (14 April 2010 to 14 September 2010).

Statistics

Data were analyzed using the software environment R (R Development Core Team 2011). Differences between paired samples were tested with the Wilcoxon matched-pairs test. Two-group comparisons were performed with a t-test. Multiple group comparisons were performed with a one-way ANOVA (F-Test) followed by Tukey's honest significant differences *post hoc* test with Bonferroni correction. Nitrogen canopy budgets were analyzed with sequential ANCOVA (Type I, sum of squares). Model development was based on the principles of marginality, backward selection and single-term deletion of a full model containing region, forest type (i.e. coniferous or deciduous), basal area, N_{min} in litter leachate, Shannon index, and all two-term interactions as explanatory variables. Preliminary correlation analysis of interactions of two continuous covariates identified predominance of at least one main effect (i.e. $r_{Pearson} > 0.6$), thus, these interactions were not included in the initial model. Main effects could only be removed from the model if they were not part of an interaction term. Model development was performed until further term deletion decreased model quality significantly (F-test). One plot in Hainich-Dün (HEW4) was identified as a highly influential observation on model results by a Cook's distance value of > 1 because of the low number of mature trees on this plot (Tab. 2.2) and thus was excluded from the model development. A second plot in Hainich-Dün (HEW10) was identified as an outlier with respect to the canopy budget of TN (-8.2 kg ha^{-1}) on a within region basis violating the assumption of homogeneity and thus was excluded from the linear model. For visualization of the biodiversity effect we calculated residuals of a linear model containing only main effects of region, forest type and stand density. For all models, Gaussian distribution of residuals and homogeneity of variances were inspected visually and verified with the Anderson-Darling and the Fligner-Killeen tests, respectively.

2.4 Results

2.4.1 Total N fluxes and differences among regions

Bulk deposition of TN was greater in Schorfheide-Chorin (11.8 ± standard deviation (SD) 1.7 kg ha^{-1}) than in Hainich-Dün (10.1 ± 0.8 kg ha^{-1}, $P = 0.011$) but similar to Schwäbische Alb 11.1 ± 0.6 kg ha^{-1}. Total deposition of TN was similar in all three regions (Tab. 2.4, Fig. 2.1). Below canopy flux of TN was lower than total deposition of TN ($P < 0.001$; Fig. 2.1). The canopy budget of TN covered a wide range from

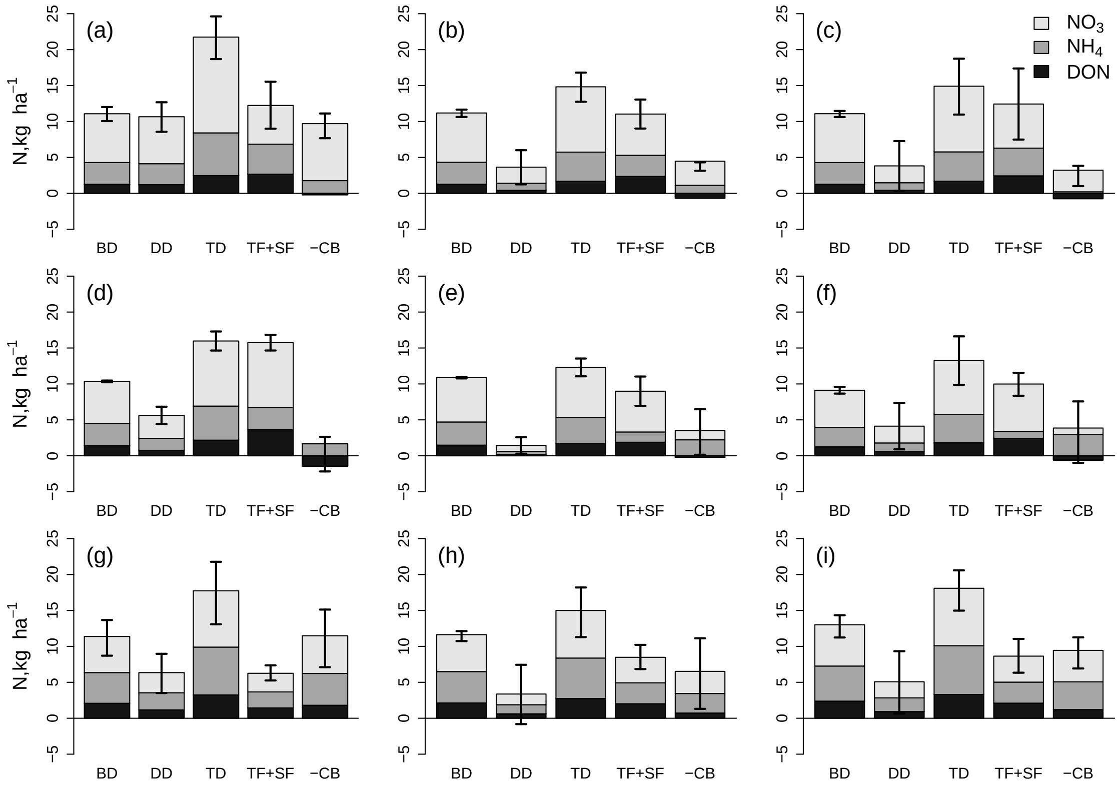

Figure 2.1: Bulk deposition (BD), dry deposition (DD), total deposition (TD), throughfall + stemflow flux (TF+SF), and the canopy budget (multiplied by –1 for better visualization; –CB) of total dissolved N (TN) separated by NO_3^--N, NH_4^+-N and DON in spruce age-class forests (a, d), pine age-class forests (g), beech age-class forests (b, e, h), and extensively managed beech forests (c, f, i) in Schwäbische Alb (a, b, c), Hainich-Dün (d, e, f), and Schorfheide-Chorin (g, h, i), respectively, for the growing season 2010. Error bars show mean ± standard deviation of TN fluxes (SD, n = 3). Note that the offset of the error bars of –CB of TN is caused by the the release of DON from the canopy.

–15.6 kg ha^{-1} to +1.5 kg ha^{-1} (Fig. 2.1) and differed among regions (Tab. 2.5). On average, 29 %, 16 %, and 51 % of total deposition of TN was retained in the canopy in Schwäbische Alb, Hainich-Dün, and Schorfheide-Chorin, respectively. The canopy budget of TN was negatively correlated with total deposition of TN (Fig. 2.2). Comparisons of dry deposition, total deposition and below canopy fluxes of TN among regions and of fractional contributions of N species in total deposition and below canopy fluxes are summarized in Tab. 2.4 and Fig. 2.1.

The charge-equivalent retention of NO_3^- was 30.2 ± 12.4 mmol$_c$ ha^{-1} in Schorfheide-Chorin, whereas NH_4^+ retention (26.2 ± 11.2 mmol$_c$ ha^{-1}) equaled leaching of K^+ from forest canopies (28.1 ± 11.3 mmol$_c$ ha^{-1}). In Schwäbische Alb, K^+ leaching from canopies (43.2 ± 14.1 mmol$_c$ ha^{-1}) exceeded NH_4^+ retention (7.4 ± 6.5 mmol$_c$ ha^{-1}) but the gap was compensated by NO_3^- retention (34.0 ± 17.6

mmol$_c$ ha^{-1}). NH_4^+ retention (16.3 ± 6.5 mmol$_c$ ha^{-1}) was smaller than K^+ leaching (50.8 ± 19.2 mmol$_c$ ha^{-1}) from canopies in Hainich-Dün where NO_3^- retention (5.3 ± 14.7 mmol$_c$ ha^{-1}) was negligible.

2.4.2 Effects of forest type and stand density

Because of the greater dry deposition, total deposition of TN was greater in coniferous than in deciduous forests of Schwäbische Alb and Hainich-Dün ($P < 0.036$), respectively (Fig. 2.1). Canopy retention of TN was greater in coniferous than in deciduous forests (Tab. 2.5). However, the interaction between forest type and region was only significant in Schwäbische Alb and Schorfheide-Chorin ($P = 0.010$). Below canopy fluxes of TN differed between coniferous and deciduous forests exclusively in Hainich-Dün (Tab. 2.4). Stand density was similar in all three regions and greater in coniferous than in deciduous forests ($P = 0.017$). The canopy budget of TN increased with the stand density in coniferous forest while the opposite was true for deciduous forests rendering the overall effect of stand density on all studied forests negligible (Tab. 2.5). Furthermore, differences in canopy N budget among coniferous age-class forests, deciduous age-class forests, and extensively managed forests only reflected differences between the forest types.

Table 2.4: Comparison of fluxes of total dissolved nitrogen (TN) among regions and forest types studied, respectively, and of canopy budgets of dissolved organic nitrogen (DON), NH_4^+-N, and NO_3^--N within regions if not presented in the results section. Logical operators indicate significant differences at the $P < 0.05$ level. Quantitative information is shown in Fig. 2.1.

Comparison	Flux	Result
Differences among regions	Bulk deposition of TN	Schwäbische Alb ≈ Hainich-Dün < Schorfheide-Chorin
	Dry deposition of TN	Schwäbische Alb ≈ Hainich-Dün ≈ Schorfheide-Chorin
	Total deposition of TN	Schwäbische Alb ≈ Hainich-Dün ≈ Schorfheide-Chorin
	Below canopy flux of TN	Schwäbische Alb ≈ Hainich-Dün > Schorfheide-Chorin
Differences among N species	Total deposition	Schwäbische Alb: DON < NH_4^+-N < NO_3^--N; Hainich-Dün: DON < NH_4^+-N < NO_3^--N; Schorfheide-Chorin: DON < NH_4^+-N ≈ NO_3^--N
	Canopy budget	Schwäbische Alb: DON > 0 > NH_4^+-N > NO_3^--N; Hainich-Dün: DON > NO_3^--N ≈ 0 > NH_4^+-N; Schorfheide-Chorin: 0 > DON > NH_4^+-N ≈ NO_3^--N
Differences among forest types	Below canopy flux of TN	Schwäbische Alb: coniferous ≈ deciduous; Hainich-Dün: coniferous > deciduous; Schorfheide-Chorin: coniferous ≈ deciduous

2.4.3 Influence of plant diversity

The diversity of trees and shrubs differed marginally among the three regions ($P = 0.057$) and tended to be lowest in Schorfheide-Chorin and highest in Hainich-Dün (Tab. 2.2). The Shannon index was higher in coniferous than in deciduous forests ($P = 0.012$). The Shannon index explained 14 % of the variance in the canopy budget of TN (Tab. 2.5) and tended to be positively correlated with the residual canopy budget of TN after accounting for region, forest type and stand density (i.e. supporting canopy N retention; Fig. 2.3). The effect of plant diversity varied significantly among regions and forest types, respectively (interaction terms in Tab. 2.5).

2.5 Discussion

2.5.1 Effects of region and forest management intensity on canopy N retention

Canopy budgets of TN were almost entirely negative indicating widespread net N retention (Fig. 2.1). Canopy N retention occurs frequently in temperate forests deficient in N and forest canopies in North America receiving low to intermediate N deposition usually retain 10 to 90 % (mean of 40 %) of annual wet N deposition (Lovett and Lindberg 1993). Foliar N uptake was estimated to provide up to 50 % of plant N demand (Sievering *et al.* 2007) and thus may counteract N limitation (Sparks *et al.* 2003). Similar to our study, canopy N retention in North America increased with N deposition (Lovett and Lindberg 1993; Fig. 2.2). Thus, regional differences in the canopy budget of TN in our study are likely related to the magnitude of N deposition and the forest N status. However, the proxy we used for N availability to roots (i.e. N_{min} in litter leachate) did not influence the canopy budget of TN. Given the sandy soil texture in Schorfheide-Chorin and the shallowness of soils in Schwäbische Alb, respectively, N availability to roots may also be limited by water-shortage resulting from the low water holding capacity of the soils in Schorfheide-Chorin or small soil N stocks in Schwäbische Alb, rendering canopy uptake of deposited N more important in Schorfheide-Chorin and Schwäbische Alb than in Hainich-Dün. Accordingly, canopy N uptake in Hainich-Dün might have been limited because local soil properties (e.g., high fertility, high water and nutrient storage capacity of the soils) render N nutrition by root uptake more efficient resulting in N accumulation within the plant and decreased foliar N uptake (Rennenberg *et al.* 1998).

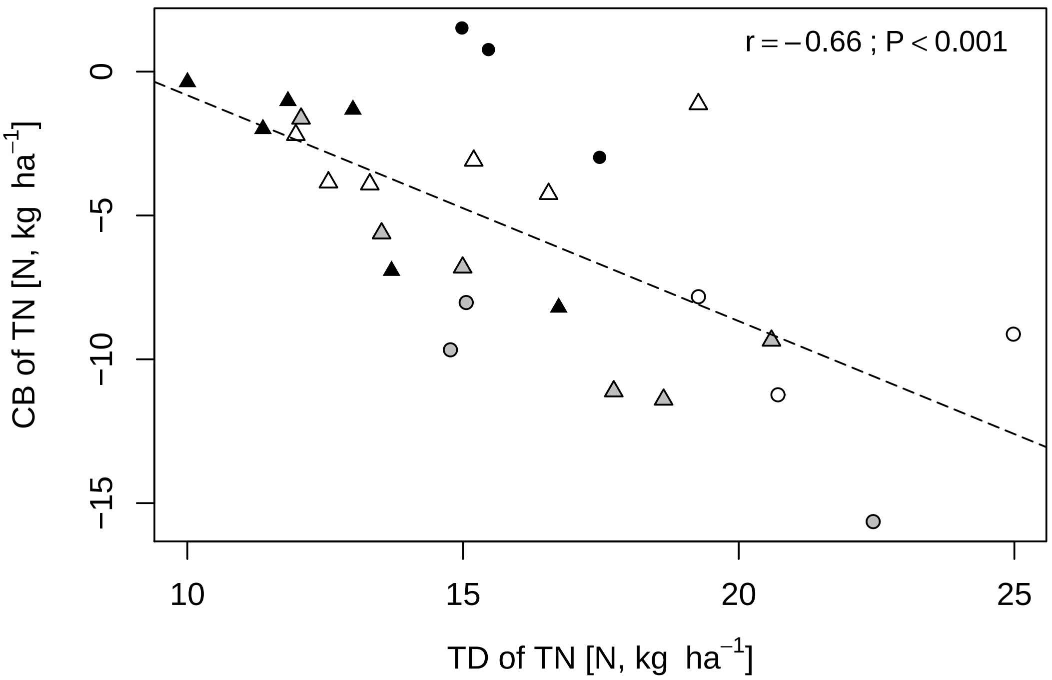

Figure 2.2: Relationship of total deposition and canopy budget of total dissolved N (TN) of the growing season 2010. Open, black, and gray symbols refer to plots from Schwäbische Alb, Hainich-Dün, and Schorfheide-Chorin, respectively. Circles and triangles refer to coniferous and deciduous forests, respectively. The dashed line is the regression line.

Deposited N is prone to chemical, biological, and physical interactions with canopy surfaces and organisms. Major sinks for deposited N in the canopy are foliar uptake by plants through stomatal penetration and cuticular diffusion (e.g., Eilers *et al.* 1992; Peuke *et al.* 1998; Lockwood *et al.* 2008) that is usually accompanied by ion exchange and leaching, assimilation by epiphytes and microbes (Papen *et al.* 2002; Gaige *et al.* 2007; Schwarz *et al.* 2011), and ion adsorption to canopy surfaces (Dail *et al.* 2009; Adriaenssens *et al.* 2012). The canopy can also be a source of dissolved N through dissolution of dry deposited particles and gases and leaching from organic tissues (e.g., DON, Fig. 2.1), respectively. All of these sinks and sources occur simultaneously and should be related to species-specific canopy surface properties or functional traits. The good agreement of K^+ leaching and $NH_4{}^+$ retention in mmol$_c$ m^{-2} in Schorfheide-Chorin suggested that foliar uptake accompanied by ion exchange is a potentially important sink for N in the canopy. The fact that K^+ leaching in Schwäbische Alb and Hainich-Dün was greater than the $NH_4{}^+$ retention in mmol$_c$ m^{-2} indicates that either we underestimated $NH_4{}^+$ retention because we did not consider gaseous NH_3 deposition or that there were additional acid inputs causing canopy H^+ buffering by K^+ leaching. Part of the acid inputs might originate from gaseous HNO_3 deposition. While NO_3^- may be taken up by the plant in a charge-neutral way by release of anions like OH^-, the H^+ is buffered by K^+ leaching. Consequently, K^+ leaching in $\mathrm{mmol}_c\ \mathrm{m}^{-2}$ matched the uptake of NH_4^+ and NO_3^- in Schwäbische Alb.

Generally, canopy surface area and roughness are greater in coniferous than in deciduous forests (Augusto *et al.* 2002). Canopy properties of spruce forest increased dry deposition of TN (Fig. 2.1) and provided a larger reactive surface for adsorption and assimilation relative to deciduous forests because of permanent foliage (Harrison *et al.* 2000) as reflected by the significant effect of forest type on the canopy budget of TN (Tab. 2.5). The effect of the forest type differed among regions (Tab. 2.5). The structural differences between coniferous and deciduous forests are unlikely to vary substantially among regions. More probably, coniferous and deciduous forests adapt their N acquisition strategies differently in relation to the regional N status. This also suggests that biotic retention (e.g., assimilation) is more important than abiotic retention (e.g., adsorption).

In line with other studies, coniferous forests retained atmospheric N more efficiently than deciduous forests in Schwäbische Alb and Schorfheide-Chorin (Rothe *et al.* 2002; De Schrijver *et al.* 2007; Tab. 2.5). This difference may have been marginalized through the greater N demand and functional traits of beech (e.g., thinner cuticle, more pronounced leaf-wettability, higher nitrate reductase activity) compared to coniferous trees (Harrison *et al.* 2000). However, the opposite was observed in Hainich-Dün, indicating that the regional N status had a profound effect on functional traits of the dominant tree species (region × forest type in Tab. 2.5). Norway spruce forests are known to be more susceptible to N saturation resulting in greater N leaching than from deciduous forests and thus having a more open N cycle (Neary and Gizyn 1994; Augusto *et al.* 2002; Rothe *et al.* 2002; De Schrijver *et al.* 2007; Berger *et al.* 2009). In Hainich-Dün, the regional susceptibility to N saturation because of the soil fertility and the more open N cycle of spruce forests could have added up and overcome the positive feedback of the larger surface area of spruce on canopy N retention while the opposite was observed in Schwäbische Alb and Schorfheide-Chorin under N scarcity. Only marginal effects of management intensity in terms of stand density on canopy N retention were observed, but these seemed to differ between deciduous and coniferous forests in our study (Tab. 2.5).

Table 2.5: Analysis of (co-)variance (sequential, type I sum of squares) with the canopy budget of total dissolved N as response variable (n = 25). Asterisks highlight significant variances.

	Df	Sum Sq	Mean Sq	F value	P (>F)	
Region	2	254.4	127.2	65.4	<0.001	***
Forest type	1	56.4	56.4	29.0	<0.001	***
Basal area	1	6.15	6.15	3.16	0.099	
Shannon index	1	70.3	70.3	36.1	<0.001	***
Region × forest type	2	19.2	9.58	4.92	0.026	*
Region × Shannon index	2	26.6	13.3	6.83	0.009	**
Forest type × basal area	1	17.8	17.8	9.13	0.010	*
Forest type × Shannon index	1	11.9	11.9	6.14	0.028	*
Residuals	13	25.3	1.95			

2.5.2 The role of plant diversity for canopy N retention

We showed, to our knowledge for the first time, a biodiversity effect on aboveground nutrient cycling in forests. In the studied forests which are representative for large parts of Central Europe, plant diversity explained a significant fraction of the variance of the canopy budget of TN and canopy N retention was positively related to the diversity of trees and shrubs. We highlight that the diversity of all canopy-forming plants of forests and not only that of trees impact the canopy budget of TN and therefore the biodiversity-ecosystem function relationship. However, because of confounding effects of region, forest type, and possibly associated species composition, the influence of the tree and shrub diversity on canopy N retention varied by region and forest type.

The Shannon index of shrubs and trees explained 14 % of the variance in the canopy budget of TN but also interacted with the study region and the forest type, respectively (Tab. 2.5). Furthermore, canopy N retention increased significantly with the Shannon index because not accounting for the effect of plant diversity would have resulted in an overestimation of the canopy budget of TN (Fig. 2.3). The fact that the strength of this relation differed by region and forest type (interaction terms in Tab. 2.5) highlights the relevance of environmental variability for the functional role of biodiversity in forest ecosystems.

Most studies on the biodiversity-nutrient cycling relationship were conducted in grassland systems. The more efficient use of N with increasing diversity of grass-

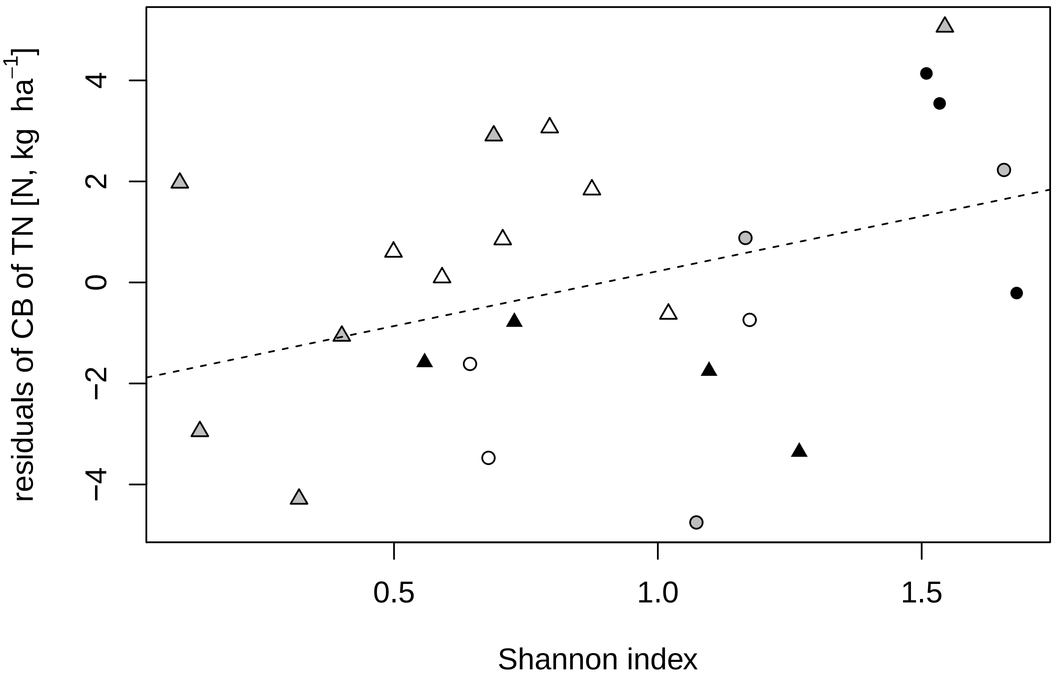

Figure 2.3: Relationship of the Shannon index and the residual canopy budget of total dissolved N (TN) of the growing season 2010 after accounting for the effects of region, forest type, and basal area, respectively. According to Tab. 2.5 this effect is significant at the $P < 0.001$ level. Open, black, and gray symbols refer to plots from Schwäbische Alb, Hainich-Dün, and Schorfheide-Chorin, respectively. Circles and triangles refer to coniferous and deciduous forests, respectively. The dashed line is the regression line.

land plant species is commonly attributed to belowground complementary use of resources (Hooper and Vitousek 1998; Scherer-Lorenzen *et al.* 2003). Thus, the effect of the diversity of canopy-forming plant species on canopy N retention suggests complementary use of bulk and fine particulate deposited N in aboveground plant parts in Central European forests.

