UNIVERSITY OF HOHENHEIM

Faculty of Agricultural Sciences

Institute of Soil Science and Land Evaluation

Dept. of Soil Biology

Master Thesis

Exploring carbon dynamics on mineral surfaces under different management scenarios in temperate forests

submitted on 18 April, 2022

by Moritz Mainka, mat. no. 794066

to Prof. Dr. Ellen Kandeler (first corrector)

and Dr. Marion Schrumpf (external supervisor)

Abstract

Forest soils are key components of global biogeochemical cycles as they stabilize large amounts of C in soils. The stabilization capacity of forests, however, is also shaped by forest management practices. This study aims to disentangle the relationship of management- and soil-related factors with the formation of mineral-associated organic matter (MAOM), nutrient cycling, and nutrient limitations. Therefore, mineral containers filled with goethite and illite were buried at 5 cm depth in forests with different management intensity over a 5-year period. Laboratory analyses of organic carbon (OC), total nitrogen (TN), β-Glucosidase, N-Acetyl-β-D-Glucosaminidase, β-Xylosidase, acid phosphatase, and respective ecoenzymatic stoichiometries revealed highest MAOM formation (OC + TN) on goethite and lower ones on illite. The same pattern was found for abs. EEAs. In turn, higher normalized EEAs (by OC) were found in mineral containers (goethite > illite) compared to soils. Further, higher MAOM formation was found under spruce stands which indicates a higher importance of dissolved organic matter (DOM) fluxes compared to deciduous forests. The key drivers of MAOM formation in mineral containers were the C:N ratio of the surrounding soil, the soil pH, and also tree species composition. EEAs were more strongly affected by the SOC content. This study shows that forest management significantly influences the SOM dynamics in forests as the flux of DOM increases and soil pH decreases in coniferous stands. At the same time, the identity of the stabilizing mineral matters.

Acknowledgement

I would like to thank the Max-Planck Institute for Biogeochemistry in Jena and the team of Dr. Marion Schrumpf for allowing me to conduct laboratory experiments within the framework of the BEmins project at their facilities. Further, I would like to thank Prof. Dr. Ellen Kandeler as head of the Department of Soil Biology at the University of Hohenheim for being the first corrector of my thesis and Dr. Marion Schrumpf for being my direct supervisor and second corrector. I highly value the fruitful discussions and the helpful comments provided by Ingo Schöning and De Shorn Bramble that further contributed to an overall excellent learning opportunity.

Contents

Figures

Tables

1 Introduction

Forests ecosystems store between 45 to 80 % of global terrestrial carbon (C) (Winjum et al., 1992; Batjes, 1996; Jobbágy and Jackson, 2000; Bonan, 2008). Yet, they are globally under pressure due to climate change and an expansion of human activities into pristine areas (FAO and UNEP, 2020). The value of intact forest ecosystems to mitigate climate change bears a large potential (Bradford et al., 2013). However, the exact drivers regulating C dynamics in forests are not well understood (Aznar-Sánchez et al., 2018). The relationship between forest management and C dynamics remains a bone of contention in the research community since trade-offs between the aboveground and belowground C stocks occur depending on the management regime (Bradford et al., 2013). Higher aboveground C stocks related to fast-growing tree species for instance result in lower belowground C storage or deadwood (Mayer et al., 2020). Thus, both above- and belowground C stocks are affected by management-related disturbances (Jobbágy and Jackson, 2000; Pan et al., 2011).

The largest portion of C entering soils is adsorbed on reactive mineral surfaces and forms mineral associated organic matter (MAOM) that prevent decomposition of organic matter (OM) by microorganisms (Von Lützow et al., 2008; Schmidt et al., 2011; Lehmann and Kleber, 2015). The heterogeneity of mineral and organic compounds, as well as the competition of living organisms for MAOM, makes the mineral-OM interface one of the most relevant yet not completely understood aspects in contemporary soil science (Jilling et al., 2018; Kleber et al., 2021). The importance of inorganic mineral surfaces for structuring soil microbial community composition was recently demonstrated in temperate forests and grasslands (Uroz et al., 2009, 2011; Vieira et al., 2020a). Thus, the nature of these microhabitats bears the potential to affect C cycling and nutrient cycling in general (Uroz et al., 2016). This relationship gave rise to new *in-situ* experiments where mineral containers (in the present case filled with illite and goethite) were buried in soils under different forest managements for five years (Kandeler et al., 2019; Vieira et al., 2020a, b).