Similar to grasslands and belowground complementary N use, aboveground complementarity in forests may result from spatial, temporal and functional niche partitioning, respectively (Tilman *et al.* 1996; Kahmen *et al.* 2006). In the context of canopy N retention in forests, spatial niche partitioning evolves most likely from canopy layering. When N is deposited, it comes first into contact with the tree canopy layer and is partially assimilated by foliage, twigs, and bark. Residual N, N falling directly through gaps of the overstory, and N released from the overstory, is translocated from the overstory to the understory of the canopy with the percolating water where further uptake may occur. Although the understory vegetation has a much lower biomass than trees in Central European forests, N incorporation from throughfall can be twice that of overstory trees (Gebauer *et al.* 2000).

Canopy N retention is greatest in the physiologically active season of the year (Harrison *et al.* 2000; Adriaenssens *et al.* 2012) when plant N demand is high. Complementary phenological species traits could therefore have lowered temporal variation in canopy N retention. Since shrub diversity exceeded tree diversity (Tab. 2.2), temporal variability of N demand was likely greater in the understory. Temporal complementarity might also have been related to micro-climatic differences between the canopy layers (e.g., higher relative humidity of the air near the ground sustaining water-films on canopy surfaces, thus supporting foliar uptake) or variation of N availability in soil and species-specific rooting depths.

Functional complementarity likely results from plant functional traits such as leaf-wettability or preference for certain N species and thus relates to different N use strategies among plant functional groups (Kahmen *et al.* 2006). Because of the greater species richness, functional diversity should be greater in the shrub layer than in the tree layer. Therefore, especially canopy N uptake in coniferous forests of Schwäbische Alb and Schorfheide-Chorin could have been supported by ${NO_3}^-$-N uptake in the shrub layer since the capability of conifers to use ${NO_3}^-$ is low. Furthermore, species dominance can correlate with N species preference (McKane *et al.* 2002). This suggests, that the plants in the understory could have adapted to high ${NO_3}^-$ availability in throughfall after ${NH_4}^+$ has been filtered out by conifers. This could also have coupled back to species composition in the understory by increasing the abundance of species efficient in foliar uptake of ${NO_3}^-$.

The interactions of the influences of region and forest type with the Shannon index on canopy budgets of TN suggested that the biodiversity-ecosystem functioning relationship depended on the regional and forest management-related species pools which determine the potential extent of temporal, spatial and functional complementarity. However, the abundance of key species can have a pronounced influence on apparent biodiversity effects (Wardle 1999). The influence of key species cannot be tested in forests because single species interactions are not thoroughly replicated. More research on the influence of environmental variability and forest management on the biodiversity-ecosystem function relationship is needed to draw conclusions on involved mechanisms.

2.6 Conclusions

We conclude that the diversity of canopy-forming plants is a control of the canopy budget of TN in Central European forests and especially diverse understorys may support canopy N retention and thus provided evidence for a relationship of plant diversity and nitrogen cycling in forests. However, the regional N status, the forest type, and interactions of both codetermine canopy N retention and couple back to the effect of plant diversity on canopy N retention. Hence, we showed for the first time that the traditional view of belowground complementarity of nutrient uptake by plant roots can be transferred to forest canopies, the ‘roots in the sky’.

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Chapter 3

Drivers of nitrogen leaching from organic layers in Central European beech forests

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3.1 Abstract

We identified the drivers of dissolved inorganic and organic nitrogen (N) fluxes through shallow mull-type organic layers in 12 beech forests on calcareous soils in two regions in Germany over three consecutive growing seasons. Our results suggest that dissolved N exports from organic layers contain significant amounts of throughfall derived NO_3^--N that flushes through the organic layer. Average growing season net fluxes (i.e. litter leachate – throughfall flux) of total dissolved N (TDN) from the organic layer were low (2.3 ± 5.6 kg ha^{-1}) but varied widely from net release (12.9 kg ha^{-1}) to net retention (–8.3 kg ha^{-1}). The small release of dissolved N from organic layers suggested that high turnover rates of Mull-type organic layers on calcareous soils coincided with high microbial N assimilation and plant N uptake. Gross and net fluxes of TDN and NO_3^--N were influenced by forest stand basal area, vascular plant diversity, and soil fauna biomass. Stand basal area had a positive feedback on N fluxes by providing litter for soil organic matter formation. Plant diversity reduced dissolved N fluxes. Especially herb diversity contributed to reduced leaching losses while herb cover had no significant effect suggesting that the diversity effect was related to synergistic diversity effects and not to a diversity-biomass relationship. Soil fauna biomass increased TDN and NO_3^--N fluxes with litter leachate by stimulating mineralization and possibly enhancing the basal area effect. Our results highlight that N leaching in organic layers is driven by the complex interplay of plants, animals and microbes and that high understory plant diversity reduces N leaching in Central European beech forests.

3.2 Introduction

While the internal recycling of nitrogen (N) in forest ecosystems through decomposition and mineralization of organic matter primarily controls plant available N (Park *et al.* 2002), continuously elevated atmospheric deposition of reactive N has become an important additional component of N relations of temperate forests (De Vries *et al.* 2006; Tørseth *et al.* 2012). Excessive atmospheric N deposition is regarded as a major threat for ecosystem functioning, stability and services like clear fresh-water supply due to nutrient retention (Millennium Ecosystem Assessment 2005). Organic layers play a key role in N retention of forests (Nadelhoffer *et al.* 1995). The latter authors found that organic layers in temperate hardwood forests contribute 40 to

80 % to total N retention. The response of the N budget of European forest ecosystems to N deposition, however, is varied. Increased NO_3^- leaching was observed mainly in coniferous forests with a low C:N ratio in the organic layer (MacDonald *et al.* 2002; Prietzel and Bachmann 2012). Durka *et al.* (1994) showed that 80 % of NO_3^- from atmospheric deposition bypasses the ecosystem N-cycle and enters into groundwater in a Norway spruce (*Picea abies* (L.) H. Karst) forest. For a range of Central European beech (*Fagus sylvatica* L.) forests, N accumulation in the soil ranged –24 to +11 kg ha^{-1} $year^{-1}$ (Brumme and Khanna 2008).

Plants influence N cycling by controlling external N inputs to soils like deposition from the atmosphere via canopy properties (Schwarz *et al.* 2014) and losses like N leaching and N uptake (Knops *et al.* 2002). About 50 to 60 % of plant-assimilated N in deciduous forests is annually returned to the soil via litterfall (Khanna *et al.* 2009). The associated flux of organic C substrates is an important energy source for soil heterotrophs and therefore enhances soil organic matter formation, and turnover (Knops *et al.* 2002; Kaiser *et al.* 2011). Although trees constitute the majority of the forest biomass, understory biomass has a strong influence on N fluxes which was ascribed to physiological and phenological differences between overstory and understory plants (Muller and Bormann 1976; Olsson and Falkengren-Grerup 2003; Schulze *et al.* 2009). While this implies a relationship with functional diversity, no study yet tested the influence of plant diversity in the canopy and the understory on N fluxes in organic layers. This is surprising given the positive relationship of plant diversity to N use efficiency in grasslands (Tilman *et al.* 1996; Kahmen *et al.* 2006) and to primary productivity and canopy N uptake in forests (Morin *et al.* 2011; Brassard *et al.* 2013; Schwarz *et al.* 2014).

In calcareous soils, which are widespread in Central Europe, biological activity is high resulting in high turnover rates of organic matter and a considerable contribution of soil microorganisms and animals to the mass of the organic layer (Scheu 1987; Frouz *et al.* 2013; Kammer *et al.* 2012). The dominant organic layer form is therefore mull consisting only of a fresh litter layer (Oi horizon) plus occasionally a thin fermented litter layer (Oe horizon) which are mineralized or incorporated into the mineral soil within a few years. The activity of soil organisms may thus strongly influence the N budget of organic layers. High gross N mineralization may for instance be out-competed by N uptake of microorganisms at slightly acidic pH values (Kooijman *et al.* 2008) thereby reducing both the risk of N leaching and N availability for plants. However, bioturbation by the soil animals may stimulate and facilitate net N mineralization in European beech forests on calcareous soils (Scheu

1987) and may counteract restricted plant N access (Scheu 1987; 1997; Verhoef and Brussaard 1990; Bardgett and Chan 1999).

Our objective was to identify controls of N leaching from organic layers in forests dominated by European beech by relating dissolved N inputs and outputs from 12 forests in two regions over three consecutive growing seasons to abiotic and biotic drivers. The study forests were exposed to a total N deposition from the atmosphere of about 15 kg ha^{-1} year^{-1} (Schwarz *et al.* 2014). We hypothesized that (1) gross N fluxes with litter leachate are dominated by throughfall-derived N while the contribution of organic layer mineralization is small, (2) the fluxes of dissolved N from organic layers increase with forest stand basal area and related litterfall providing major resources for decomposition, (3) vascular plant diversity reduces dissolved N fluxes in organic layers, and (4) the soil fauna increases dissolved N fluxes in litter leachate by accelerating soil organic matter decomposition.

3.3 Materials and methods

3.3.1 Site description

This study was conducted in the Schwäbische Alb (48° 24′ N, 9° 24′ E; 740 – 788 m a.s.l.) and in Hainich-Dün (51° 10′ N, 10° 23′ E; 333 – 491 m a.s.l) in Germany. The two study regions are similar in climate, parent materials and soil types (Tab. 3.1) and represent typical conditions in Central European mid-mountain ranges. The organic layers consist of Oi and Oe horizons, except on one plot (AEW8) where a thin discontinuous Oa horizon was detected additionally. Total N deposition in the growing season 2010 was 17.1 ± standard deviation (SD) 4.3 kg ha^{-1} in the Schwäbische Alb and 13 ± SD 2.5 kg ha^{-1} in Hainich-Dün (Schwarz *et al.* 2014).

In both regions, we investigated 6 forest plots (100 m × 100 m) dominated by European beech (i.e., $>$ 70 % of stand basal area). Other species in the tree and shrub layer comprised sycamore maple (*Acer pseudoplatanus* L.), hornbeam (*Carpinus betulus* L.), and European ash (*Fraxinus excelsior* L.). In some forests in the Schwäbische Alb, few Norway spruce trees were admixed to beech. The herb layer harbored mainly Amaryllidaceae, Brassicaceae, Cyperaceae, Euphorbiaceae, Lamiaceae, Oxalidaceae, Poaceae, Ranunculaceae, Rubiaceae, and Violaceae families. Wild garlic *Allium ursinum* (L.) is the dominant herb in spring, especially in Hainich-Dün, and collapses in early summer.

Table 3.1: Site characteristics of the studied regions and forests. Soil classification according to IUSS Working group WRB (2006). MAT and MAP is mean annual temperature and mean annual precipitation, respectively. C:N ratios refer to the whole organic layer, pH is the mean of litter leachate over three growing seasons. stand density and basal area (G) were registered by a forest inventory of the whole plot area (1 ha, caliper limit > 7 cm; except for a thicket beech stand HEW4, where G was estimated). The Shannon index was calculated based on cover values of vascular plant species and averaged over three years.

Region	Bedrock	MAT [°C]	MAP [mm]	Plot ID	Soil type	C:N	pH	stand density [trees ha^{-1}]	stand basal area [m^2 ha^{-1}]	Shannon index
Schwäbische Alb	jurassic limestone	6 - 7	700 - 1000	AEW4	Cambisol	28	6.6	2219	29.7	1.77
				AEW5	Cambisol	48	6.6	139	27.6	2.38
				AEW6	Cambisol	29	6.7	374	26.5	2.13
				AEW7	Leptosol	28	6.1	199	33.2	0.77
				AEW8	Cambisol	28	6.7	277	40.2	2.01
				AEW9	Leptosol	32	6.7	376	32.2	2.20
Hainich-Dün	lacustrine limestone / loess	6.5 - 8	500 - 800	HEW4	Luvisol	39	6.2	1	7	1.82
				HEW5	Luvisol	29	6.2	487	25.6	2.34
				HEW6	Luvisol	37	6.4	283	35.3	2.09
				HEW10	Stagnosol	35	6.2	379	34.8	1.66
				HEW11	Luvisol	31	6.3	565	36.9	1.60
				HEW12	Luvisol	27	5.8	326	36.5	1.29

3.3.2 Sampling and chemical analysis

Cumulative throughfall and litter leachate was collected fortnightly in the years 2010 to 2012 when daily mean temperatures were > 0°C and samples could be collected in liquid state (roughly from March to November). For convenience, we refer to the sampling period as growing seasons. Because of differences in meteorological conditions, growing season length differed among regions and years with 266, 280 and 266 days in the Schwäbische Alb and 252, 266 and 238 days in Hainich-Dün for 2010, 2011 and 2012, respectively. The plots were inaccessible due to frost or hunting at few planned sampling campaigns which could not be realized (1 of 58 in the Schwäbische Alb; 4 of 54 in Hainich-Dün) and samples from these campaigns were included in the following sampling. We cannot fully exclude N transformations inside the collectors between sampling campaigns. Other studies, however, revealed that the majority of N transformations only occurs after storage times longer than two weeks in the field (Michalzik *et al.* 1997). The composition of dissolved N in samples that were collected over 28 days might have changed though. Nevertheless, we included these samples in our analysis as the number of sampling campaigns concerned was small.

Precipitation during the growing seasons was measured with 5 collectors at 9 grassland sites distributed throughout each of the two study regions. Throughfall was sampled with 20 funnel-type collectors (diameter of 0.12 m; polyethylene) per forest site in a subplot (20 m × 20 m) 0.3 m above the soil surface; thus canopy interactions of small herbs might not be fully reflected in throughfall. Throughfall collectors were wrapped with aluminum foil to prevent photochemical reactions and algae growth. Funnels were equipped with a 1.6 mm polyester mesh and a table-tennis ball to prevent contamination with coarse particulate matter and to minimize evaporation, respectively. Litter leachate was sampled with three circular zero-tension lysimeters (diameter of 0.2 m, polyvinyl chloride) per site which were installed horizontally below the soil organic layer in summer 2009. Polyethylene hoses attached to the lysimeter outlet drained the collected sample into polyethylene bottles stored in the dark below ground.

During each sampling campaign, the volume of water in each collector was measured and a volume-weighted aliquot of each sample type per plot was taken in the field. All samples were filtered through pre-rinsed (at least 0.05 L distilled water and 0.05 L sample) folded paper filters (low N concentration, 5 – 8 μm, 292, Munktell & Filtrak, Bärenstein, Germany, and Sartorius, Göttingen, Germany) and stored at –18°C until chemical analysis.

Total dissolved nitrogen (TDN) concentrations were determined after catalytic oxidation with TOC/TN analyzers (Schwäbische Alb: Vario TOC cube, Elementar, Hanau, Germany; Hainich-Dün: VPCN, Shimadzu, Düsseldorf, Germany). Concentrations of NH_4^+-N and NO_3^--N were determined photometrically after a modified Berthelot reaction and colorimetrically after Cd reduction to NO_2^- and reaction to an azo-dye, respectively, with a continuous flow analyzer (AutoAnalyzer 3, Seal Analytical GmbH, Norderstedt, Germany). The concentrations of dissolved organic N (DON) were calculated as the difference in TDN and inorganic N forms. Concentrations of Cl^- were determined with an ion-specific electrode (Orion 9417BN, Thermo Scientific, Nijkerk, The Netherlands).

3.3.3 Forest and vegetation properties, arthropod biomass and organic layer properties

Species and diameter at breast height (dbh; measured to the millimeter) of all trees with a dbh $\geq$ 7 cm growing on a plot were surveyed within two vegetation periods between September 2008 and April 2010, and used for the calculation of forest stand basal area. For plot AEW4 we used forest inventory data sampled in November 2012 because initial inventory at this site was incomplete due to high tree numbers. The basal area of HEW4 had to be estimated as 7 m^2 ha^{-1} because this stand is a thicket with only few individuals exceeding the caliper limit of the forest inventory (Schall and Ammer 2013). For comparative purposes, litterfall was collected from September 24, 2013 to June 03, 2014 in the Schwäbische Alb and from October 09, 2013 to June 17, 2014 in Hainich-Dün with 5 litterfall traps (sampling area of 0.25 m^2) per plot. Litterfall mass was determined after drying at 60°C and removing coarse woody litter (> 20 mm).

Vascular plant species richness of trees, shrubs (woody species, height < 5 m) and herbs was determined annually in each forest in early summer between 2010 and 2012 in a 20 m × 20 m subplot and plant diversity was quantified by the Shannon index (H') according to Eq. 3.1.

$$H' = -\sum_{i=1}^{S} p_i \times ln(p_i) \ , \tag{3.1}$$

where S denotes the total number of vascular plant species present, i identifies an individual species, and p_i is the cover value of species i. Additionally, Shannon indexes were calculated individually for trees, shrubs and herbs. The Shannon indexes (using antilogarithm) and cover values were averaged over the study period.

Soil fauna was sampled to a depth of 0.05 m in spring 2008. Soil macrofauna and mesofauna was extracted by heat from two to four soil cores of 0.2 m and 0.05 m diameter, respectively. *Lumbricidae* were extracted separately *in situ* with a mustard solution (area = 0.25 m^2). Soil fauna was determined to the species level, average weight per species was determined after drying at 60°C or mass-length regression and population biomass in mg dry weight m^{-2} calculated as detailed in (Ehnes *et al.* 2014). For statistical analysis, soil fauna species were aggregated to the functional groups macro detritivores, including the taxonomic groups *Coleoptera*, *Diplopoda*, *Isopoda*, *Lumbricidae*, and *Symphyla*, and meso detritivores, including *Collembola* and *Oribatida*. Additionally, microbial biomass in a fresh subsample of the litter layer was determined by measuring maximum initial respiratory response (Anderson and Domsch 1980).

Organic layers were sampled at 14 sampling points along two 36 m transects in each forest site using a rectangular metal frame of 0.15 m side length in May 2011. Organic layers were separated into horizons, and thickness and dry mass was recorded. For each horizon, composite subsamples dried at 70°C were analyzed for C and N concentrations with an elemental analyzer (Vario EL, Elementar). The C:N ratios of the organic layers were calculated as mass-weighted mean of all organic layer horizons.

3.3.4 Calculation of water and element fluxes

Water input into the soil was quantified by volumetric measurements of throughfall precipitation. Missing throughfall amounts were substituted by the average throughfall of the sampling period in the respective area (the Schwäbische Alb: 1 %; Hainich-Dün: 5 %). We did not include stemflow fluxes because we believe that stemflow is of limited importance for the budget of the organic layers because it is spatially concentrated around trees where it causes erosion of the litter layer and thus infiltrates directly into the mineral soil at the base of trunks (Levia and Frost 2003). However, stemflow deposition of TDN in the growing season 2010 was only 0.27 ± SD 0.15 kg ha^{-1} in the Schwäbische Alb and 0.71 ± SD 0.28 kg ha^{-1} in Hainich-Dün (Schwarz *et al.* 2014).

Water fluxes through organic layers cannot be inferred directly from the collected water amount by zero-tension lysimeters because of the interface effect (i.e. the artificial barrier prevents water drainage until water saturation of the organic layer is reached). We thus used a two-step Cl^- balance approach of throughfall and litter leachate to estimate water fluxes through the organic layer. Given sufficient water flow, Cl^- is inert in soils (Beese and van der Ploeg 1979) and water flux can be calculated according to Eq. 3.2.

$$q_{LL}[mm] = q_{TF}[mm] \times Cl^-_{TF}/Cl^-_{LL}, \tag{3.2}$$

where q_{LL} is the water flux through the organic layer, q_{TF} is the throughfall precipitation, Cl^-_{TF} and Cl^-_{LL} is the Cl^- concentration in throughfall and litter leachate, respectively. We then calculated a linear regression function of throughfall precipitation on water leaching through the organic layer for all available samples to infer water fluxes through the organic layer directly from throughfall precipitation ($R^2 = 0.46$; Fig. 1.7). For this calculation, we excluded low and high precipitation sampling periods (5 mm (14 days)$^{-1}$ < throughfall < 80 mm (14 days)$^{-1}$; 6 % of available cases) to minimize Cl^- imbalances because of transient retention and spontaneous release of Cl^- and insufficient drainage of the lysimeters. The linear regression revealed an interception loss of 1.03 mm and a fractional water loss of throughfall precipitation due to evapotranspiration in the organic layer of 27 % on a 14 days basis. These estimates are similar to values of interception and evapotranspiration in organic layers under European beech in Luxembourg (Gerrits *et al.* 2010).

Prior to flux calculations, we removed outliers that were outside 1.5 × inter-quartile range of log-transformed concentrations for each plot and N form separately while accounting for seasonality patterns. In throughfall, 1.8 %, 0.6 % and 1.9 %, and in litter leachate, 0.6 %, 1.2 % and 0.6 % of TDN, NH_4^+-N and NO_3^--N concentrations, respectively, were removed. These samples were probably contaminated (e.g., leaching from coarse debris or dead insects in the funnel of the collectors) and mostly matched for the three N forms. Gross fluxes of TDN, NH_4^+-N and NO_3^--N with throughfall and litter leachate were calculated by multiplying water flux with volume-weighted mean concentrations. Because of seasonal concentration patterns, volume weighted means and fluxes were calculated for spring, summer, and fall separately and then summed over the growing seasons. Because of insufficient sample volume, volume weighted mean concentrations of NH_4^+-N and NO_3^--N in litter leachate at HEW11 and HEW12 in spring 2011 could not be determined and were substituted by multiplying TDN concentration with the respective average fractional contribution of NH_4^+-N and NO_3^--N to TDN in spring 2010 and 2012 at the same sites. Net fluxes of TDN, NH_4^+-N and NO_3^--N in the organic layer were calculated by subtracting throughfall fluxes from gross fluxes in litter leachate of the respective N form.

3.3.5 Statistics

Annual differences of throughfall precipitation and deposition were tested for each region separately with an F-test followed by Tukey's honest significant difference test. Regional differences of water fluxes in the organic layer, throughfall precipitation and deposition were tested with a pairwise t-test grouped by growing season. Pearson's coefficient of correlation was used to test correlations among covariates.

Because our data represent repeated measures over time from the same plots, we used general least squares models including a first-order auto-regressive correlation structure to account for dependence among observations from the same site. Gross fluxes of TDN, NH_4^+-N, NO_3^--N and DON, and net fluxes of NH_4^+-N (absolute value) were log-transformed to obtain Gaussian distributed residuals. Model development was performed by stepwise backward selection from a beyond optimal model based on Aikaike's information criteria adjusted for small sample size (AICc) using maximum likelihood estimation. The initial models contained growing season, region, C:N of the organic layer, stand basal area (squared, for distributional reasons) as a proxy for tree biomass, the Shannon index, soil macro and meso fauna biomass, respectively, and a growing season × region interaction. Models of gross fluxes additionally included throughfall deposition (log-transformed) of the respective N form. No other interaction terms were included because coefficient estimates of interaction terms were correlated with the coefficient estimate of a main effect. We did not include estimates of microbial biomass because of collinearity with C:N ratios as indicated by a variance inflation factor ≥ 10 and the C:N ration was preferred over microbial biomass as en explanatory variable because of greater spatial and temporal representativeness. Gaussian distribution and homogeneity were inspected with the Shapiro-Wilk test, diagnostic plots and the Bartlett test (for factors), respectively. To overcome heterogeneity in the model of net DON fluxes, we performed backward selection only up to the best model (in terms of AICc) without heterogeneity. The significance of effects was tested with analysis of covariance after refitting the model with restricted maximum likelihood estimation.

To analyze the relationship between fluxes of TDN and NO_3^--N and plant diversity more closely, we re-fitted the optimal models after substitution of the Shannon index of all vascular plants by the individual Shannon index of the functional groups trees, shrubs and herbs. We further fitted models with cover values of functional plant groups instead of Shannon indexes to differentiate between biomass and diversity effects.

3.4 Results

3.4.1 Annual and regional variation of gross and net fluxes of dissolved N

Precipitation in the growing season 2010, 2011 and 2012 was 1006 mm, 803 mm and 839 mm in the Schwäbische Alb and 734 mm, 568 mm and 492 mm in Hainich-Dün, respectively. Throughfall precipitation in the growing seasons was higher in the Schwäbische Alb (552 ± SD 44 mm) than in Hainich-Dün (347 ± SD 57 mm; $P < 0.001$). Throughfall composition was similar in the Schwäbische Alb (26 ± SD 4 % NH_4^+-N, 52 ± SD 4 % NO_3^--N, 20 ± SD 1 % DON) and in Hainich-Dün (23 ± SD 9 % NH_4^+-N, 57 ± SD 12 % NO_3^--N, 20 ± SD 11 % DON). Consequently, throughfall deposition in the Schwäbische Alb exceeded that in Hainich-

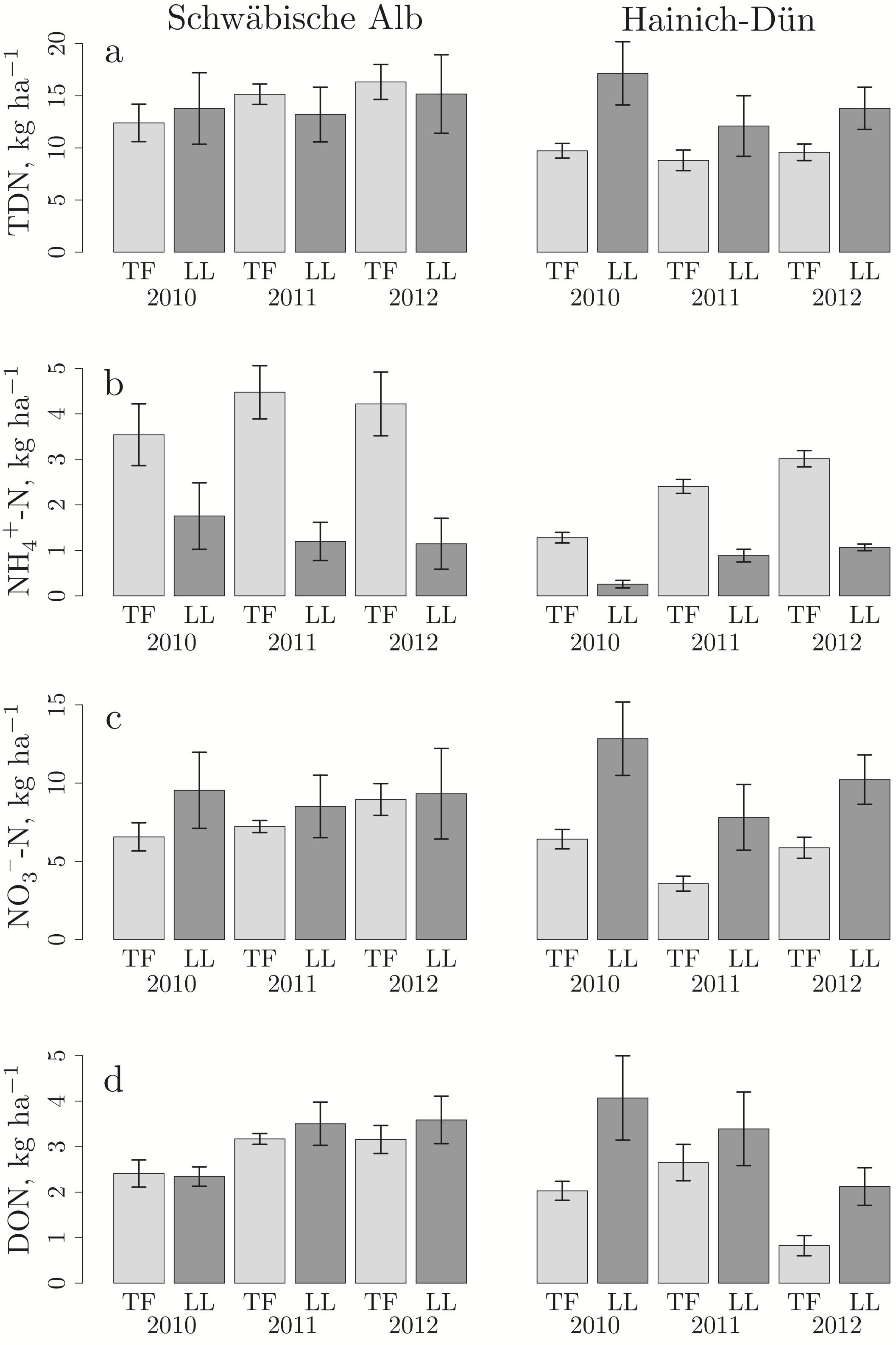

Figure 3.1: Gross fluxes of TDN (a), NH$_4$$^+$-N (b), NO$_3$$^-$-N (c), and DON (d) with throughfall (TF) and litter leachate (LL) for the growing seasons 2010, 2011, and 2012 in the Schwäbische Alb (n=6) and in Hainich-Dün (n = 6), respectively. Error bars indicate mean ± standard error.

Dün for all N forms ($P < 0.05$; Fig. 3.1). Deposition of NH_4^+-N with throughfall increased significantly in Hainich-Dün from 2010 to 2012 (Fig. 3.1b). The deposition of NO_3^--N was lower in 2011 compared with the other growing seasons in Hainich-Dün (Fig. 3.1c; $P < 0.05$), probably because of lower precipitation in 2011 compared with other seasons. In Hainich-Dün, throughfall fluxes of DON were significantly lower in the growing season 2012 compared with the other growing seasons ($P < 0.01$, log-transformed; Fig. 3.1d). There were no differences in N fluxes with throughfall among growing seasons in the Schwäbische Alb.

Gross fluxes of TDN with litter leachate were dominated by NO_3^--N in the Schwäbische Alb (61 ± SD 12 %) and in Hainich-Dün (71 ± SD 9 %). The contribution of NH_4^+-N to gross fluxes of TDN in litter leachate in the Schwäbische Alb (8 ± SD 3 %) and in Hainich-Dün (6 ± SD 4 %) was lower than in throughfall. The fraction of DON in litter leachate was only slightly greater than in throughfall and similar in both regions (Schwäbische Alb: 22 ± SD 5 %; Hainich-Dün: 22 ± SD 6 %). In contrast to throughfall deposition and despite greater water fluxes in organic layers of the Schwäbische Alb (386 ± SD 32 mm) compared with Hainich-Dün (241 ± SD 40 mm; $P < 0.001$), gross fluxes of TDN and NO_3^--N with litter leachate were similar in both regions and varied only slightly among growing seasons (Tab. 3.2, Fig. 3.1a, c). Within regions, gross NH_4^+-N and DON fluxes varied significantly within regions among the growing seasons (interaction term in Tab. 3.2). In 2010, gross NH_4^+-N fluxes were an order of magnitude lower in Hainich-Dün than in the Schwäbische Alb (Fig. 3.1b). Likewise, gross DON fluxes were lower in Hainich-Dün than in the Schwäbische Alb in 2012 (Fig. 3.1d). Gross fluxes of all dissolved N forms in litter leachate except DON were correlated with the respective throughfall deposition (Tab. 3.2, Fig. 3.2a).

Net fluxes (i.e. throughfall – litter leachate) of TDN varied among the growing seasons (Tab. 3.2) and were greater in 2010 than in 2011 and 2012 (Fig. 3.3). Intraregional variation of net TDN (Schwäbische Alb: –2.3 ± SD 4.3 kg ha^{-1}; Hainich-Dün: 5.9 ± SD 5.4 kg ha^{-1}) and net NO_3^--N fluxes (Schwäbische Alb: 0.1 ± SD 3.1 kg ha^{-1}; Hainich-Dün: 5.7 ± SD 4.0 kg ha^{-1}) was large rendering differences between regions insignificant (Tab. 3.2). In Hainich-Dün, however, net fluxes of TDN and NO_3^--N were positive in all cases indicating release from the organic layers while both positive and negative net fluxes were observed in the Schwäbische Alb (Fig. 3.3). Net fluxes of NH_4^+-N with litter leachate decreased from to 2010 to 2012 and were generally negative (Fig. 3.3) indicating retention or transformation in organic layers. The temporal trend of net NH_4^+-N fluxes (Tab. 3.2) was related to the variation in throughfall NH_4^+-N deposition (r = –0.73, $P < 0.001$). Net fluxes of NH_4^+-N and DON were lower in the Schwäbische Alb than in Hainich-Dün (Tab. 3.2, Fig. 3.3). Similar to TDN and NO_3^--N, DON was quantitatively released from all organic layers in Hainich-Dün while organic layers in the Schwäbische Alb exhibited both retention and release of DON (Fig. 3.3).

3.4.2 Factors influencing gross and net fluxes of dissolved N

Stand basal area was positively related to gross and net fluxes of both TDN and NO_3^--N (Tab. 3.2, Fig. 3.2c, d) suggesting that the source function of trees for dissolved N dominates over the sink function. Furthermore, stand basal area correlated positively with gross DON fluxes (Fig. 3.2c) but not with gross and net fluxes of NH_4^+-N (Tab. 3.2).

The Shannon index of vascular plants explained a significant fraction of the variation of gross and net fluxes of TDN and NO_3^--N in litter leachate (Tab. 3.2). Gross and net fluxes of TDN and NO_3^--N both correlated negatively with the Shannon index (Fig. 3.2e, f). The Shannon index, however, did not explain a significant part of the variation in gross and net fluxes of NH_4^+-N and DON, respectively.

Separating the Shannon index into different plant functional groups indicated that the diversity effect on gross and net fluxes of TDN and NO_3^--N was mainly attributable to the diversity of herbaceous species (Tab. 3.3). Cover values of herbs were not correlated with stand basal area ($P = 0.81$) and did not explain variation of net and gross fluxes of TDN and NO_3^--N (Tab. 3.4) suggesting that the diversity effect did not result from a diversity-biomass relationship. Cover values of trees were not correlated with stand basal area ($P = 0.79$) and explained an additional part of the variation in net fluxes of TDN and NO_3^--N (Tab. 3.4).

While the biomass of macrofauna influenced net fluxes of TDN, NO_3^--N and DON in litter leachate, mesofauna biomass explained part of the variation in both gross and net fluxes of TDN and NO_3^--N (Tab. 3.2). There was, however, no direct correlation of soil mesofauna biomass with fluxes of TDN and NO_3^--N in litter-leachate ($P >$ 0.41) but soil mesofauna influenced gross and net fluxes of TDN and NO_3^--N conditionally on other effects included in the model (Fig. 3.2g, h). Surprisingly, the C:N ratio of the organic layer was not a significant predictor of gross and net fluxes of TDN, NH_4^+-N, NO_3^--N, and DON in litter leachate, respectively. Likewise, microbial biomass was not correlated with the net and gross fluxes of dissolved N in litter leachate ($P >$ 0.29).

Table 3.2: Analysis of covariance results of optimal generalized least squares models of gross and net fluxes of total dissolved nitrogen (TDN), NH_4^+-N, NO_3^--N, and DON in litter leachate (n=36), respectively. Models include a first order correlation structure to account for correlation among multiple observations from the same plots. Gross fluxes (all N forms) and net NH_4^+-N fluxes (absolute value) were log transformed. Throughfall deposition refers to the respective N form and was not included in models of net fluxes (n.i.) because it is already accounted for in the calculation of net fluxes. Insignificant terms (n.s.) were dropped during model development, ϕ is the estimated correlation among repeated measures, asterisks depict the level of significance.

Source of variation	gross TDN		gross NH_4^+-N		gross NO_3^--N		gross DON		net TDN		net NH_4^+-N		net NO_3^--N		net DON	
	Df	*F*	Df	*F*	Df	*F*	Df	*F*	Df	*F*	Df	*F*	Df	*F*	Df	*F*
Intercept	1	3278^{***}	1	10.8^{**}	1	960^{***}	1	190^{***}	1	19.9^{***}	1	67.1^{***}	1	42.1^{***}	1	8.48^{**}
Throughfall deposition (log)	1	28^{***}	1	56.6^{***}	1	22.7^{***}		n.s.		n.i.		n.i.		n.i.		n.i.
Growing season	2	5^{*}	2	0.336	2	1.69	2	2.97	2	6.07^{**}	2	12.6^{***}		n.s.		n.s.
Region		n.s.	1	2.85		n.s.	1	0.203		n.s.	1	13.4^{***}		n.s.	1	4.61^{*}
Stand basal area^2	1	29.4^{***}		n.s.	1	12^{**}	1	13.2^{**}	1	29^{***}		n.s.	1	13.8^{***}		n.s.
Shannon index	1	12^{**}	1	2.88	1	7.4^{*}		n.s.	1	23^{***}		n.s.	1	13.7^{***}	1	2.09
Soil macrofauna	1	2.29		n.s.	1	1.01		n.s.	1	16.4^{***}		n.s.	1	4.9^{*}	1	5.4^{*}
Soil mesofauna	1	18.2^{***}	1	1.96	1	11.5^{**}		n.s.	1	37.3^{***}		n.s.	1	19.1^{***}		n.s.
Growing season × region		n.s.	2	9.12^{***}		n.s.	2	10.5^{***}		n.s.		n.s.		n.s.		n.s.
Denominator Df	28		27		28		29		29		32		31		32	
ϕ	0.293		0.318		0.366		0.548		0.099		0.396		0.15		0.362	

n.i. not included; n.s. not significant; $^{*}P < 0.05$; $^{**}P < 0.01$; $^{***}P < 0.001$

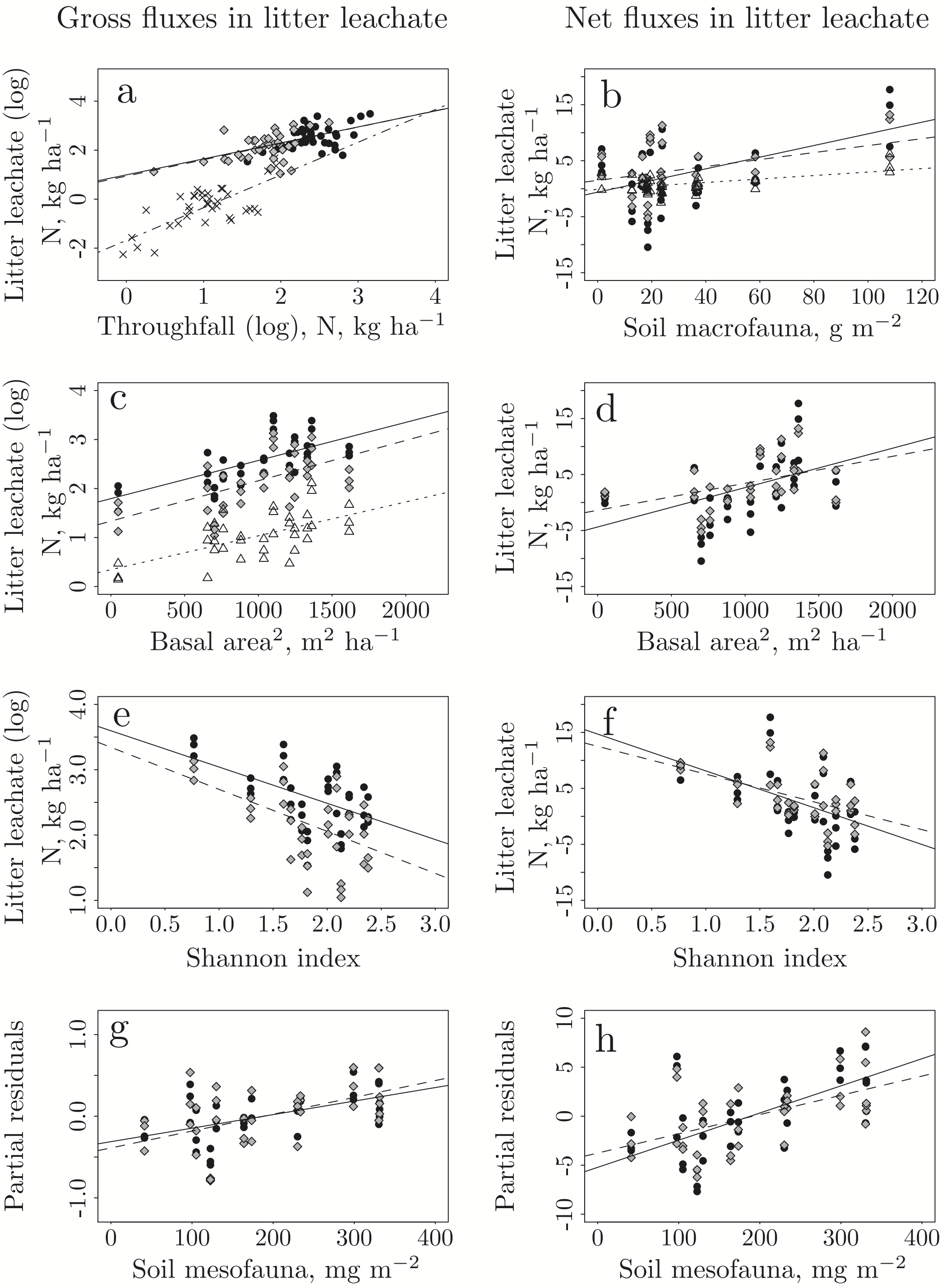

Figure 3.2: Graphical representation of significant effects on gross (left column) and net fluxes (right column) of TDN (black circles), NH_4^+-N (crosses), NO_3^--N (filled diamonds), and DON (open triangles) with litter leachate according to the optimal models as presented in Tab. 3.2. The effect of the soil mesofauna is visualized as a partial regression according to the model structure in Tab. 3.2 because of an insiginificant direct relationship. Solid (TDN), dotdashed (NH_4^+-N), dashed (NO_3^--N), and dotted (DON) lines represent regression estimates including an autoregressive correlation structure to account for dependence among multiple observations from the same site.

3.5 Discussion

3.5.1 Throughfall N retention and N release from organic layers

Net fluxes of dissolved N in the organic layers indicated both retention of throughfall derived N and net N release from soil organic matter, respectively (Fig. 3.3). The conclusion differed with the considered N form with ${NH_4}^+$-N being generally retained (by adsorption, microbial immobilization, or plant uptake) or nitrified and ${NO_3}^-$-N and DON tended to be formed and leached in organic layers (by mineralization, nitrification, and hydrolysis; Fig. 3.3). The correlation of gross fluxes of dissolved N in litter leachate with throughfall deposition suggested a partial throughflow of deposited N, especially of ${NO_3}^-$ (Tab. 3.2, Fig. 3.2a).

Although the studied organic layers did not indicate long-term accumulation of soil organic matter (i.e. formation of an Oa horizon), release of TDN (Fig. 3.3) was low representing < 10 % of the typical aboveground litterfall of 63 – 75 kg N ha^{-1} $year^{-1}$ in Central European beech forests (Khanna *et al.* 2009). Our budget is constrained to the vegetation period and thus misses processes occurring in winter. Winter accounted for 10 to 15 % of annual net nitrification and 96 % of deposited and soil produced ${NO_3}^-$ was retained in soils in a hardwood forest in New Hampshire (Judd *et al.* 2007). Likewise, net N mineralization in O horizons and litter turnover was reduced in Central European deciduous forests in winter (Hentschel *et al.* 2008; Kammer *et al.* 2012). Furthermore, microbial N immobilization is increased in autumn and winter because of greater C availability after litterfall (Kaiser *et al.* 2011), at least below snow and in phases in which the soil is not frozen which are common at the study sites in winter. Moreover, we did not quantify N transport into the mineral soil via biological mixing which is likely the dominant transport path for N into the mineral soil at our highly biologically active sites and accounts for most of the gap between quantified dissolved N exports from the organic layer and N addition by litterfall.