Therefore, this study aims to investigate the formation of MAOM (organic carbon (OC) and total nitrogen (TN)) on goethite and illite that were buried over a 5-year period in forest ecosystems with different management regimes. Moreover, changes in nutrient cycling and nutrient limitations were assessed through measuring extracellular enzyme activity of hydrolytic enzymes involved in SOM decomposition. In Chapter 2, the governing mechanisms and processes are examined in an extensive literature review that ultimately leads to the development of a conceptual framework and the formulation of research hypotheses. Chapter

3 explains the experimental design of the study, which data resources were used and which statistical methods employed. Chapter 4 describes the results of the measurements and is followed by Chapter 5 which interprets the outcomes and relates them to the research questions and hypotheses. Finally, a conclusion and outlook are provided in Chapter 6.

2 Literature review and conceptual framework

2.1 Forests as natural C sink

Temperate forests alone are estimated to store 119 ± 6 Pg C which equal 14 % of total forest C stocks (861 ± 66 Pg C; Pan et al., 2011). The global forest C stock stores 383 ± 30 Pg C (44 %) in soil organic carbon (SOC), followed by 363 ± 28 Pg C (42 %) in above- and belowground biomass, 73 ± 6 Pg C (12 %) in deadwood, and 43 ± 3 Pg C (5 %) in litter (see Table 1) (Pan et al., 2011). Yet, exact stocks and shares can vary across forest types (Fahey et al., 2011).

Soil carbon stocks and forest vegetation thereby represent the most important storage compartment of forest ecosystems since they consistently sequester carbon and thus offset anthropogenic greenhouse gas emissions (Gaudinski et al., 2000; Liski et al., 2002; Pan et al., 2011). Temperate forests in the northern hemisphere alone sequestered annually around 0.6-0.8 Pg C of 2.5-2.7 Pg C yr^{-1} on global scale (Goodale et al., 2002; Magnani et al., 2007; Pan et al., 2011; Le Quéré et al., 2014).

Table 1 : Data on global and temperate forest C stocks from Pan et al. (2011). The uncertainties for temperate forest were not provided for each compartment but only in general.

	Global forest C stock [Pg C]	Temperate forest C stock [Pg C]
Litter	43 ± 3	12
Biomass (above- and belowground)	363 ± 28	47
Soil C	383 ± 30	57
Deadwood	73 ± 6	3
Total C	861 ± 66	119 ± 6

2.2 Soil organic matter dynamics in forest soils

2.2.1 Input pathways

Living and dead OM build up the SOM stock. The OM originates from aboveground living and dead biomass such as plant tissues, i.e. leaves and woody parts, as well as bodies and faeces of

animals but also from root exudates, microbial bio- and necromass and other ground-dwelling organisms. The major aboveground input comes from plant litter and totals around 2-50 t C ha^{-1} (1-5 t ha^{-1} yr^{-1}) (Baldrian, 2017). However, the efficiency of litter incorporation into soils is low and most C is respired as CO_2 before entering the soil (Liebmann et al., 2022). Still, the overall importance of aboveground C input in forests is reflected in the low root-to-shoot ratios of temperate forests (~ 0.25) that indicates a much higher biomass aboveground than belowground compared to temperate grasslands for instance (~ 4.22) (Mokany et al., 2006; Ye et al., 2021). The root-to-shoot ratios are however also influenced by stand characteristics and management practices which can be determined by the specific tree species (Pérez-Cruzado et al., 2012; Purahong et al., 2014; Shanin et al., 2014).

The C stocks are further supplied by belowground C inputs as trees allocate photosynthates to their roots to sustain their water and nutrient supply and to gain mechanical stability. There are multiple exchanges between plant roots and the microbiome in the soil matrix that lead to substantial belowground C input through root exudates, rhizodeposits, microbial bio- and necromass (Hari et al., 2013). The belowground C input thus is central to the formation of stable SOC stocks in temperate forests whereas aboveground sources help to maintain high stocks (Bowden et al., 2014).

2.2.2 Accumulation processes

In theory, the accumulation rate of C in soils equals the rate of C input subtracted by the C losses (Olson, 1963). Carbon that enters forest soils accumulates in two compartments: the forest floor and the mineral topsoil that are equivalent to the O and A horizon. Radiocarbon measurements showed that O (equals forest floor) and A horizons (mineral topsoil) in a two-century-old forest succession patch stored most C with turnover times between 40 to over 100 years (Gaudinski et al., 2000).