The C:N ratios of the studied organic layers (Tab. 3.1) did not explain a significant part of the variation in gross and net N fluxes because it was above the threshold value of 25 for which a linear relationship with N leaching was described (MacDonald *et al.* 2002). Studies simulating deposition using isotope tracers revealed that organic layers are sinks for throughfall N. In a mixed hardwood stand in Massachusetts, highest recovery of applied tracers among ecosystem pools was found

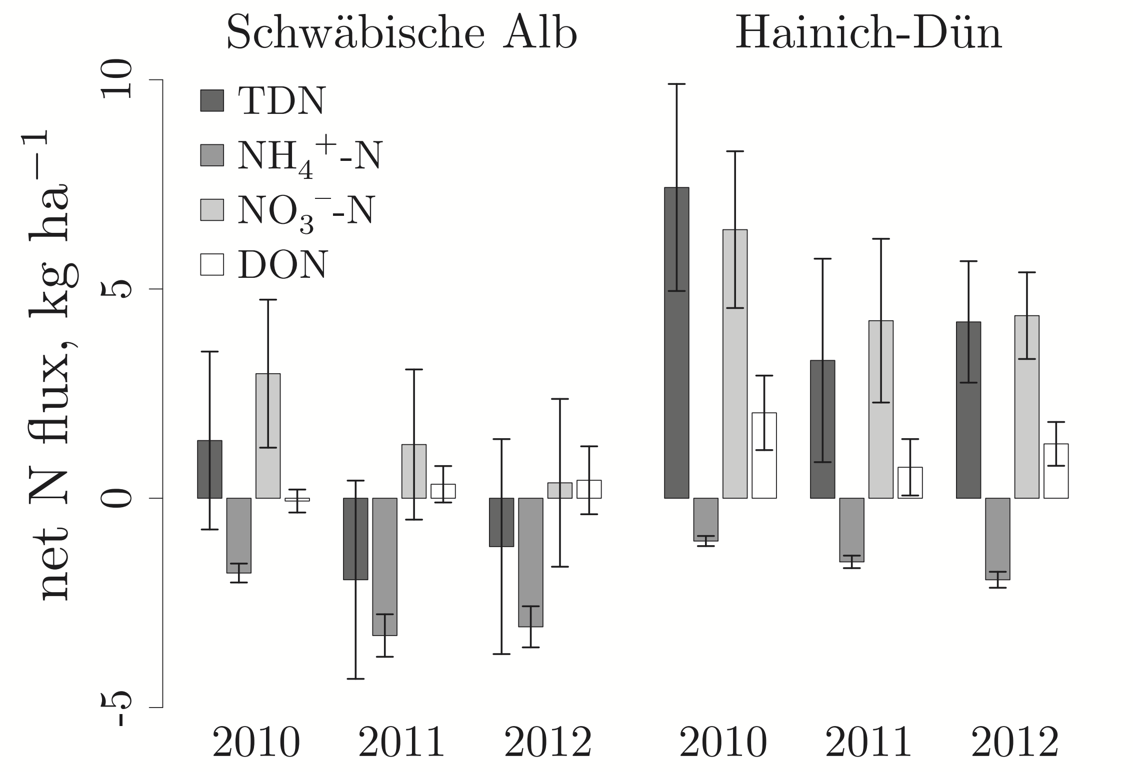

Figure 3.3: Net fluxes of TDN, NH_4^+-N, NO_3^--N, and DON through the organic layers in the growing seasons 2010, 2011, and 2012 in the Schwäbische Alb (n = 6) and Hainich-Dün (n = 6), respectively. Net fluxes were calculated as gross flux minus throughfall deposition of the respective N form and negative fluxes therefore represent retention in the organic layer. Error bars indicate mean ± standard error.

in Oi and Oa horizons (Nadelhoffer *et al.* 1999). In sugar-maple (*Acer saccharum* Marsh.) forests in Massachusetts, applied $^{15}NO_3^-$ was rapidly assimilated by the microbial community, subsequently released as NH_4^+-N, taken up by the plants, and accumulated in organic layers 6 years after the beginning of the treatment (Zak *et al.* 2008). In our study, throughfall N retention was more apparent in the Schwäbische Alb (where organic layers exhibited both release and retention of TDN and NO_3^--N) than in Hainich-Dün (Fig. 3.3a, c). This corroborates with Schwarz *et al.* (2014) who reported greater canopy N retention in the Schwäbische Alb than in Hainich-Dün and attributed this to insufficient root N uptake because of the shallow mineral soils in the Schwäbische Alb.

3.5.2 Functional relationship between plants and dissolved N fluxes

Stand basal area effect

Greater biomass (as approximated by stand basal area) coincided with greater gross and net fluxes of TDN, NO_3^--N and DON (Fig. 3.2c, d) suggesting that trees are a source for N in litter leachate but also the basis for higher growth. In contrast, stand basal area had no significant effect on fluxes of NH_4^+-N (Tab. 3.2) probably because of great immobilization and nitrification in the studied organic layers.

Trees contribute to N leaching from organic layers by providing above- and below-ground litter for soil organic matter formation and N release during decomposition. Soluble N compounds are leached from litter immediately after senescence (Berg 2000). Litterfall mass as measured from October 2013 to June 2014 correlated closely with stand basal area ($r_{Pearson} = 0.82$, $P = 0.001$) and also with gross fluxes of TDN and NO_3^--N ($r_{Pearson} = 0.62$, $P > 0.030$). Furthermore, C and N stocks in the organic layer were positively correlated with basal area ($r_{Pearson} = 0.70$ and $r_{Pearson} = 0.65$, respectively, $P < 0.05$) but including these terms did not improve the explanatory power of the models ($P > 0.2$; Likelihood Test). The slow decomposition rates of beech litter (De Vries *et al.* 2006; Vesterdal *et al.* 2008) and because fresh litter acts as a sink for N released during decomposition (Berg 2000; Gebauer *et al.* 2000; Scheu 1997) likely limited net N release.

The carbon flux associated with litterfall could also have fed back on the microbial and the decomposer community thereby affecting N fluxes indirectly (Knops *et al.* 2002). In a beech forest in Austria, C supply by litterfall increased microbial N immobilization in winter. The N stored in microbial biomass was released in the following growing season when C availability for microbes decreased (Kaiser *et al.* 2011). The authors reported that one third of annual plant N demand was resupplied by this process. However, microbial biomass was not correlated with gross and net fluxes of N in our study.

The role of the ground vegetation diversity for N fluxes

Gross and net fluxes of TDN and NO_3^--N decreased with increasing plant diversity (Fig. 3.2e, f) which indicates either a decrease in the source (i.e. N release during decomposition) or an increase in the sink function (i.e. plant N uptake) of vascular plants in diverse communities. Decreased N release during decomposition seems

Table 3.3: Analysis of covariance results of re-fitted generalized least squares models of gross and net fluxes of total dissolved nitrogen (TDN) and NO_3^--N in litter leachate (n = 36), respectively. Models correspond to the models presented in Tab. 3.2 but the Shannon index of vascular plants was substituted by the Shannon index of the functional groups trees, shrubs and herbs. Throughfall deposition refers to the respective N form and was not included in models of net fluxes (n.i.) because it is already accounted for in the calculation of net fluxes. Insignificant terms (n.s.) were dropped during original model development, ϕ is the estimated correlation among repeated measures and asterisks depict the level of significance.

Source of variation	gross TDN		gross NO_3^--N		net TDN		net NO_3^--N	
	Df	*F*	Df	*F*	Df	*F*	Df	*F*
Intercept	1	3540^{***}	1	1596^{***}	1	19.6^{***}	1	50.1^{***}
Throughfall deposition (log)	1	30^{***}	1	28.9^{***}		n.i.		n.i.
Growing season	2	5.04^{*}	2	1.96	2	6.02^{**}		n.s.
Stand basal area^2	1	31.9^{***}	1	20.9^{***}	1	28.6^{***}	1	16.5^{***}
Shannon index trees	1	2.37	1	5.01^{*}	1	8.61^{**}	1	6.98^{*}
Shannon index shrubs	1	1.3	1	0.089	1	7.72^{**}	1	2.06
Shannon index herbs	1	12.8^{**}	1	13.2^{**}	1	19.2^{***}	1	14.8^{***}
Soil macrofauna	1	1.97	1	0.221	1	10.6^{**}	1	2.23
Soil mesofauna	1	19.4^{***}	1	22.8^{***}	1	31.1^{***}	1	23^{***}
Denominator Df	26		26		27		29	
ϕ	0.266		0.165		0.103		0.068	

n.i. not included; n.s. not significant; $^{*}P < 0.05$; $^{**}P < 0.01$; $^{***}P < 0.001$

unlikely because several studies on the relationship between plant diversity and organic matter turnover reported no or a positive effect of plant diversity on N release (e.g., Blair *et al.* 1990; Wardle *et al.* 1997; Fornara *et al.* 2009; Rosenkranz *et al.* 2012). Lower dissolved N fluxes in more diverse forests could instead have resulted from increased N demand of the vegetation as related to the greater productivity of more diverse forests (Morin *et al.* 2011; Paquette and Messier 2011; Brassard *et al.* 2013). However, forest biomass consists largely of trees which had an opposing effect in our study (Fig. 3.2c, d) and cover values of herbs and shrubs, as a surrogate for understory biomass, were poorly related with dissolved N fluxes (Tab. 3.4). Fluxes of TDN and NO_3^--N with litter leachate therefore could instead have been affected by diversity effects like complementary N uptake through facilitation and functional, spatial and temporal niche partitioning. Because some herbs were smaller than the throughfall collectors, the decreasing effect of herb diversity on net TDN and NO_3^--N fluxes could also have partly been attributable to canopy uptake in herb layer.

Table 3.4: Analysis of covariance results of re-fitted generalized least squares models of gross and net fluxes of total dissolved nitrogen (TDN) and NO_3^--N in litter leachate (n = 36), respectively. Models correspond to the models presented in Tab. 3.2 but the Shannon index of vascular plants was substituted by the cover values of the functional groups trees, shrubs and herbs. Throughfall deposition refers to the respective N form and was not included in models of net fluxes (n.i.) because it is already accounted for in the calculation of net fluxes. Insignificant terms (n.s.) were dropped during original model development, ϕ is the estimated correlation among repeated measures and asterisks depict the level of significance.

Source of variation	gross TDN		gross NO_3^--N		net TDN		net NO_3^--N	
	Df	F	Df	F	Df	F	Df	F
Intercept	1	1856^{***}	1	806^{***}	1	9.53^{**}	1	23.6^{***}
Throughfall deposition (log)	1	17.6^{***}	1	21.4^{***}		n.i.		n.i.
Growing season	2	4.97^{*}	2	1.66	2	5.66^{**}		n.s.
Stand basal area^2	1	16^{***}	1	9.93^{**}	1	12^{**}	1	7.63^{**}
Cover value trees	1	2.27	1	2.94	1	6.31^{*}	1	4.66^{*}
Cover value shrubs	1	0.045	1	1.32	1	0.457	1	0.221
Cover value herbs	1	0.0139	1	0.246	1	0.0544	1	0.644
Soil macrofauna	1	0.692	1	0.3	1	2.05	1	0.571
Soil mesofauna	1	14^{***}	1	12.8^{**}	1	18.1^{***}	1	13^{**}
Denominator Df	26		26		27		29	
ϕ	0.492		0.435		0.453		0.403	

n.i. not included; n.s. not significant; $^{*}P < 0.05$; $^{**}P < 0.01$; $^{***}P < 0.001$

The N release during litter decomposition differs among functional plant groups because leaf traits like N and lignin content impact both litter decomposition and N immobilization (Wardle *et al.* 1997; Berg 2000). Functional traits other than growth form (e.g., leaf N, nitrate reductase activity) were not determined in the studied communities and could thus not be examined directly. In temperate forests, understory plants like herbs usually produce N rich litter (Schulze *et al.* 2009). While the decomposition of wild garlic increased N leaching losses from temperate forests (Jandl *et al.* 1997), beech litter instead reduced NO_3^--N leaching compared to control and nettle (*Urtica dioica* L.) litter treatments (Scheu 1997). A basic functional relationship between plant diversity and dissolved N fluxes in the studied forests could therefore reflect the buffering of N release from N-rich litter or soil organic matter by N transfer to litter with lower N content (Berg 2000; Xiong *et al.* 2014).

Despite its low biomass compared to the tree layer, the understory of temperate forests has a great nitrogen retention capacity (Schulze *et al.* 2009) and is highly efficient in taking up throughfall derived N (Gebauer *et al.* 2000). Furthermore, the understory in northern hardwood forests can act as a sink for N and reduces N leaching at the end of the dormant season when nitrification rates are high and tree demand is still low (Muller and Bormann 1976). The N release associated with the decomposition of herbaceous litter in the later growing season may have been buffered by tree uptake or immobilization in tree litter. With respect to the observed diversity effect, the 'vernal dam' hypothesis (Muller and Bormann 1976) may be translated into temporal, spatial and functional niche partitioning and facilitation. Spatial niche complementarity would most likely be related to rooting traits. In boreal forests, fine-root productivity increased with tree species evenness by more horizontal and vertical space filling in the organic layer in mixtures of deep-rooting and shallow-rooting species (Brassard *et al.* 2013). Additional functional niche partitioning would be related to the preference and ability of various plant species and their mycorrhizal associations to use different N forms. For instance, NO_3^--N leaching was negatively correlated with understory biomass in Swedish oak forests because of the high nitrate reductase activity in this stratum (Olsson and Falkengren-Grerup 2003). Our results suggest, however, that the diversity and not only biomass or the mere presence of understory plants decreases N leaching in forest soils (Tab. 3.3, Tab. 3.4). Different mycorrhizal associations of plant species (e.g., ectomycorrhiza in beech, arbuscular mycorrhiza in ash, maple, herbs and grasses) potentially further increased resource use of N in more diverse forests.

3.5.3 Effects of soil fauna on N fluxes

Soil macrofauna biomass increased gross and net fluxes of TDN, NO_3^--N and DON in litter leachate (Fig. 3.2b) likely through leaching from fecal pellets, stimulation and facilitation of mineralization, and structural changes in the organic layers induced by bioturbation. The soil macrofauna comprised mainly earthworms in this study bioturbation by earthworms likely fostered the effect of stand basal area on N release (Scheu 1987; Frouz *et al.* 2013). Furthermore, the burrowing activity of earthworms could have resulted in a higher throughflow rate of throughfall N, reducing the residence time and availability for microorganisms of throughfall N, respectively, and facilitated decomposition by increasing porosity and aeration, respectively (Curry and Schmidt 2007). In line with the observed relationship between soil macrofauna and net NO_3^--N fluxes (Tab. 3.2, Fig. 3.2b), short-term laboratory studies indicated a positive effect of earthworms on nitrification in soils treated with beech litter (Scheu 1997). While the effect diminished in mixed litter treatments (beech, nettle) because of N transfer among litter species, other studies reported increased mineralization and leaching due to mixing of soil organic matter and mineral soil (Hector *et al.* 2000; Xiong *et al.* 2014).

The subsequent decomposition of fragmented litter by soil mesofauna might have further increased N mineralization and increased the availability of litter-derived C for microorganisms (Verhoef and Brussaard 1990; Jandl *et al.* 1997; Chamberlain *et al.* 2006). The latter potentially contributes to the seasonality of microbial N dynamics in beech forests (Kaiser *et al.* 2011). In a factorial microcosm experiment, the presence of *Collembola*, the most abundant mesofauna group in our study, increased N mineralization, NO_3^- leaching and plant N uptake (Bardgett and Chan 1999). The effect of soil mesofauna on dissolved N fluxes in litter leachate was only significant conditional on other covariates (Fig. 3.2g, h) suggesting an indirect relationship, possibly because of trophic interactions. In addition, *Collembola* grazing on fungi (Pollierer *et al.* 2007) could have decreased fungal N immobilization or stimulated mineralization of N-rich fungal biomass after digestion and excretion. However, our results suggest that soil mesofauna biomass is an important control for plant N availability in studied forests where net N mineralization is assumed to be low.

3.6 Conclusions

- Strong NH_4^+-N retention, small NO_3^--N and DON release from organic layers in beech forests on calcareous soil probably because of high microbial N immobilization at a high C:N ratio.
- Dissolved N release from organic layers increased with forest basal area probably because of greater litterfall and resource availability.
- N leaching increased with soil fauna biomass possibly by stimulation and facilitation of mineralization.
- N leaching decreased with increasing plant diversity either because of decreasing N release during decomposition or through complementary N use particularly in the understory.

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Chapter 4

Abiotic and biotic controls of the dissolved P cycle in Central European beech forests

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4.1 Abstract

Phosphorus (P) is expected to become an increasingly limiting resource in Central European forests because of global change. We studied the cycling of P by determining fluxes of P with rainfall, throughfall and litter leachate in 12 in European beech forests in two regions in Germany. Atmospheric inputs of reactive P (i.e. to Central European beech forests were < 0.03 kg ha^{-1} (growing season)$^{-1}$ and concentrations of reactive P in mineral soil solution 6 ± standard deviation 4 μg L^{-1} indicating low leaching losses and limited P availability. Foliar leaching was the most important source of dissolved P in the studied forests (0.16 – 1.86 kg ha^{-1} (growing season)$^{-1}$) and correlated with the foliar P stock and the NaOH-extractable P concentration in the mineral topsoil. A net release of P from the organic layer occurred at only two sites and the reactive P flux with litter leachate (0.12 – 2.28 kg ha^{-1})growing season)$^{-1}$) correlated with the NaOH-extractable P fraction suggesting P retention in the mineral soil. Canopy P leaching was restricted to the foliated period of the year and decreased before senescence indicating P resorption. Canopy P losses were greatest in years with a remarkable deficit in spring precipitation highlighting the susceptibility of P recycling to water stress in beech forests on calcareous soils. Throughfall fluxes of reactive P and the foliar carbon to phosphorus ratio were correlated with the diversity of ectomycorrhiza suggesting that P nutrition is improved by diverse fungal communities.

4.2 Introduction

Phosphorus (P) limits biomass productivity in many ecosystems (Elser *et al.* 2007). Temperate forests usually have negligible external P sources and the plant P supply depends mainly on slow mineral weathering, i.e. dissolution of primary and secondary phosphate salts and mineralization of soil organic matter (Wood *et al.* 1984; Attiwill and Adams 1993; Yanai 1992). The P cycle of temperate forests is assumed to be almost closed because losses of P by leaching and erosion are small compared with P pools (Attiwill and Adams 1993). Thus, the bioavailable ecosystem P is cycled with water fluxes such as throughfall, stemflow, and organic layer leachate between the vegetation and the soil in an almost closed loop. Variations in these fluxes among regions and in time are indicative of the P nutritional status of a forest ecosystem and determining abiotic and biotic controls of these fluxes is essential to predict the response and elasticity of forest functioning to changing environmental conditions and to progressive impoverishment of available P in soil (Walker and Syers 1976; Cross and Schlesinger 1995).

Concentrations of directly plant-available orthophosphate ($H_2PO_4{}^{-}$-P and $HPO_4{}^{2-}$-P) in soil solution are usually low because of the limited solubility of phosphate-containing minerals at both high and low pH. In Central Europe, this is especially true for forests on calcareous soils because orthophosphate is precipitated as amorphous apatite ($Ca_{10}[PO_4]_6[F,Cl,OH]_2$) in the presence of high calcium (Ca) concentrations. Trees loose P through litterfall and leaching from tissues and these losses can escape rapid recycling when trapped in recalcitrant P forms in the soil. Temperate deciduous tree species hence reduce the P loss associated with litterfall by P resorption (Aerts 1996). Additionally, plants have developed strategies to gain access to recalcitrant organic and inorganic P sources via rhizosphere acidification, exudation of extracellular enzymes (e.g., phosphatases), and mutualistic associations with mycorrhizal fungi (Wallander 2000; Blum *et al.* 2002; Lambers *et al.* 2008). Baxter and Dighton (2001) showed that increased P uptake of *Betula populifolia* Marshall seedlings was more affected by ectomycorrhizal fungal diversity than by composition and colonization rate. The roots of European beech (*Fagus Sylvatica* L.) are almost fully colonized by a highly diverse and exclusively ectomycorrhizal community (Lang *et al.* 2011) suggesting a great dependence of P nutrition on mutualistic associations (Smith 2003; van Schöll *et al.* 2008) as well as potential benefits for P resource exploitation through complementary ectomycorrhiza traits in P acquisition and transfer to host plants (Buscot *et al.* 2000).

Climate change and nitrogen (N) deposition are assumed to increase P limitation of forest ecosystems in the future due to their effects on physiological tree performance, litter decomposition and mineralization as a consequence of stochiometric imbalances (Gessler *et al.* 2004; Bréda *et al.* 2006; Vitousek *et al.* 2010). Although evidence for a shift from N to P limitation of temperate forests is contradictory (Finzi 2009; Weand *et al.* 2009; Marklein and Houlton 2012), decreasing trends of foliar P concentrations in European beech forests suggest that P supply rates do not keep pace with the enhanced biomass production (Duquesnay *et al.* 2000; Pretzsch *et al.* 2014). Additionally, the frequency, intensity and duration of water stress during the growing season is expected to increase in the Northern temperate region (IPCC 2014) and thus will challenge the functioning of temperate forests dominated by European beech because of its sensitivity to drought (Ellenberg 1996). The published studies on nutrient cycling in beech forests do not yet reveal a predictable response (Kreuzwieser and Gessler 2010) but indicate a great susceptibility of P status to drought (Peuke and Rennenberg 2004). A disturbance of P cycling associated with global change may be amplified in forests on shallow soils with low water storage capacity developed on permeable limestone by the limited P availability.

We used the seasonal and regional variation of the dissolved P fluxes in beech stands on calcareous soils along a gradient from high (Schwäbische Alb, 1000 mm) to intermediate precipitation (Hainich-Dün, 650 mm), to infer responses of the forest P cycle to climate change and elucidate the controls of P cycling. We investigated water-bound fluxes of P with rainfall, throughfall and through the organic layer in 12 beech-dominated forests over three growing seasons (2010 – 2012), foliar P stocks, soil P fractions, and ectomycorrhizal fungal diversity. We hypothesized that (i) the canopy and the organic layer are sources of dissolved P and P availability in the mineral soil is low because of fast recycling of P from the organic layer to the plants and geochemical P fixation, (ii) P fluxes with throughfall and litter leachate are modified by weather conditions (particularly strong rainfall and drought), and (iii) canopy leaching of P is controlled by the P stock in foliage, the size of the bioavailable P Pool in the mineral soil and by ectomycorrhizal fungal diversity which facilitates the use of little soluble P resources.

4.3 Materials and methods

4.3.1 Study site

This study was conducted in the Schwäbische Alb (48° 24′ N, 9° 24′ E; 740 – 788 m a. s. l.) and the Hainich-Dün area (51° 10′ N, 10° 23′ E, 333 – 491 m a. s. l.) in Germany. The two study regions are located on limestone (Jurassic [Malm] in the Schwäbische Alb and Triassic [Muschelkalk] with loess cover in Hainich-Dün). Tab. 4.1 summarizes climate and soil types. We investigated 6 forest plots (100 m × 100 m) dominated by European beech (i.e. $>$ 70 % of stand basal area) in each region. Further tree species comprised sycamore maple (*Acer pseudoplatanus* L.), hornbeam (*Carpinus betulus* L.), and European ash (*Fraxinus excelsior* L.). Additionally, few Norway spruce (*Picea abies* (L.) H. Karst) trees were present in some forests in the Schwäbische Alb. The organic layers consist of Oi and Oe horizons and thus are of a mull humus form, except in one forest stand (AEW8) where a thin discontinuous Oa horizon was detected. Total N deposition to the forests from April to November 2010 was 15 kg ha^{-1} in the Schwäbische Alb and 13 kg ha^{-1} in Hainich-Dün (Schwarz *et al.* 2014).

Table 4.1: Site characteristics of the studied regions and forests. Soil classification according to IUSS Working group WRB 2006. Total P concentrations and pH values refer to the A horizon, foliar C:P ratios (mass) and foliar P refer to beech leaves. Stand basal area was registered by forest inventories of the whole plot area (1 ha, caliper limit > 7 cm) except for the thicket beech stand HEW4, where basal area was estimated. Foliar biomass was estimated from litterfall measurements.

Region	Bedrock	Plot ID	Soil type	pH	Total P	Basal area	Foliar biomass	Foliar	Foliar P
					[g kg^{-1}]	[m^2 ha^{-1}]	[Mg ha^{-1}]	C:P	[g kg^{-1}]
Schwäbische Alb	jurassic	AEW4	Cambisol	6.4	1.26	29.7	3.7	472	1.00
	limestone	AEW5	Cambisol	4.5	0.60	27.6	4.7	710	0.67
		AEW6	Cambisol	5.4	0.53	26.5	5.0	561	0.84
		AEW7	Leptosol	4.9	0.77	33.2	6.3	672	0.71
		AEW8	Cambisol	5.1	0.56	40.2	5.5	628	0.74
		AEW9	Leptosol	6.4	0.54	32.2	5.4	576	0.83
Hainich-Dün	Triassic	HEW4	Luvisol	6.2	0.54	7	2.5	543	0.88
	limestone /	HEW5	Luvisol	4.8	0.51	25.6	4.9	818	0.59
	loess	HEW6	Luvisol	4.2	0.49	35.3	5.8	589	0.81
		HEW10	Stagnosol	4.8	0.71	34.8	7.2	672	0.71
		HEW11	Luvisol	4.8	0.68	36.9	6.4	570	0.83
		HEW12	Luvisol	3.9	0.36	36.5	6.2	655	0.73

4.3.2 Sampling and chemical analysis

Water-bound fluxes

Samples of rainfall, throughfall, litter leachate and mineral soil solution were collected cumulatively every 14 days between 2010 and 2012. Because of frost, inaccessibility of the plots or staff illness one sampling campaign in the Schwäbische Alb and eight sampling campaigns in Hainich-Dün lasted 28 days. Sampling started each year when daily average temperature exceeded 0°C, so that water samples could be collected in liquid state, and lasted until the onset of winter. We considered this sampling period as the growing season (GS) which varied slightly in length by region and year (Tab. 4.2). In 2010, stemflow was also sampled using three collar-type collectors. However, data from that growing season revealed a small contribution of stemflow to the water cycle at the stand scale (3 % of precipitation).

In each forest, throughfall was sampled with 20 funnel-type collectors (diameter of 0.12 m; polyethylene) in a subplot (20 m × 20 m) 0.3 m above the soil surface. To prevent growth of algae and photochemical reactions, throughfall collectors were wrapped with aluminum (Al) foil. Funnels were equipped with a 1.6 mm polyester

Table 4.2: Growing seasons (GS), leaf development and coloring dates, annual precipitation, precipitation and throughfall (standard deviation in parenthesis, n = 6) during the growing season in the Schwäbische Alb and Hainich-Dün for the years 2010, 2011 and 2012. Phenology data was obtained for the nearest stations from the Pan European Phenology Database (www.pep725.eu). Precipitation was calculated as mean of two nearby stations per region of the German Weather Service.

Region	Year	Growing season	Leaf development	Leaf coloring	Annual precipitation	Precipitation GS^{-1}	Throughfall GS^{-1}
Schwäbische Alb	2010	03 Mar – 23 Nov	04 May	7 Oct	1107	827	585 (36)
	2011	02 Mar – 06 Dec	22 Apr	13 Oct	886	665	510 (32)
	2012	29 Feb – 06 Nov	08 May	7 Oct	1021	689	521 (31)
Hainich-Dün	2010	31 Mar – 09 Nov	29 Apr	17 Oct	725	447	408 (40)
	2011	16 Mar – 06 Dec	20 Apr	22 Oct	526	382	315 (40)
	2012	14 Mar – 06 Nov	29 Apr	18 Oct	672	437	349 (29)

mesh and a table-tennis ball to prevent contamination with coarse particulate matter and to minimize evaporation, respectively. Litter leachate was sampled with three circular zero-tension lysimeters (diameter of 0.2 m; polyvinyl chloride) per site which were installed horizontally below the soil organic layer in summer 2009. The lysimeters were connected to polyethylene sampling bottles with polyethylene hoses. The sampling bottles were stored in the dark below ground. Rainfall was sampled at 9 grassland sites distributed throughout the research areas using 5 samplers per site. The construction of rainfall samplers was similar to throughfall samplers and collected bulk deposition because they were continuously open. Regional precipitation was calculated as the mean of data from two nearby stations of the German Weather Service (DWD, Offenbach, Germany; Schwäbische Alb: Sonnenbühl-Genkingen, Münsingen-Apfelstetten; Hainich-Dün: Leinefelde, Mühlhausen-Windeberg). In each forest, mineral soil solution was sampled with 3 suction cups (0.45 μm pore width, polyamide membrane and polyethylene body, ecoTech Umwelt-Messsysteme GmbH, Bonn, Germany) at 0.2 m depth of the mineral soil in the Schwäbische Alb and at 0.15 m depth in Hainich-Dün. Suction cups were connected to polypropylene bottles with a polytetrafluorethane tubing. Vacuum was set to approximately 500 mbar after sampling and dropped only little during the sampling interval. However, during large parts of the growing seasons, no samples of mineral soil solution could be collected because of drought.

The volume of sample in each collector was measured and a volume-weighted aliquot of each sample type per plot was created in the field. Immediately after sampling, pH was measured in an subsample with a pH electrode (Sentix 41, WTW GmbH, Weilheim, Germany) and another subsample was filtered through pre-rinsed (at least 0.05 L distilled water and 0.05 L sample) folded paper filters (5 – 8 μm, 292, Munktell & Filtrak, Bärenstein, Germany, and Sartorius, Göttingen, Germany) and frozen within 48 hours after sampling. Samples were stored at –18°C until chemical analysis. Soil moisture was measured 0.1 m below the surface with a time-domain reflectometry probe (DeltaT ML2X, DeltaT Devices Ltd, Cambridge, UK) connected to a datalogger (ADL-MX, Meier-NT GmbH, Zwönitz, Germany) at a temporal resolution of 1 hour and were aggregated to daily means.

Concentrations of orthophosphate were determined photometrically with a continuous flow analyzer (CFA; AutoAnalyzer 3, Seal Analytical GmbH, Norderstedt, Germany) according to Murphy and Riley (1962). Denison *et al.* (1998) showed that inorganic P is overestimated by this method because of a PO_4^{3-} release due to the hydrolysis of labile organic sugars in the acidic reaction environment when samples had been stored for $>$ 72 hours. Since the sampling interval was beyond this critical storage time, we regard this fraction as reactive P comprising inorganic and labile organic P (which is probably bioavailable). Total dissolved phosphorous (TDP) concentrations were determined as orthophosphate after $K_2S_2O_8$-UV digestion with CFA. The limit of detection (LOD) was 6 μg L^{-1} and 9 μg L^{-1} for reactive P and TDP, respectively, and concentrations below the LOD were adjusted to half the LOD. Dissolved organic P (DOP) was calculated as the difference of TDP and reactive P concentrations, however, we acknowledge that DOP in this study reflects only a residual dissolved organic P fraction. Because of measurements close to the LOD, few negative DOP concentrations were calculated (8 % of throughfall and litter leachate samples). In such cases, TDP was adjusted to equal reactive P and DOP concentrations were set to zero. Chloride (Cl^-; LOD: 46 μg L^{-1}) concentrations were determined with an ion-specific electrode (Orion 9417BN, Thermo Scientific, Nijkerk, The Netherlands).

Site properties

The A horizon of the mineral soil was sampled in spring 2008 with a soil corer (diameter of 55 mm) in 5 replicates per forest stand. Immediately after sampling, a composite subsample (free of roots) was frozen and stored at –20°C to analyze fungal community composition using Internal Transcribed Spacer (ITS) rDNA pyrotag sequencing (methodological details on DNA extraction, amplicon library preparation and amplicon sequencing using the 454 GS FLX genome sequencer, and extraction of the ectomycorrhizal fungal groups are described in Wubet *et al.* 2012). The Shannon diversity index of ectomycorrhiza species was calculated using the sequence relative abundance as the abundance measure. Air-dried and sieved (< 2 mm) composite subsample was used to determine P concentration and partitioning among Hedley P fractions in soil (Hedley *et al.* 1982; Alt *et al.* 2011). Briefly, soil samples were sequentially extracted with $NaHCO_3$, NaOH, HCl, and H_2SO_4 and the extracts were analyzed with CFA for organic P (only $NaHCO_3$ and NaOH fractions) and inorganic P (see further details in Alt *et al.* 2011).

The dates of leaf unfolding and coloring were obtained from the Pan European Phenology Database (www.pep725.eu) for the nearest stations in the Schwäbische Alb (Genkingen, 48° 24′ N, 9° 12′ E, 800 m a. s. l.) and in Hainich-Dün (Mühlhausen, 51° 12′ N, 10° 28′ E, 230 m a. s. l.). Leaves of mature beech trees were sampled between June 25 and August 20, 2009 from the sun-exposed part of the upper canopy with a crossbow. Of each of five trees per plot one branch with 50 leaves was harvested (details of the sampling technique are given in Gossner *et al.* 2014). Composite leaf samples of each plot were dried at 70°C and milled with a swing mill (MM300, Retsch, Haan, Germany). Subsequently, 5 mg of each sample were analyzed for carbon (C) concentrations with an elemental analyzer (Vario EL, Elementar GmbH, Hanau, Germany) and for P concentrations after HNO_3 digestion with CFA. To estimate foliar biomass, litterfall was sampled from September 24, 2013 to June 03, 2014 in the Schwäbische Alb and from October 09, 2013 to June 17, 2014 in Hainich-Dün in 2-week intervals in autumn, cumulatively over the winter season, and in 4-week intervals in spring with 5 litterfall traps (area of 0.25 m^2) per plot. Subsamples of litterfall per plot and date were combined and branches > 20 mm were removed. Litterfall mass was determined after drying at 60°C, summed over the sampling period and multiplied with the P concentration in leaves to give an estimate of the P stock in foliage.

4.3.3 Calculations

Because of inaccessibility of the plots, few fluxes of throughfall and litter leachate were missing and were substituted by the average throughfall flux in the respective region and sampling period (Schwäbische Alb: 1 % of data; Hainich-Dün: 4 % of data). Water fluxes through organic layers cannot be inferred directly from the collected water amount by zero-tension lysimeters because of the interface effect (i.e. the artificial barrier prevents water drainage until water saturation of the organic layer is reached). We used a two-step Cl^- balance approach of throughfall and litter leachate to estimate water fluxes through the organic layer according to Equation 4.1.

$$q_{LL}[mm] = q_{TF}[mm] \times \frac{Cl^{-}_{TF}}{Cl^{-}_{LL}}, \tag{4.1}$$

where q_{LL} is the water flux through the organic layer, q_{TF} is the throughfall precipitation, Cl^{-}_{TF} and Cl^{-}_{LL} is the Cl^{-} concentration in throughfall and litter leachate, respectively. We then calculated a linear regression function of throughfall precipitation on water leaching through the organic layer for all available samples to infer water fluxes through the organic layer directly from throughfall precipitation (R^2 = 0.46). For this calculation, we excluded low and high precipitation sampling periods (5 mm $(14 \text{ days})^{-1}$ < throughfall < 80 mm $(14 \text{ days})^{-1}$ representing 6 % of available cases) to minimize Cl^{-} imbalances because of transient retention of Cl^{-} and insufficient drainage of the lysimeters. The linear regression revealed an interception of 1.03 mm and an average fractional water loss of throughfall precipitation due to evapotranspiration in the organic layer of 27 % on a 14 days basis. These estimates are similar to values of interception and evapotranspiration in organic layers under European beech in Luxembourg (Gerrits *et al.* 2010).

Fluxes of P were calculated by multiplying water flux and reactive P, TDP and DOP concentration, respectively, and were summed for the growing season. Missing concentrations of P species in throughfall and litter leachate because of insufficient sample amount for analysis were substituted by the volumetric mean concentration per sample type and plot. To obtain an equally spaced time series for the analysis of seasonality, fluxes with throughfall which referred to 28 days were split into two 14-day intervals weighted by the corresponding regional precipitation.

Because of the great proportion of measurements below the LOD and the susceptibility to contamination in rainfall, the median of reactive P concentrations of each sampling campaign was used to calculate the region-specific bulk P deposition. We removed two rainfall samples from the data that deviated by a factor of > 10 in reactive P concentrations from available replicates. We did not calculate leaching fluxes of P in mineral soil because for some forest sites only few samples of soil solution were available which were restricted to early spring. Because of the uncertainty caused by the low concentrations near or below LOD and the small sample size, we used median concentrations of reactive P in soil solution per plot to calculate regional means as a qualitative estimate of P leaching.

4.3.4 Statistics

Statistical analysis was performed with R 3.1 (R Core Team 2014). Fluxes of P with throughfall and litter leachate were $\log_{10}$-transformed prior to statistical analysis. Figures and averages are presented in original scale and means and standard deviations thus refer to geometric means (μ_g) and geometric standard deviations (σ_g), respectively. No transformation of bulk deposition flux and mineral soil solution concentrations was necessary and these data are reported as arithmetic means with standard deviations (SD). Differences in throughfall and litter leachate P fluxes between regions and among growing seasons were investigated with linear mixed effects models (LME) from the package nlme (Pinheiro *et al.* 2014) with a random plot effect to account for repeated measures from the same forest. Gaussian distribution of residuals and homogeneity of variances were inspected visually using diagnostic plots. The significance of differences was determined with sequential ANOVA (Type I; F-test). The significance of differences among individual growing seasons was further investigated with general linear hypothesis testing including a sandwich estimator using Tukey's contrasts of the LME with the package multcomp (Hothorn *et al.* 2008) to adjust P-values for multiple testing. Because most environmental properties were not repeatedly measured and would thus be redundant to the random plot effect, we used ordinary least squares regression analysis and correlation analysis of potential environmental controls on log-transformed geometric plot means to describe reactive P flux response to environmental conditions instead of including the covariates in the LME. Whenever linear model assumptions were violated, we used non-parameteric Spearman correlation ($\mathrm{r}_{Spearman}$) instead of the Pearson's coefficient of correlation ($\mathrm{r}_{Pearson}$). However, in some cases dislocated growing season fluxes were excluded to hold the assumptions of linear regression but qualitative explanation for the deviation from the remaining sample will be provided in such cases. Generalized additive models (Wood 2006) were used as an exploratory method of the temporal course of throughfall reactive P fluxes using a smooth term for the day of the year. Cubic regression spline with shrinkage was used as smoothing technique and smoothing parameters were estimated with generalized cross-validation. To this end, we centered single-event log-scaled throughfall fluxes by plot to remove the offset induced by different scales of fluxes and set up individual models for each region × growing season combination because of different sampling periods (Tab. 4.2).

4.4 Results

4.4.1 Dissolved P fluxes in beech forests

Bulk deposition of reactive P was 0.027 ± SD 0.005 kg ha^{-1} GS^{-1} in the Schwäbische Alb and 0.016 ± SD 0.004 kg ha^{-1} GS^{-1} in Hainich-Dün. Because reactive P in rainfall was only detectable in 10 % of the sampling campaigns, our estimation of bulk deposition has a high uncertainty and tends to be too high. Surplus deposition of DOP was primarily resulting from the difference of the LOD of TDP compared to reactive P and could thus not be reasonably estimated.

Reactive P contributed 84 ± SD 8 % to TDP throughfall fluxes. Because of the great intra-regional variation, throughfall fluxes of reactive P did not differ between the Schwäbische Alb (0.55 kg ha^{-1} GS^{-1}, $\sigma_g = 2.01$) and Hainich-Dün (0.36 kg ha^{-1} GS^{-1}, $\sigma_g = 1.91$; $P = 0.312$). A particularly great throughfall flux of reactive P was consistently measured in the forest stand AEW4 (1.88 kg ha^{-1} GS^{-1}, $\sigma_g = 1.05$; Fig. 4.1). Excluding this site from the data reduced the reactive P throughfall flux in the Schwäbische Alb to 0.43 kg ha^{-1} GS^{-1} ($\sigma_g = 1.47$) and marginalized regional differences further ($P = 0.628$). Unlike reactive P, throughfall DOP fluxes varied little within regions and were significantly greater in the Schwäbische Alb (0.09 kg ha^{-1} GS^{-1}, $\sigma_g = 1.1$) than in Hainich-Dün (0.04 kg ha^{-1} GS^{-1}, $\sigma_g = 1.16$; $P = 0.001$).

Reactive P comprised 79 ± SD 18 % of TDP in litter leachate in the Schwäbische Alb and 93 ± SD 4 % of TDP in Hainich-Dün. The fluxes of reactive P with litter leachate were similar in the Schwäbische Alb (0.51 kg ha^{-1} GS^{-1}, $\sigma_g = 2.91$) and Hainich-Dün (0.55 kg ha^{-1} GS^{-1}, $\sigma_g = 2.71$; $P = 0.911$). A comparison of litter leachate with throughfall fluxes indicated an enrichment in reactive P during the passage through the organic layer in Hainich-Dün. The large intra-regional variation in reactive P fluxes resulted from a great release of reactive P in organic layers of the forest stands AEW7 and HEW11, respectively, while reactive P fluxes changed little from throughfall to litter leachate in the other studied forest stands (Fig. 4.1). The change in DOP flux from throughfall to litter leachate ranged -0.06 to 0.12 kg ha^{-1} GS^{-1}.

Concentrations of reactive P in mineral soil solution were below the LOD in 53 % of the available samples (n = 278) and averaged 4.5 ± SD 2.5 μg L^{-1} for sites in the Schwäbische Alb and 7.5 ± SD 5.4 μg L^{-1} for Hainich-Dün sites. An even greater

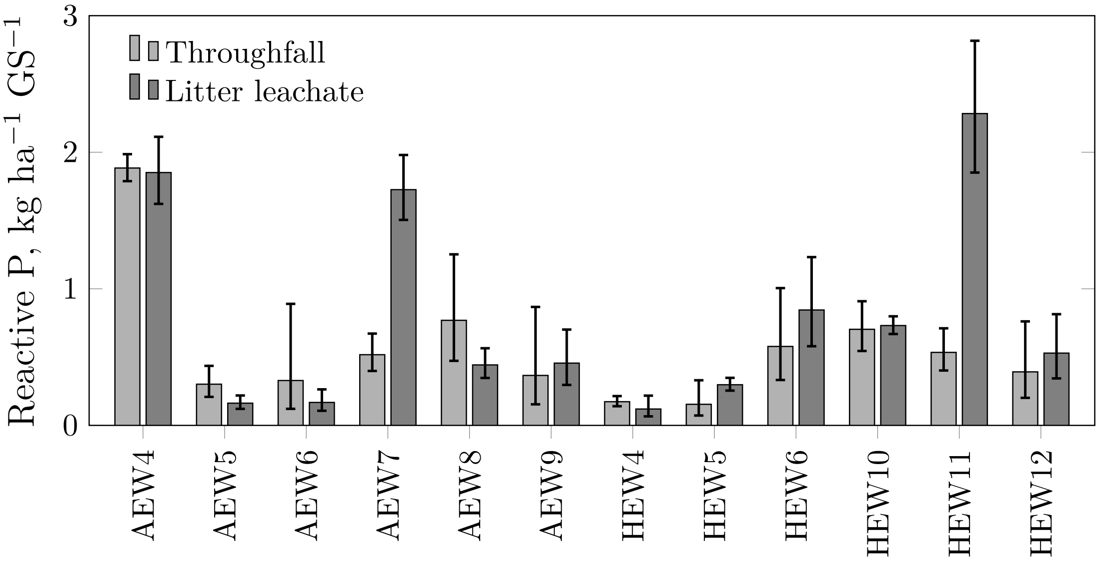

Figure 4.1: Fluxes of reactive P (i.e. phosphate-P + easily hydrolyzed organic P) with throughfall and litter leachate at six study sites in each of the Schwäbische Alb (AEW#) and Hainich-Dün (HEW#) in the growing seasons (GS) 2010, 2011, and 2012 (see Tab. 4.2 for the precise periods). Bars are geometric means, errors reflect the antilog of mean ± standard deviation on the log scale.

fraction of samples was below the LOD of TDP (65 %) and resulting in mean concentrations of 9.1 ± SD 1.2 μg L^{-1} in the Schwäbische Alb and 8.2 ± SD 4.9 μg L^{-1} in Hainich-Dün. Similar to rainfall, the differences between reactive P and TDP were strongly biased by the different LODs of the analytical methods. Concentrations of dissolved P species in mineral soil solution were especially uncertain for the Hainich-Dün region because of the small sample size ($n = 53$) due to the challenge of abstracting soil water under limited rainfall and the resulting drier soil conditions. In the Schwäbische Alb, gaps of the soil solution data were less common and revealed no temporal variation of concentrations, however, some randomly distributed high concentrations occurred (data not shown).