Aboveground C accumulates in the first place in the forest floor compartment. In boreal and temperate forest ecosystems the C accumulation in forest floor is highest (compared for instance to tropical forest ecosystems) (Vogt et al., 1995). Slower C turnover in cooler climates favours the accumulation of litter in the forest floor (Trumbore et al., 1996; Davidson and Janssens, 2006; Tewksbury and Van Miegroet, 2007). The forest floor C accumulation also depends on litter chemistry which in turn is determined by the dominant tree species (Pérez-Cruzado et al., 2012; Purahong et al., 2014; Shanin et al., 2014). Coniferous forest stands tended to accumulate more C in the forest floor compared to broadleaved forest stands (Schulp et al., 2008; Shanin et al., 2014). The wider C:N ratio of coniferous needles (40-80) constrained the decomposition

relative to leaf litter of beech trees (30-50) (Albers et al., 2004; Wu et al., 2011; Kögel-Knabner, 2018). On the contrary, narrower litter C:N ratios also favour the incorporation of litter into SOC stocks (Zhou et al., 2019). Narrower litter C:N ratios have also been reported in more diverse stands that exhibited higher SOC stocks on the large scale (Li et al., 2020). This is complemented by the observations that litter decomposition is faster in older forest stands (Albers et al., 2004; Zhang et al., 2020). Through litter decomposition, dissolved organic carbon (DOC) is released. Chemical analyses of DOC showed differences regarding DOC concentrations and pH values in dependence of tree species identity. Under Norway spruce (*Picea abies*) highest DOC concentrations but also lowest soil pH values were found (Strobel et al., 2001) (see Section 2.4.1).

Next to DOC flows from the forest floor, litter is subsequently incorporated into the mineral soil through bioturbation. Litter-dwelling (epigeic) and burrowing (endogeic) earthworms in acidic temperate forest ecosystems play crucial roles in incorporating forest floor C into the mineral soil. Thereby, these organisms are affected by the nutrient content of litter but also enhance the habitat conditions in topsoils in their favour by increasing the soil pH through litter incorporation (Desie et al., 2020). In addition, evidence from laboratory experiments with artificial soils showed that C transport at hotspots of microbial activity (and consequently decomposition) may also occur along fungal hyphae (Vidal et al., 2021).

The important contribution of leaf litter to the forest floor C stocks and subsequently to the mineral soil C is accompanied by belowground C inputs which enter the soil directly through root activity or root senescence. The importance of root C to SOC stocks is high since root C is stabilized more easily in the soil matrix (Rasse et al., 2005). A manipulative experiment quantified the higher efficiency to be 2 to 13 times higher compared to litter inputs in forming stable SOC (Sokol et al., 2019). The importance of root-derived C inputs may be even higher for subsoil C accumulation (Tefs and Gleixner, 2012).

2.2.3 Formation of mineral-associated organic matter

Mineral surfaces interact with the organic phase and form mineral-associated OM (MAOM) which becomes either physically protected within aggregates or chemically protected against microbial decomposition when sorbed on mineral colloids (Six et al., 2002; Kögel-Knabner et al., 2008; Schmidt et al., 2011; Lehmann and Kleber, 2015). The fate of SOM (OC + TN) therefore relies on three components: the amount and composition of OM entering soils, the desorption and decomposition activity, and the properties and amount of mineral surfaces available to form MAOM (Cotrufo et al., 2015).

The SOM composition can be differentiated based on the chemical or molecular structure as well as by the energetic signatures (Barré et al., 2016). Persistent OM which constitutes MAOM was found to be less related to molecular structures but highly related to energy content that was measured as energy release during combustion of OM (Barré et al., 2016; Williams et al., 2018). MAOM is thus characterized by longer mean residence times, higher radiocarbon ages, and narrower C:N ratios (Torn et al., 1997; Baisden et al., 2002; Basile-Doelsch et al., 2005; Kaiser et al., 2016). Narrower C:N ratios were also reported for microbial biomass suggesting that not only plant- but also microbially-derived OM is frequently attached to mineral surfaces (Chenu and Stotzky, 2002).

Microbial-derived SOM found in MAOM is preferentially fixated in the fine silt and clay texture fractions (Han et al., 2016). However, there is no uniform type of SOM that exclusively associates with mineral surfaces (Wagai et al., 2009) and the dependence on mineral surface and soil properties may be the overriding factor in different ecosystems (Han et al., 2016). In forests, tree species composition controls the composition of SOM and thus potentially affects the formation of MAOM (Quideau et al., 2001). However, the differences in dissolved organic matter (DOM) which carries the material that eventually attaches to mineral surfaces did not differ in composition in mineral soils (Kalbitz et al., 2005; Thieme et al., 2019). The transformation of DOM in mineral soils is linked to microbial activity that transforms it (Kaiser et al., 2002).

The importance of MAOM increases with soil depth as with increasing depth the share of litter-derived OM decreases (Schrumpf et al., 2013; Jackson et al., 2017). Further, the reduced influence of root exudates that mobilize sorbed OM in the main rooting zone via addition of labile OM input may play a role (Keiluweit et al., 2015; Jilling et al., 2018). Lower soil pH values that are frequently observed in the rhizosphere may in turn contribute to increase sorption capacity and strength especially on iron oxides (Strahm and Harrison, 2008; Kleber et al., 2015). Conversely, the strength of MAOM binding decreases at higher pH values which in turn increases the turnover of OM (Kleber et al., 2015).