4.4.2 Reactive P fluxes as related to weather conditions

Annual precipitation as well as precipitation and throughfall precipitation during the GS were lowest in 2011 (Tab. 4.2). Precipitation in the observation period exhibited a more pronounced temporal variation than the long-term average (Fig. 4.2). Especially, the period from February to May 2011 was drier than average years with monthly precipitation close to the 10th percentile of the normal period (1961 – 1990). Above average precipitation in December and January as well as rainstorms

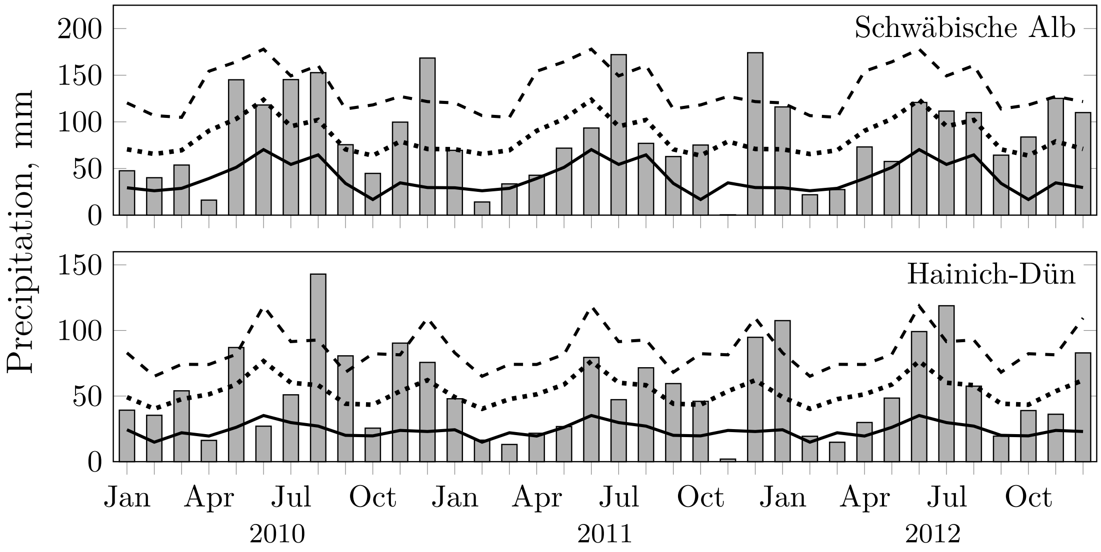

Figure 4.2: Regional mean monthly precipitation in the years 2010, 2011 and 2012 (bars) and mean (dotted line), 10th (solid line) and 90th percentile (dashed lines) of precipitation during the normal period (1961 – 1990) at two nearby meteorological stations of the German Weather Service in the Schwäbische Alb and Hainich-Dün (data from only one station was available for the period 1961 – 1969), respectively.

in summer compensated partly for dry spells on an annual scale (Fig. 4.2). Soil water content decreased after leaf unfolding and with the onset of transpiration (cf. Fig. 4.4). Low precipitation in the first half of 2011 led to an early decrease in soil moisture and prolonged period of soil drought in 2011 in Hainich-Dün while the soil in the Schwäbische Alb was intermittently re-wetted in 2011.

Throughfall fluxes of reactive P were lower in 2010 than in 2011 and 2012 ($P < 0.001$; Fig. 4.3). This inter-annual difference was consistent irrespective whether the forest stand AEW4 was excluded from the data or not. Throughfall fluxes of DOP were greater in 2011 than in 2010 and 2012 ($P < 0.002$). Reactive P fluxes with litter leachate were only greater in 2012 than in 2010 ($P = 0.018$; Fig. 4.3). On the contrary, DOP fluxes with litter leachate were only marginally greater in 2011 than in 2010 ($P = 0.058$).

Fluxes of reactive P with throughfall varied widely within the GS and exhibited a strong seasonality (Fig. 4.4). Fluxes of reactive P with throughfall were low in March and early April and increased after leaf unfolding and thus with canopy development (Fig. 4.4). Canopy leaching of reactive P peaked in the mid of the GS and decreased from end of August towards the end of the GS (Fig. 4.4). An additional flush of reactive P with throughfall occurred in late autumn of 2012 in the Schwäbische Alb and in autumn 2010 and 2011 in Hainich-Dün (Fig. 4.4). Autumnal canopy leaching of reactive P accounted for most of the throughfall fluxes at the P-richest forest stand AEW4 (Fig. 4.5).

The seasonal pattern of throughfall fluxes of reactive P varied among years and regions. In 2012, the temporal course of throughfall fluxes of reactive P roughly followed the distribution of precipitation. However, in the other years the peak of the reactive P flux did not necessarily coincide with high precipitation, although great throughfall fluxes were associated with high precipitation after periods of reduced soil water content (e.g., Hainich-Dün 2010, Schwäbische Alb 2010; Fig. 4.4). Especially in the early GS, the temporal course of throughfall reactive P fluxes was clearly distinct from that of precipitation (e.g., Schwäbische Alb 2010 and 2011, Hainich-Dün 2010) while low precipitation restricted throughfall fluxes in autumn (Fig. 4.4). The greatest intra-seasonal fluxes occurred in 2011 during low to intermediate precipitation. This was especially pronounced for forests in the Schwäbische Alb (all forest stands except AEW4), where the the greatest reactive P flux occurred briefly after leaf unfolding and coincided with a an early drop of soil water content (Fig. 4.5). In Hainich-Dün, precipitation around the date of leaf unfolding was probably too low to result in similar throughfall fluxes of reactive P. Because litter leachate fluxes of reactive P mainly resembled throughfall fluxes (see previous section), seasonal patterns were similar (Fig. 4.6).

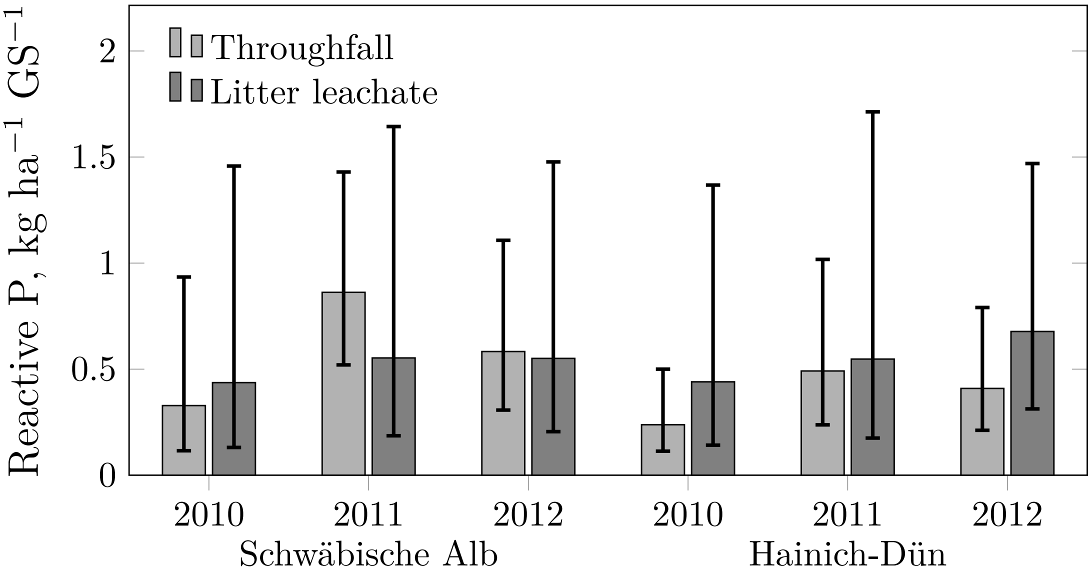

Figure 4.3: Fluxes of reactive P (i.e. phosphate-P + easily hydrolyzed P) with throughfall and litter leachate in the Schwäbische Alb (n = 6) and Hainich-Dün (n = 6) in the growing seasons (GS) 2010, 2011, and 2012 (see Tab. 4.2 for the precise periods). Bars are geometric means, errors reflect the antilog of mean ± standard deviation on the log scale.

4.4.3 Other controls of reactive P fluxes

Growing season throughfall fluxes of reactive P were correlated with the P stock in foliage and the Shannon diversity index of ectomycorrhizal fungi (Fig. 4.7a, b). The plot AEW4 was excluded from regressions of throughfall fluxes of P against P stocks in foliage and the Shannon diversity index of ectomycorrhizal fungi because of dislocation (Fig. 4.7a, b). Notably, the foliar C:P ratio was lowest and the soil total P concentration was greatest at AEW4 (Tab. 4.1). There were concurring effects of foliar P status and foliar biomass on throughfall reactive P fluxes. The throughfall reactive P flux correlated only with the foliar C:P ratio when the bias introduced by the low foliar biomass of the thicket stand HEW4 was excluded ($r_{Pearson} = -0.731$, $P = 0.011$) and only with foliar biomass when forests with extreme foliar C:P ratios were excluded (i.e. AEW4, HEW5; $r_{Spearman} = 0.745$, $P = 0.018$). Throughfall reactive P fluxes were correlated with the NaOH-extractable inorganic P in the A horizon ($r_{Spearman} = 0.674$, $P = 0.023$), while other Hedley P fractions and soil properties (e.g., soil pH, phosphatase activity) were not correlated with throughfall fluxes of reactive P. The NaOH-extractable inorganic P concentrations in the A horizon in turn correlated with the Shannon diversity index of ectomycorrhizal fungi ($r_{Spearman} = 0.595$, $P = 0.041$). Furthermore, the foliar C:P ratio correlated marginally with the Shannon diversity index ($r_{Spearman} = -0.516$, $P = 0.086$), but the correlation was highly significant when the thicket stand HEW4 was excluded ($r_S = -0.784$, $P = 0.004$). We assume that stand development of HEW4 (approximately 15 years, Peter Schall, personal communication) was too short to yield a comparable fungal community structure at this site. We did not detect any significant correlation of P stock in foliage, foliar C:P ratio, NaOH-extractable inorganic P concentrations in the A horizon, and the Shannon diversity index of ectomycorrhizae with throughfall fluxes of DOP.

Flux of both, the reactive P ($r_{Pearson} = 0.718$, $P = 0.009$) and DOP ($r_{Pearson} = 0.741$, $P = 0.006$) in litter leachate correlated significantly with the respective flux in throughfall, partly because water fluxes of litter leachate were derived from throughfall precipitation using a fixed average fraction of evapotranspiration litter layer. Therefore, correlations of environmental conditions with litter leachate fluxes largely paralleled those with throughfall fluxes. For instance, the reactive P flux with litter leachate correlated with the P stock of foliage ($r_{Pearson} = 0.798$, $P = 0.003$), but there was no correlation between the reactive P flux with litter leachate and the Shannon diversity index of ectomycorrhizal fungi ($r_{Pearson} = 0.36$, $P = 0.277$). The litter leachate flux of reactive P correlated closely with the NaOH-extractable inorganic P concentrations in the A horizon (Fig. 4.7c; log-log scale). We tried to disentangle the controls of litter leachate and throughfall fluxes by analyzing the net flux of reactive P (i.e. litter leachate – throughfall), but the net flux for reactive P from the litter layer was not significantly correlated with any considered soil or soil organic layer property.

4.5 Discussion

4.5.1 Dissolved P fluxes in beech forests

In line with other studies in forests, inputs and outputs of P were small compared to the internal recycling (e.g., Attiwill and Adams 1993; Yanai 1992; Finzi 2009). Bulk deposition of reactive P was low and in the typical range reported for Europe (0.027 ± SD 0.034 kg ha^{-1} $year^{-1}$; Tipping *et al.* 2014). However, we did not estimate dry deposition of P. Lequy *et al.* (2014) showed that particulate P deposition (> 0.45 μm) contributed 17 to 32 % to total P deposition in deciduous forests in northeastern France. Thus, total P deposition to the studied forest stands might have been greater than our estimate in spite of the possible overestimation of bulk deposition.

The low concentrations of reactive P in mineral soil solution suggested that dissolved P losses with drainage from the solum are small and that the availability of P for plants by uptake from the soil solution is limited in the studied forests. Small P concentrations in soil water and a limited P availability likely resulted from geochemical and biological P retention in the soil (Wood *et al.* 1984). Based on the observations in the Schwäbische Alb and in line with Weand *et al.* (2009), we assume that reactive P concentrations in soil solution were also held constantly low by fast plant uptake after P release by mineral dissolution or organic matter mineralization throughout the GS in Hainich-Dün. Given the mostly acidic soil pH in the Al oxide buffer range of most A horizons (Tab. 4.1), reactive P was likely also bound to Al and iron oxides or precipitated as Al phosphates. At greater soil depths, leached reactive P was likely precipitated as amorphous apatite because of the high pH and Ca concentrations of mineral soil solution (Schwäbische Alb: pH 7.4 to 8.1, 12.9 to 40.5 mg Ca L^{-1}; Hainich-Dün: pH 6.7 to 7.8, 4 to 47.2 mg Ca L^{-1}; own unpublished data).

Our results suggest that the canopy was the quantitatively most important source of dissolved P and that water bound P fluxes were dominated by reactive P in European beech forests on calcareous bedrock. The high contribution of reactive P to TDP in throughfall probably resulted from the greater mobility of inorganic P relative to ester-bound P and polyphosphates in plants and because P is predominantly stored as inorganic P in tissue cells (Lauer *et al.* 1989). Reactive P fluxes with throughfall (Fig. 4.1) were much greater than with bulk precipitation and similar to stand deposition in a mixed hardwood forest in New Hampshire (0.57 kg ha^{-1} $year^{-1}$; Yanai 1992) and in three deciduous forest stands adjacent to Hainich-Dün (0.73 to 1.46 kg ha^{-1} $year^{-1}$; Talkner *et al.* 2010). The large range of reactive P stand deposition fluxes reported in the study of Talkner *et al.* (2010) is in line with our finding that throughfall P fluxes vary considerably on regional scales, probably in relation to P status and availability. Growing season throughfall fluxes of reactive P accounted for approximately 5 to 19 % of the estimated P stock in foliage (AEW4 excluded) and thus represented a substantial P loss for the trees.

Fluxes of reactive P with litter leachate were greater than in a beech forest on dolomite in Bavaria (0.1 kg ha^{-1} $year^{-1}$; Kaiser *et al.* 2003). Moreover, P leaching from the organic layer in the study of Kaiser *et al.* (2003) was dominated by DOP (61 to 81 %), while DOP contributed only 5 to 30 % of TDP in litter leachate in our study. In most studied forests, reactive P fluxes with litter leachate resembled the fluxes with throughfall (Fig. 4.1, Fig. 4.3). This suggested that throughfall-derived reactive P flushed nearly quantitatively through organic layers and a small net P mineralization with exception of the sites AEW7 and HEW10. In a mor-type organic layer of a mixed deciduous forest in North Carolina, Qualls *et al.* (1991) similarly found that throughfall-derived reactive P was poorly retained and release of reactive P was small. Small apparent net-retention and net-release likely resulted from a short contact time of throughfall with the shallow mull-type organic layers, P accumulation in decomposing beech litter (Colpaert and van Tichelen 1996) and an efficient P recycling by plants and microbes (Walbridge *et al.* 1991; Yanai 1992). The typically high bioturbation in soils with mull-type organic layers might have transported organic matter into the mineral soil before significant net mineralization occurred. However, the reason for the great release of reactive P from organic layers in the forests AEW7 and HEW10 remain unresolved.

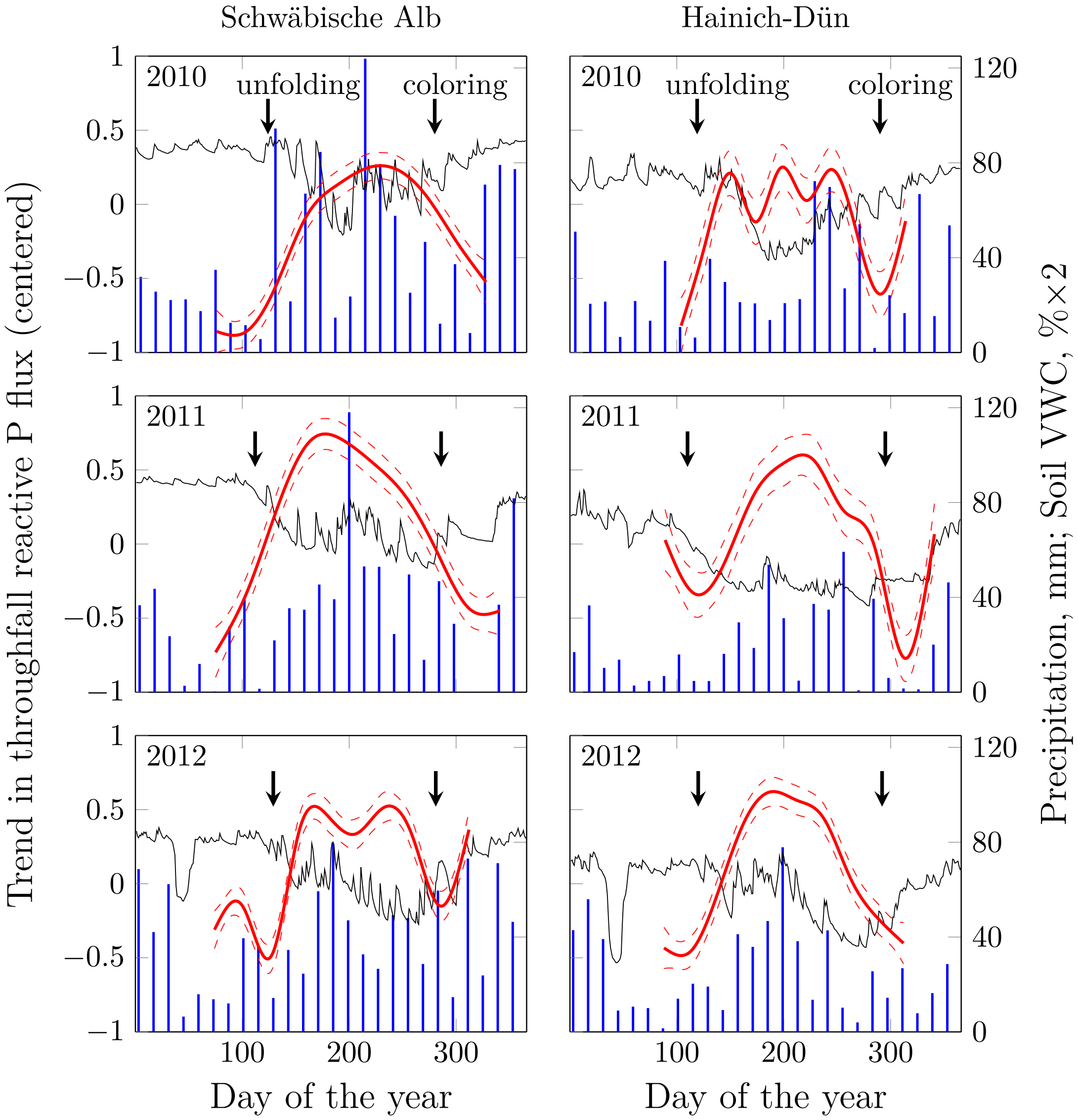

Figure 4.4: Temporal course of reactive P (i.e. phosphate-P + easily hydrolyzed organic P) fluxes with throughfall (red line) as estimated by cubic regression splines of day of the year and centered log-scale throughfall fluxes of reactive P during the growing seasons 2010, 2011, and 2012 in the Schwäbische Alb and Hainich-Dün, respectively. The dashed lines are the mean ± standard error of the smooth fit. Bars represent the cumulative precipitation between sampling campaigns (14 days). The black line is the mean daily volumetric soil water content (exaggerated by a factor of 2) at the 0.1 m depth averaged for the 6 sites per region. Arrows mark the days of leaf unfolding and leaf coloring at the nearest observation available in the Pan European Phenology Database (www.pep725.eu).

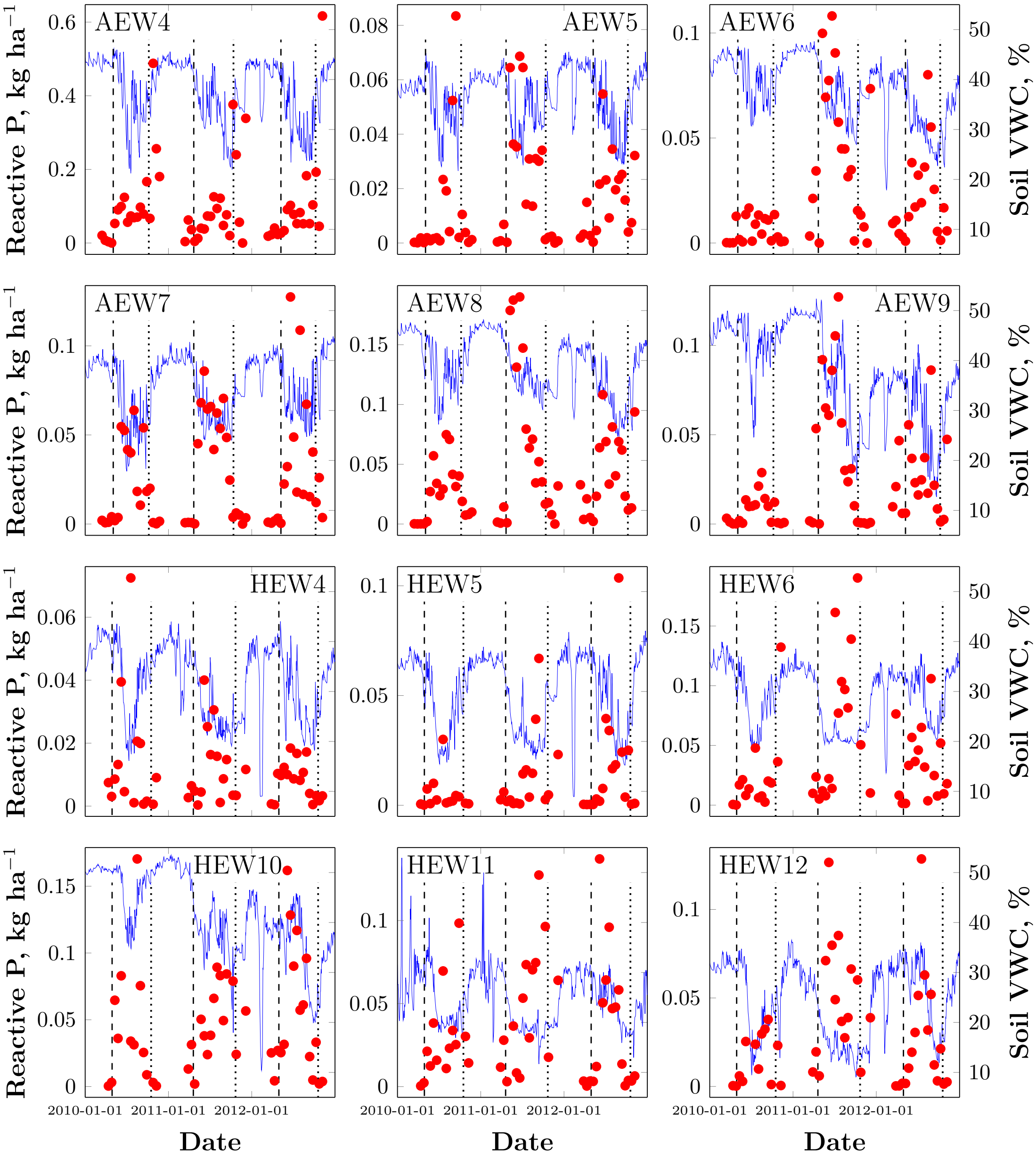

Figure 4.5: Temporal course of reactive P (i.e. phosphate-P + easily hydrolyzed organic P) fluxes with throughfall (red dots, cumulative over 14 days) and volumetric soil water content at the 0.1 m depth (blue lines) from 2010–01–01 to 2012–12–31 in forests of the Schwäbische Alb (AEW#) and Hainich-Dün (HEW#). Note that the scale of reactive P flux differs among subfigures to improve readability. The dashed and dotted vertical lines indicate the date of leaf unfolding and coloring, respectively, at the nearest station in the Pan European Phenology Database (www.pep725.eu).

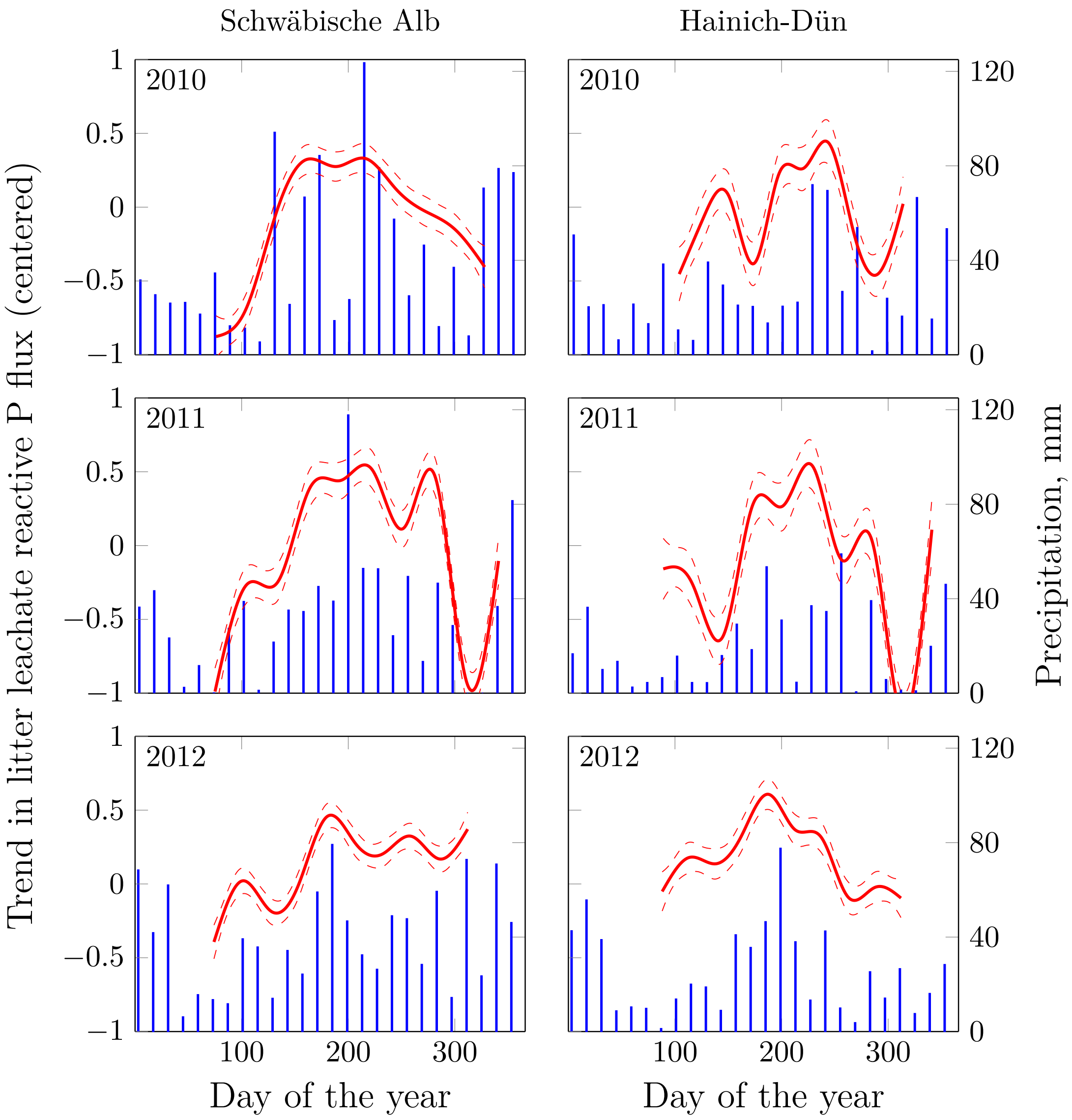

Figure 4.6: Temporal course of reactive P (i.e. phosphate-P + easily hydrolyzed organic P) fluxes with litter leachate (red line) as estimated by cubic regression splines of day of the year and centered log-scale litter leachate fluxes of reactive P during the growing seasons 2010, 2011, and 2012 in the Schwäbische Alb and Hainich-Dün, respectively. The dashed lines are the mean ± standard error of the smooth fit. Bars represent the cumulative precipitation between sampling campaigns (14 days).

4.5.2 Reactive P fluxes as related to weather conditions

In both regions, throughfall and litter leachate fluxes of reactive P varied widely (Fig. 4.3) and were similar. However, the cumulative throughfall fluxes of reactive P were only 20 % greater in the Schwäbische Alb than in Hainich-Dün although throughfall volume was 50 % greater. This might be attributable to a limited pool of reactive P in the canopy being diluted at higher precipitation amounts. Moreover, cumulative GS throughfall fluxes of reactive P were greatest in 2011 and 2012 (Fig. 4.3) which were characterized by a pronounced deficit in precipitation between February and May (Fig. 4.2) and thus suggested a positive response of canopy P leaching to reduced water availability in spring. Within growing seasons, high precipitation was associated with great throughfall fluxes of reactive P especially after dry spells (Fig. 4.4). The throughfall flux of DOP varied marginally in both regions illustrating that DOP leaching was less sensitive to site specific controls of P cycling than reactive P. However, canopy DOP leaching also increased in the driest year 2011. Regional and annual differences in reactive P fluxes tended to be more expressed in throughfall than in litter leachate because of an apparent reactive P release from organic layers in Hainich-Dün and more efficient buffering of temporal variation in the organic layer compared to the canopy. The greater throughfall-derived reactive P input in 2011 than in other years was partly retained in organic layers of the Schwäbische Alb (Fig. 4.3), probably because of low water fluxes.

The dry and warm first half of the year 2011 led to an earlier beginning of canopy development (Tab. 4.2) and drop in soil moisture (Fig. 4.4), and the most intense fructification and crown transparency ever observed for beech in Germany (BMELV 2011). The greater throughfall fluxes of reactive P and DOP in 2011 may thus have resulted from the longer growing season and leaching of pollen while the increase in litter leachate reactive P fluxes in 2012 (Fig. 4.3) may reveal P release from fruiting components deposited in the preceding year. Canopy P leaching decreased before leaf coloring (Fig. 4.4), probably because of P resorption (Aerts 1996). In view of the low P availability in soil, resorption is likely an important trait of trees in the studied forest for maintaining P supply because residual foliar P was leached from the canopy during autumn storms (Fig. 4.4).

The meteorologic conditions in spring 2011 and 2012 could also have coupled back to P uptake and availability. After leaf unfolding, soil moisture decreased (Fig. 4.4) in response to transpiration which is the driving process for P allocation from roots to shoots. Hence, P leaching might have been facilitated by P allocation and stomatal aperture during high transpiration rates. Soil drought was more exacerbated in 2011 in Hainich-Dün, potentially impairing stomatal conductance and nutrient uptake (Bréda *et al.* 2006; Gessler *et al.* 2004), however, the delayed peak of throughfall reactive fluxes relative to the Schwäbische Alb may also have resulted from the low precipitation in April and May in Hainich-Dün. Peuke and Rennenberg (2004) observed a 16 % decrease of P concentration and a 31 % decrease in phosphate concentration in beech seedling leaves which were exposed to short-term experimental drought compared to control treatments. The authors attributed the decreasing leaf concentration to reduced concentrations of exchangeable orthophosphate in the soil. However, the leaves were washed before analysis and potential P leaching and wash-off losses were not considered.

On the short run, trees can buffer reduced P availability by mobilization from internal P storage pools. Sardans and Peñuelas (2007) showed that P mobilization from woody to green plant parts increased under experimental drought in a Mediterranean *Quercus ilex* L. forest resulting in a 30 % decrease in the biomass P after 6 years. In combination with our findings this suggests long-term implications of the predicted higher drought frequency (IPCC 2014) for P nutrition of Central European beech forests because the tree P pool is finite and remobilized P will be increasingly leached from the canopy and be immobilized in the soil in sparingly available forms. Further mechanistic studies are thus needed to assess the adaptability of P cycling in European beech forests under changing climatic conditions.

4.5.3 Other controls of reactive P fluxes

Growing season throughfall fluxes of reactive P correlated with the P stock in foliage (Fig. 4.7a). Furthermore, throughfall reactive P fluxes increased just after leaf unfolding and decreased before leaf coloring (Fig. 4.4, Fig. 4.5) and thus before senescence, i.e. when the scavenging capacity of the canopy for particles was still high. This temporal decoupling of particle scavenging and throughfall reactive P fluxes suggested that leaching from leaves drove the growing season throughfall flux of reactive P while dry deposition contributed to a lesser extent to P enrichment in throughfall. For a subset of forests, the throughfall fluxes of reactive P correlated with the foliar C:P ratio and NaOH-extractable inorganic P concentrations in the A horizon indicating that a high bioavailability of P accelerated P cycling. The foliar P concentrations were below the critical value of 1 g kg^{-1} (except at AEW4, Tab. 4.1)

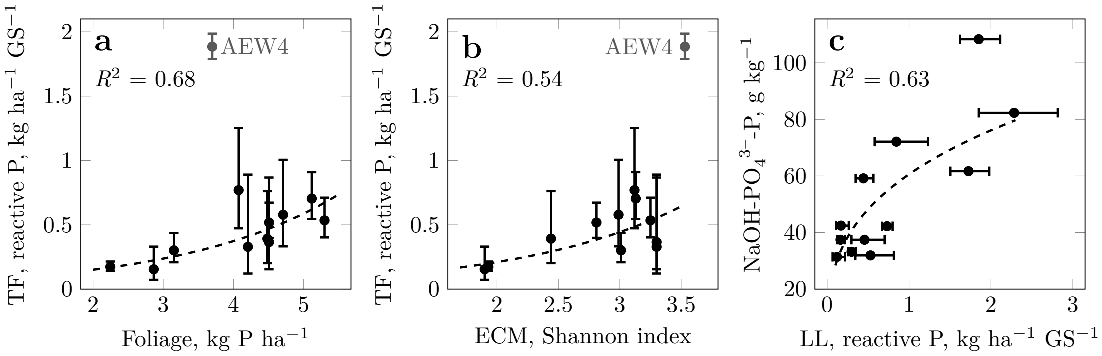

Figure 4.7: Relationship of (a) the P stock in foliage and (b) the Shannon index of ectomycorrhizae (ECM) with geometric mean fluxes per growing season (GS) of reactive P (i.e. phosphate-P + easily hydrolyzed organic P) with throughfall (TF), and (c) the reactive P flux with litter leachate (LL) and the NaOH-extractable inorganic P concentration in the A horizon, respectively. The dashed lines are the linear regressions based on log-transformed fluxes and additionally log-transformed NaOH-extractable inorganic P. R^2 is the goodness of fit and error bars are geometric standard deviations based on transformed data. Forest plot AEW4 in (a) and (b) was excluded from the regression as an outlier.

indicating P deficiency (Stefan *et al.* 1997). Therefore, it may be hypothesized that under P scarcity, beech is only able to downregulate P leaching from foliage to a limited extent or only during the period of resorption. The greatest canopy P leaching occurred in the forest stand AEW4 with the highest P concentration in the mineral soil and lowest C:P ratios of foliage (Tab. 4.1). The different P nutritional status potentially resulted in different dynamics of P cycling at this site compared to the other studied forests. In the forest AEW4, canopy leaching of reactive P accounted for 50 % of the estimated P stock in foliage, the majority of which occurred in autumn (cf. Fig. 4.7; Fig. 4.5). We speculate that trees have adapted to the greater P availability at this site by reducing P resorption in autumn (Vergutz *et al.* 2012).

Our data suggest that reactive P leached from the canopy and subsequently through the organic layer was partly immobilized in the moderately labile soil P pool (i.e. NaOH-extractable inorganic P; Negassa and Leinweber 2009). Additionally, leached P was likely also bound to organic matter in the mineral soil, directly or after microbial recycling (Wood *et al.* 1984; Walbridge *et al.* 1991). The moderately labile soil P and the soil organic P are temporary storage pools which are accessible for plants by rhizosphere acidification, extracellular enzymes and mycorrhizal associations (Wallander 2000; Blum *et al.* 2002; Lambers *et al.* 2008).

Alt *et al.* (2013) reported a phosphate release from soils in the Schwäbische Alb after H^+ addition from a fast-reactive pool consisting of poorly-crystalline Ca phosphates and a slow reactive pool consisting of hydroxylapatite. Among the Hedley P fractions, both pools were most closely correlated with the NaOH-extractable P (Alt *et al.* 2013), supporting the idea that root acidification was an effective strategy to solubilize moderately labile P fractions and improve P availability in the studied forests. Ectomycorrhizal fungi can mine the soil for P bound in organic matter by the release of hydrolytic and oxidative enzymes, for P bound in minerals by the release of organic acids and chelators (e.g., oxalate), and by increasing the explored volume of soil (Griffiths *et al.* 1994; Wallander 2000; Smith 2003; van Schöll *et al.* 2008). The ectomycorrhizal colonization rate of beech roots in the studied forests was 99.7 ± 0.5 % (A. Polle, personal communication), hence, nutrient and water uptake of trees was mainly mediated by ectomycorrhiza. The observed significant correlation of the Shannon diversity index of ectomycorrhizal fungi with the foliar C:P ratios suggested that P nutrition of beech was improved by a diverse fungal community, potentially through complementary P acquisition (Jones *et al.* 2010), supplementing spatial foraging patterns through species-specific hyphal densities (Agerer 2001), and interactions with the associated bacterial community structure among different ectomycorrhizal fungal species (Uroz *et al.* 2007), respectively. If so, canopy P leaching losses could be compensated for by a greater P uptake from soil because of a more diverse ectomycorrhizal fungal community and possibly a stimulation of mycelial production by apatite formation under P limited conditions (Hagerberg *et al.* 2003).

4.6 Conclusions

The forest canopy is the largest source of dissolved P because of P leaching from plants. European beech forests loose 5 to 50 % of the P stored in foliage by canopy leaching every growing season. In most beech forests, this throughfall P flushed quantitatively through the shallow organic layers on calcareous soils indicating small net mineralization, and was retained in the mineral soil, likely mainly in the NaOH-extractable pool. We suggest that the NaOH-extractable inorganic P fraction in the mineral soil reflects both a sink and a source of recycled P in ecosystems.

The fluxes of reactive P in throughfall show a strong seasonality with low fluxes before leaf unfolding and high ones during summer storms and autumn senescence. Our results showed a significant increase in canopy P leaching in years with deficit precipitation in spring and thus suggested a susceptibility of P cycling to water stress. In the view of the predicted climate change and increasing P scarcity this finding suggests a further enhanced P stress of Central European beech forests if frequency and duration of spring droughts increase.

The phosphorus status of European beech stands benefited from a diverse ectomycorrhizal fungal community probably because of a greater exploitation of recalcitrant P sources in the soil. The phosphorus status of European beech stands benefited from a diverse ectomycorrhizal fungal community probably because of a greater exploitation of recalcitrant P sources in the soil. However, the better P supply also resulted in greater canopy leaching of P and a high diversity of ectomycorrhizal fungi might be necessary to maintain recycling of P between trees and sparingly available soil P fractions.

4.7 Acknowledgements

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Appendix A

Data appendix

The appendix is attached as a CD.

A.1 Contents of the attached CD

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- ReadMe.pdf

  Copyright notice, list of data appendices and structure of files on CD.

- VariableDescription.xlsx

  Metadata and explanation of acronyms used in the data appendix.

Chapter2\\

Chapter2**ALB**\\

- 02_01_ALB_RF_2010_rawdata.xlsx

  Precipitation, concentrations of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, K, Na, and TP, Na to Cl ratio, and electrical conductivity in rainfall samples from the Schwäbische Alb in the growing season 2010 (unprocessed).

- 02_02_ALB_RF_2010_outlier.xlsx

  Identified outliers and respective criteria in rainfall samples from the Schwäbische Alb in the growing season 2010.

- 02_03_ALB_RF_2010_nooutlier.xlsx

  Precipitation, concentrations of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, K, Na, and TP, Na to Cl ratio, and electrical conductivity in rainfall samples from the Schwäbische Alb in the growing season 2010 (outlier removed).

- 02_04_ALB_RF_2010_meanperdate.xlsx

  Concentrations of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K per sampling in rainfall samples from the Schwäbische Alb in the growing season 2010 (averaged over available samples).

- 02_05_ALB_RF_2010_vwm.xlsx

  Volume weighted mean concentration of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in rainfall samples from the Schwäbische Alb in the growing season 2010.

- 02_06_ALB_RF_2010_radolandep.xlsx

  Radar derived precipitation and bulk deposition of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K with rainfall in the Schwäbische Alb in the growing season 2010 (RADOLAN × volume-weighted mean concentration).

- 02_07_ALB_TF_2010_rawdata.xlsx

  Throughfall volume, concentrations of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in throughfall samples from the Schwäbische Alb in the growing season 2010 (unprocessed).

- 02_08_ALB_TF_2010_negativeDON.xlsx

  Throughfall samples from the Schwäbische Alb in the growing season 2010 with negative DON concentration and applied correction.

- 02_09_ALB_TF_2010_vwm.xlsx

  Volume weighted mean concentration of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in throughfall samples from the Schwäbische Alb in the growing season 2010.

- 02_10_ALB_TF_2010_corrected.xlsx

  Throughfall volume, concentrations and fluxes of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K per sampling in the Schwäbische Alb in the growing season 2010 (processed).

- 02_11_ALB_TF_2010_fluxes.xlsx

  Cumulative throughfall volume and fluxes of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in the Schwäbische Alb in the growing season 2010.

- 02_12_ALB_SF_2010_rawdata.xlsx

  Stemflow volume, concentrations of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in stemflow samples from the Schwäbische Alb in the growing season 2010 (unprocessed).

- 02_13_ALB_SF_2010_negativeDON.xlsx

  Stemflow samples from the Schwäbische Alb in the growing season 2010 with negative DON concentration and applied correction.

- 02_14_ALB_SF_2010_vwm.xlsx

  Volume weighted mean concentration of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in stemflow samples from the Schwäbische Alb in the growing season 2010.

- 02_15_ALB_SF_2010_corrected.xlsx

  Stemflow volume, concentrations and fluxes of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K per sampling in the Schwäbische Alb in the growing season 2010 (processed).

- 02_16_ALB_SF_2010_fluxes.xlsx

  Cumulative throughfall volume and fluxes of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in the Schwäbische Alb in the growing season 2010.

- 02_17_ALB_DD_2010.xlsx

  Cumulative dry deposition of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in the Schwäbische Alb in the growing season 2010.

- 02_18_ALB_2010_fluxesbudgets.xlsx

  Cumulative fluxes of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K with rainfall, throughfall stemflow, dry deposition, total deposition and canopy budgets in the Schwäbische Alb in the growing season 2010.

\Chapter 2\HAI

- 02_01_HAI_RF_2010_rawdata.xlsx

  Precipitation, concentrations of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, K, Na, and TP, Na to Cl ratio, and electrical conductivity in rainfall samples from Hainich-Dün in the growing season 2010 (unprocessed).

- 02_02_HAI_RF_2010_negativeDON.xlsx

  Rainfall samples from Hainich-Dün in the growing season 2010 with negative DON concentration and applied correction.

- 02_03_HAI_RF_2010_outlier.xlsx

  Identified outliers and respective criteria in rainfall samples from Hainich-Dün in the growing season 2010.

- 02_04_HAI_RF_2010_nooutlier.xlsx

  Precipitation, concentrations of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, K, Na, and TP, Na to Cl ratio, and electrical conductivity in rainfall samples from Hainich-Dün in the growing season 2010 (outlier removed).

- 02_05_HAI_RF_2010_meanperdate.xlsx

  Concentrations of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K per sampling in rainfall samples from Hainich-Dün in the growing season 2010 (averaged over available samples).

- 02_06_HAI_RF_2010_vwm.xlsx

  Volume weighted mean concentration of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in rainfall samples from Hainich-Dün in the growing season 2010.

- 02_07_HAI_RF_2010_radolandep.xlsx

  Radar derived precipitation and bulk deposition of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K with rainfall in Hainich-Dün in the growing season 2010 (RADOLAN × volume-weighted mean concentration).

- 02_08_HAI_TF_2010_rawdata.xlsx

  Throughfall volume, concentrations of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in throughfall samples from Hainich-Dün in the growing season 2010 (unprocessed).

- 02_09_HAI_TF_2010_negativeDON.xlsx

  Throughfall samples from Hainich-Dün in the growing season 2010 with negative DON concentration and applied correction.

- 02_10_HAI_TF_2010_vwm.xlsx

  Volume weighted mean concentration of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in throughfall samples from Hainich-Dün in the growing season 2010.

- 02_11_HAI_TF_2010_TFsub.xlsx

  Substitution of missing throughfall volume at HEW4 based on regional mean precipitation.

- 02_12_HAI_TF_2010_corrected.xlsx

  Throughfall volume, concentrations and fluxes of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K per sampling in Hainich-Dün in the growing season 2010 (processed).

- 02_13_HAI_TF_2010_fluxes.xlsx

  Cumulative throughfall volume and fluxes of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in the Hainich-Dün in the growing season 2010.

- 02_14_HAI_SF_2010_rawdata.xlsx

  Stemflow volume, concentrations of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in stemflow samples from Hainich-Dün in the growing season 2010 (unprocessed).

- 02_15_HAI_SF_2010_negativeDON.xlsx

  Stemflow samples from Hainich-Dün in the growing season 2010 with negative DON concentration and applied correction.

- 02_16_HAI_SF_2010_corrected.xlsx

  Stemflow volume, concentrations and fluxes of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K per sampling in Hainich-Dün in the growing season 2010 (processed).

- 02_17_HAI_SF_2010_fluxes.xlsx

  Cumulative throughfall volume and fluxes of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in Hainich-Dün in the growing season 2010.

- 02_18_HAI_DD_2010.xlsx

  Cumulative dry deposition of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K in Hainich-Dün in the growing season 2010.

- 02_19_HAI_2010_fluxesbudgets.xlsx

  Cumulative fluxes of Cl^-, TN, NH_4^+-N, NO_3^--N, DON, and K with rainfall, throughfall stemflow, dry deposition, total deposition and canopy budgets in Hainich-Dün in the growing season 2010.

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- 02_01_SCH_RF_2010_rawdata.xlsx

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- 02_02_SCH_RF_2010_negativeDON.xlsx

  Rainfall samples from Hainich-Dün in the growing season 2010 with negative DON concentration and applied correction.

- 02_03_SCH_RF_2010_outlier.xlsx

  Identified outliers and respective criteria in rainfall samples from Schorfheide-Chorin in the growing season 2010.

- 02_04_SCH_RF_2010_nooutlier.xlsx

  Precipitation, concentrations of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, K, Na, and TP, Na to Cl ratio, and electrical conductivity in rainfall samples from Schorfheide-Chorin in the growing season 2010 (outlier removed).

- 02_05_SCH_RF_2010_meanperdate.xlsx

  Concentrations of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K per sampling in rainfall samples from Schorfheide-Chorin in the growing season 2010 (averaged over available samples).

- 02_06_SCH_RF_2010_vwm.xlsx

  Volume weighted mean concentration of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in rainfall samples from Schorfheide-Chorin in the growing season 2010.

- 02_07_SCH_RF_2010_radolandep.xlsx

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- 02_08_SCH_TF_2010_rawdata.xlsx

  Throughfall volume, concentrations of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in throughfall samples from Schorfheide-Chorin in the growing season 2010 (unprocessed).

- 02_09_SCH_TF_2010_negativeDON.xlsx

  Throughfall samples from Schorfheide-Chorin in the growing season 2010 with negative DON concentration and applied correction.

- 02_10_SCH_TF_2010_vwm.xlsx

  Volume weighted mean concentration of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K in throughfall samples from Schorfheide-Chorin in the growing season 2010.

- 02_11_SCH_TF_2010_corrected.xlsx

  Throughfall volume, concentrations and fluxes of Cl^-, TN, $NH_4{}^+$-N, $NO_3{}^-$-N, DON, and K per sampling in Schorfheide-Chorin in the growing season 2010 (processed).

- 02_12_SCH_TF_2010_fluxes.xlsx

  Cumulative throughfall volume and fluxes of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, DON, and K in the Schorfheide-Chorin in the growing season 2010.

- 02_13_SCH_SF_2010_rawdata.xlsx

  Stemflow volume, concentrations of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, DON, and K in stemflow samples from Schorfheide-Chorin in the growing season 2010 (unprocessed).

- 02_14_SCH_SF_2010_negativeDON.xlsx

  Stemflow samples from the Schorfheide-Chorin in the growing season 2010 with negative DON concentration and applied correction.

- 02_15_SCH_SF_2010_vwm.xlsx

  Volume weighted mean concentration of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, DON, and K in stemflow samples from the Schorfheide-Chorin in the growing season 2010.

- 02_16_SCH_SF_2010_corrected.xlsx

  Stemflow volume, concentrations and fluxes of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, DON, and K per sampling in Schorfheide-Chorin in the growing season 2010 (processed).

- 02_17_SCH_SF_2010_fluxes.xlsx

  Cumulative throughfall volume and fluxes of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, DON, and K in Schorfheide-Chorin in the growing season 2010.

- 02_18_SCH_DD_2010.xlsx

  Cumulative dry deposition of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, DON, and K in Schorfheide-Chorin in the growing season 2010.

- 02_19_SCH_2010_fluxesbudgets.xlsx

  Cumulative fluxes of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, DON, and K with rainfall, throughfall stemflow, dry deposition, total deposition and canopy budgets in Schorfheide-Chorin in the growing season 2010.

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- 03_00_ALBHAI_data_for_waterflux_LL.xlsx

  Cl^- concentrations, throughfall volume, and litter leachate volume as used for the calculation of water fluxes through the organic layers.

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- 03_01_ALB_2010_12_seasons.xlsx

  Dates used to separate the growing seasons 2010 to 2012 into seasons (spring, summer, autumn) as used for volume weighted mean concentration calculation in the Schwäbische Alb.

- 03_02_ALB_TF_2010_12_rawdata.xlsx

  Throughfall volumes, concentrations of Cl^-, TN, NH_4^+-N and NO_3^--N in throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 03_03_ALB_TF_2010_12_subsTFprecmm.xlsx

  Substitution of missing throughfall volumes in the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 03_04_ALB_TF_2010_12_negDON.xlsx

  Throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with negative DON concentration and applied correction.

- 03_05_ALB_TF_2010_12_outlier.xlsx

  Identified outliers and respective criteria in throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 03_06_ALB_TF_2010_12_nooutlier.xlsx

  Throughfall volumes, concentrations of Cl^-, TN, NH_4^+-N, NO_3^--N, and DON in throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (corrected).

- 03_07_ALB_TF_2010_12_vwm_seasonal.xlsx

  Seasonal volume weighted mean concentrations of TN, NH_4^+-N, NO_3^--N, and DON in throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 03_08_ALB_TF_2010_12_seasonalfluxes.xlsx

  Seasonal fluxes of TN, NH_4^+-N, NO_3^--N, and DON in throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 03_09_ALB_TF_2010_12_fluxesXyear.xlsx

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- 03_10_ALB_LL_2010_12_rawdata.xlsx

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- 03_11_ALB_LL_2010_12_negDON.xlsx

  Litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with negative DON concentration and applied correction.

- 03_12_ALB_2010_12_LL_outlier.xlsx

  Identified outliers and respective criteria in litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 03_13_ALB_LL_2010_12_nooutlier.xlsx

  Litter leachate volumes, concentrations of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, and DON in litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (corrected).

- 03_14_ALB_LL_2010_12_vwm_seasonal.xlsx

  Seasonal volume weighted mean concentrations of TN, ${NH_4}^+$-N, ${NO_3}^-$-N, and DON in litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 03_15_ALB_LL_2010_12_seasonalfluxes.xlsx

  Seasonal fluxes of TN, ${NH_4}^+$-N, ${NO_3}^-$-N and DON in litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 03_16_ALB_LL_2010_12_FluxesBudgets.xlsx

  Cumulative leaching through organic layers and gross and net fluxes of TN, ${NH_4}^+$-N, ${NO_3}^-$-N, and DON with litter leachate in the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

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- 03_01_HAI_2010_12_seasons.xlsx

  Dates used to separate the growing seasons 2010 to 2012 into seasons (spring, summer, autumn) as used for volume weighted mean concentration calculation in Hainich-Dün.

- 03_02_HAI_TF_2010_12_rawdata.xlsx

  Throughfall volumes, concentrations of Cl^-, TN, ${NH_4}^+$-N and ${NO_3}^-$-N in throughfall samples from Hainich-Dün in the growing seasons 2010, 2011and 2012 (unprocessed).

- 03_03_HAI_TF_2010_12_subsTFprecmm.xlsx

  Substitution of missing throughfall volumes in Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 03_04_HAI_TF_2010_12_negDON.xlsx

  Throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with negative DON concentration and applied correction.

- 03_05_HAI_TF_2010_12_outlier.xlsx

  Identified outliers and respective criteria in throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 03_06_HAI_TF2010_12_nooutlier.xlsx

  Throughfall volumes, concentrations of Cl^-, TN, ${NH_4}^+$-N, ${NO_3}^-$-N, and DON in throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (corrected).

- 03_07_HAI_TF_2010_12_vwm_seasonal.xlsx

  Seasonal volume weighted mean concentrations of TN, NH_4^+-N, NO_3^--N, and DON in throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 03_08_HAI_TF_2010_12_seasonalfluxes.xlsx

  Seasonal fluxes of TN, NH_4^+-N, NO_3^--N, and DON in throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 03_09_HAI_TF_2010_12_fluxesXyear.xlsx

  Cumulative throughfall volumes and fluxes of TN, NH_4^+-N, NO_3^--N, and DON in Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 03_10_HAI_LL_2010_12_rawdata.xlsx

  Litter leachate volumes and concentrations of Cl^-, TN, NH_4^+-N and NO_3^--N in litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 03_11_HAI_LL_2010_12_negDON.xlsx

  Litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with negative DON concentration and applied correction.

- 03_12_HAI_LL_2010_12_outlier.xlsx

  Identified outliers and respective criteria in litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 03_13_HAI_LL_2010_12_nooutlier.xlsx

  Litter leachate volumes, concentrations of Cl^-, TN, NH_4^+-N, NO_3^--N, and DON in litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (corrected).

- 03_14_HAI_LL_2010_12_vwm_seasonal.xlsx

  Seasonal volume weighted mean concentrations of TN, NH_4^+-N, NO_3^--N, and DON in litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 03_15_HAI_LL_2010_12_seasonalfluxes.xlsx

  Seasonal fluxes of TN, NH_4^+-N, NO_3^--N, and DON in litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 03_16_HAI_LL_2010_12_FluxesBudgets.xlsx

  Cumulative leaching through organic layers and gross and net fluxes of TN, NH_4^+-N, NO_3^--N, and DON with litter leachate in Hainich-Dün in the growing seasons 2010, 2011 and 2012.

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- 04_00_ALBHAI_2013_14_litterfall.xlsx

  Litterfall fluxes in the Schwäbische Alb and Hainich-Dün between October 2013 and July 2014.

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- 04_01_ALB_RF_2010_2012_rawdata.xlsx

  Precipitation, concentrations of reactive P and TDP in rainfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 04_02_ALB_RF_2010_12_belowLOD.xlsx

  Rainfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with reactive P or TDP concentrations below the limit of detection and applied correction.

- 04_03_ALB_RF_2010_12_negativeDOP.xlsx

  Rainfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with negative DOP concentration and applied correction.

- 04_04_ALB_RF_2010_12_perdate.xlsx

  Median concentrations and fluxes of reactive P, TDP and DOP per sampling date in rainfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012. Precipitation was obtained from two DWD stations.

- 04_05_ALB_BD_2010_12.xlsx

  Bulk deposition of reactive, TDP and DOP in the the growing seasons 2010, 2011 and 2012. Precipitation was obtained from two DWD stations.

- 04_06_ALB_TF_2010_12_rawdata.xlsx

  Throughfall volumes, concentrations of reactive P and TDP in throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 04_07_ALB_TF_2010_12_belowLOD.xlsx

  Throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with reactive P or TDP concentrations below the limit of detection and applied correction.

- 04_08_ALB_2010_12_TF_negativeDOP.xlsx

  Throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with negative DOP concentration and applied correction.

- 04_09_ALB_2010_12_missingTFprecsubs.xlsx

  Substitution of missing throughfall volumes in the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 04_10_ALB_TF_2010_12_adjust2reftime14.xlsx

  Precipitation weighted split of throughfall volume for samples with a sampling interval of 28 days to two samplings with a 14 day interval in order to obtain a equally spaced time-series. Precipitation was obtained from two DWD stations.

- 04_11_ALB_TF_2010_2012_vwm.xlsx

  Volume weighted mean concentrations of reactive P and TDP in throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 04_12_ALB_TF_2010_12_corrected.xlsx

  Throughfall volumes, concentrations and fluxes of reactive P, TDP and DOP in throughfall samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (corrected).

- 04_13_ALB_TF_2010_12_fluxesXyear.xlsx

  Cumulative throughfall volume and fluxes of reactive P, TDP and DOP in the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 04_14_ALB_LL_2010_12_rawdata.xlsx

  Litter leachate volumes and concentrations of reactive P and TDP in litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 04_15_ALB_LL_2010_12_LL_belowLOD.xlsx

  Litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with reactive P or TDP concentrations below the limit of detection and applied correction.

- 04_16_ALB_2010_12_LL_negativeDOP.xlsx

  Litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with negative DOP concentration and applied correction.

- 04_17_ALB_LL_2010_12_vwm.xlsx

  Volume weighted mean concentrations of reactive P and TDP in litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 04_18_ALB_LL_2010_12_negDOP2.xlsx

  Litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with negative DOP concentration after substitution of missing concentrations by volume weighted mean concentrations and applied correction.

- 04_19_ALB_LL_2010_12_corrected.xlsx

  Litter leachate volumes, concentrations and fluxes of reactive P, TDP and DOP in litter leachate samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (corrected).

- 04_20_ALB_LL_2010_12_fluxesXyear.xlsx

  Cumulative litter leachate volumes and fluxes of reactive P, TDP and DOP in the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

- 04_21_ALB_SS_top_2010_12_rawdata.xlsx

  Volumes, reactive P and TDP concentrations and pH in mineral soil solution (topsoil) samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 04_22_ALB_SS_top_2010_12_belowLOD.xlsx

  Mineral soil solution (topsoil) samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with reactive P or TDP concentrations below the limit of detection and applied correction.

- 04_23_ALB_SS_top_2010_12_negativeDOP.xlsx

  Mineral soil solution (topsoil) samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012 with negative DOP concentration and applied correction.

- 04_24_ALB_SS_top_2010_12_medians.xlsx

  Median concentrations of reactive P, TDP and DOP per study plot in mineral soil solution (topsoil) samples from the Schwäbische Alb in the growing seasons 2010, 2011 and 2012.

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- 04_01_HAI_RF_2010_12_rawdata.xlsx

  Precipitation, concentrations of reactive P and TDP in rainfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 04_02_HAI_RF_2010_12_belowLOD.xlsx

  Rainfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with reactive P or TDP concentrations below the limit of detection and applied correction.

- 04_03_HAI_RF_2010_12_negativeDOP.xlsx

  Rainfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with negative DOP concentration and applied correction.

- 04_04_HAI_RF_2010_12_perdate.xlsx

  Median concentrations and fluxes of reactive P, TDP and DOP per sampling date in rainfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012. Precipitation was obtained from two DWD stations.

- 04_05_HAI_BD_2010_12.xlsx

  Bulk deposition of reactive, TDP and DOP in the the growing seasons 2010, 2011 and 2012. Precipitation was obtained from two DWD stations.

- 04_06_HAI_TF_2010_12_rawdata.xlsx

  Throughfall volumes, concentrations of reactive P and TDP in throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 04_07_HAI_TF_2010_12_belowLOD.xlsx

  Throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with reactive P or TDP concentrations below the limit of detection and applied correction.

- 04_08_HAI_TF_2010_12_negative_DOP.xlsx

  Throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with negative DOP concentration and applied correction.

- 04_09_HAI_2010_12_missingTFprecsubs.xlsx

  Substitution of missing throughfall volumes in Hainich-Dün in the growing seasons 2010, 2011, 2012.

- 04_10_HAI_TF_2010_12_adjust2reftime14.xlsx

  Precipitation weighted split of throughfall volume for samples with a sampling interval of 28 days to two samplings with a 14 day interval in order to obtain a equally spaced time-series. Precipitation was obtained from two DWD stations.

- 04_11_HAI_TF_2010_2012_vwm.xlsx

  Volume weighted mean concentrations of reactive P and TDP in throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 04_12_HAI_TF_2010_12_corrected.xlsx

  Throughfall volumes, concentrations and fluxes of reactive P, TDP and DOP in throughfall samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (corrected).

- 04_13_HAI_TF_2010_12_fluxesXyear.xlsx

  Cumulative throughfall volumes and fluxes of reactive P, TDP and DOP in Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 04_14_HAI_LL_2010_12_rawdata.xlsx

  Litter leachate volumes and concentrations of reactive P and TDP in litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 04_15_HAI_LL_2010_12_belowLOD.xlsx

  Litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with reactive P or TDP concentrations below the limit of detection and applied correction.

- 04_16_HAI_LL_2010_12_negativeDOP.xlsx

  Litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with negative DOP concentration and applied correction.

- 04_17_HAI_LL_2010_12_vwm.xlsx

  Volume weighted mean concentrations of reactive P and TDP in litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 04_18_HAI_LL_2010_12_corrected.xlsx

  Litter leachate volumes, concentrations and fluxes of reactive P, TDP and DOP in litter leachate samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (corrected).

- 04_19_HAI_LL_2010_12_fluxesXyear.xlsx

  Cumulative litter leachate volumes and fluxes of reactive P, TDP and DOP in Hainich-Dün in the growing seasons 2010, 2011 and 2012.

- 04_20_HAI_SS_top_2010_12_rawdata.xlsx

  Volumes, reactive P and TDP concentrations and pH in mineral soil solution (topsoil) samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 (unprocessed).

- 04_21_HAI_SS_top_2010_12_belowLOD.xlsx

  Mineral soil solution (topsoil) samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with reactive P or TDP concentrations below the limit of detection and applied correction.

- 04_22_HAI_SS_top_2010_12_negativeDOP.xlsx

  Mineral soil solution (topsoil) samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012 with negative DOP concentration and applied correction.

- 04_23_HAI_SS_top_2010_12_medians.xlsx

  Median concentrations of reactive P, TDP and DOP per study plot in mineral soil solution (topsoil) samples from Hainich-Dün in the growing seasons 2010, 2011 and 2012.

Appendix B

Properties of dissolved and total organic matter in throughfall, stemflow and forest floor leachate of Central European forests

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B.1 Abstract

For the first time, we investigated the composition of dissolved organic matter (DOM) compared to total OM (TOM, consisting of DOM, < 0.45 μm and particulate OM, 0.45 μm $<$ POM $<$ 500 μm) in throughfall, stemflow and forest floor leachate of common beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) H. Karst.) forests using solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. We hypothesized that the composition and properties of OM in forest ecosystem water samples differ between DOM and TOM and between the two tree species.

The ^{13}C NMR results, derived from 21 samples, point to pronounced differences in the composition of DOM and TOM in throughfall solution at the beech sites with TOM exhibiting higher relative intensities for the alkyl C region, representing aliphatic C from less decomposed organic material compared to DOM. Furthermore, TOM shows lower intensities for lignin-derived and aromatic C of the aryl C region resulting in lower aromaticity indices and a diminished degree of humification. Along the ecosystem compartments, differences in the structural composition of DOM and TOM under beech lessened in the order throughfall $>$ stemflow $\approx$ forest floor leachate.

In contrast to the broadleaved sites, differences between DOM vs. TOM in throughfall solution under spruce were only less pronounced and spectra were overall dominated by the alkyl C region, representing aliphatic C. Explanations to the reported results might be substantiated in differences in tree species-specific structural effects, leaching characteristics or differences in the microbial community of the tree speciesÂ´ phyllosphere and cortisphere. However, the fact that throughfall DOM under beech showed the highest intensities of recalcitrant aromatic and phenolic C among all samples analyzed, likely points to a high alleleopathic potential of beech trees negatively affecting other organisms and hence ecosystem processes and functions.

Appendix C

Response of Al concentrations and speciation in soil solution to Ca amendment in a tropical montane forest in southern Ecuador

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C.1 Abstract

Soils of tropical montane forests frequently have low pH values and thus toxic Al might affect ecosystem functioning. However, toxicity of Al depends on Al speciation and concentrations of antagonistic ions like Ca^{2+} and Mg^{2+}. We analyzed organic layer leachate (LL) and mineral soil solutions (at the 0.15 and 0.3 m soil depths, SS15 and SS30) from four replicate plots of each of untreated control and $CaCl_2$ amendment at a rate of 10 kg ha^{-1} $year^{-1}$ of Ca. We determined Al, Ca, Cl^-, dissolved organic carbon (DOC), F^-, K, Mg, Na, ${NH_4}^+$, ${NO_3}^-$, pH, ${PO_4}^{3-}$, and ${SO_4}^{2-}$ concentrations and electrical conductivity (EC) to model Al speciation. Additionally, we determined free Al concentrations with the Donnan Membrane Technique (DMT). Modeled (mean ± SE: LL 0.56 ± 0.21 %; SS15 0.53 ± 0.25 %; SS30 0.87 ± 0.32 % of total Al are cationic Al species) and DMT-measured free Al concentrations (LL 0.68 ± 0.41 %; SS15 0.52 ± 0.20 %; SS30 0.93 ± 0.26 % of total Al are cationic Al species) showed good agreement. The degree of organic complexation of Al was very high (99.58 ± 0.09 %). The resulting very low free Al concentrations are not likely to affect plant growth. The concentrations of potentially toxic Al^{3+} increased with soil depth (0.00 ± 0.00 μmol L^{-1}, 0.01 ± 0.01 μmol L^{-1} and 0.25 ± 0.06 μmol L^{-1} in LL, SS15, and SS30, respectively), because of higher total Al and lower DOC concentrations in soil solutions. The Ca additions caused an increase of Al in LL, probably because Al^{3+} was exchanged against the added Ca^{2+} ions while pH remained constant. The total Ca:total Al molar ratios were close to 1 and sometimes < 1 which is usually interpreted as indication of the risk of Al toxicity. However, free ion ratios of Ca^{2+}:Al^{3+} were wide (mean ratio 374 ± 69), because of a much higher degree of organo-complexation of Al than Ca. We conclude that dissolved organic matter concentrations detoxify Al in acidic tropical forest soils.

Erklärung

gemäss Art. 28 Abs. 2 RSL 05

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Leiter der Arbeit: Prof. Dr. W. Wilcke

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Bern, den ....

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Martin Thilo Schwarz