Organic matter attached to mineral surfaces, especially clays and pedogenic oxides, forms MAOM (Gu et al., 1994; Barré et al., 2014; Schrumpf et al., 2021). In general, mineral properties, i.e. surface charge or specific surface area determine the potential to form MAOM (Kaiser and Guggenberger, 2003). These mineral properties are strongly related to the degree of weathering and soil age (Mikutta et al., 2009; Kramer et al., 2012; Doetterl et al., 2018). Soil pH is driven by precipitation and evapotranspiration patterns (Slessarev et al., 2016) and

explains global patterns of MAOM protected by pedogenic oxides (Kramer and Chadwick, 2018). The association of OM with pedogenic oxides is strongest in acidic soils and occurs via ligand exchange reactions. Further, the soil texture plays a key role in stabilizing OM since adsorption of OM occurs on clay minerals with permanent negative charge or by weak associations via van der Waals forces (Lehmann and Kleber, 2015; Kögel-Knabner, 2018; Kleber et al., 2021).

2.2.4 Mineralosphere

Only recently the notion of minerals as inert components of the soil matrix was revised and with this the importance of mineral surfaces for soil microbial communities (Uroz et al., 2012; Vieira et al., 2020a) and multiple ecological processes such as the supply of plants with inorganic nutrients (Uroz et al., 2015) or the storage of OM in soils (Singh et al., 2018; Gartzia-Bengoetxea et al., 2020). For that, the nutrient content, dissolution rates, and weatherability of mineral surfaces play a crucial but poorly understood role (Ahmed et al., 2017; Carson et al., 2007; Uroz et al., 2009, 2015). To better understand which processes occur on mineral surfaces, studies that target the *mineralosphere* have received increasing attention (e.g. Uroz et al., 2015; Vieira et al., 2020a).

Clay minerals are recognized as key factors for SOM stabilization and MAOM formation in soils (Oades, 1988). Illite is a main clay mineral of central European soils and contributes to SOM stabilization. It is characterized by having a lower CEC and smaller specific surface area compared to expandable 2:1 clay minerals (e.g. smectite) but still offers a higher stabilization potential compared to 1:1 clay minerals (Hassink, 1997; Wiseman and Püttmann, 2005; Singh et al., 2018, 2019). The formation of mineral-organic associations by clay minerals was shown for overall C stocks but also for specific fractions such as DOC (Kahle et al., 2003). However, the pivotal role of iron oxides is also increasingly recognized (Rasmussen et al., 2018; Kramer and Chadwick, 2018).

Next to clay minerals, iron oxides are central for the formation of MAOM (Kramer et al., 2012). Goethite (α-FeOOH) is an iron oxide that plays a central role in SOM stabilization and is well studied (Liu et al., 2014). The binding capacity of goethite is mostly electrostatic but ligand exchange may also occur to a certain extent. The sorption depends on the soil pH. Low pH values increase the sorptive capacity in dependence of the OM compound. High pH values decrease the sorption capacity (Liu et al., 2014). In addition, the sorption on goethite can be enhanced as it promotes the formation of microaggregates and thereby greatly enhances OM stabilization (Saidy et al., 2013; Jeewani et al., 2021; Zhu et al., 2022). An interesting aspect of

goethite as potential stabilizator of OM is that it associates with phosphate in a strong manner (Liu et al., 2014). However, phosphate additions to soils have recently been shown to increase desorption of MAOM (Spohn et al., 2022). Thus, the potential for MAOM may be reduced by the phosphate presence in proximity to goethite.

2.2.5 SOM decomposition and ecoenzymatic stoichiometry

SOM is subject to continuous decomposition through microbial activity. In order to take up nutrients or energy sources, extracellular enzymes destinated to cleave macromolecules need to be produced (Sinsabaugh and Moorhead, 1994) (see Chapter 2.3). Yet, the synthesis of extracellular enzymes requires resources and must therefore be adapted to the nutrient availability. Thus, the microbial metabolism is moderated by nutrient limitations and energy balances that are coupled with habitat conditions.

First evidence for regularities in the nutrient ratios of organisms (stoichiometry) was found in marine ecosystems (Redfield, 1960). Since then many theories around the interactions and dependencies between nutrients in ecosystems were postulated (Zechmeister-Boltenstern et al., 2015). They have in common that multiple chemical cycles, e.g. the C, N, and P cycles, are coupled (Sterner and Elser, 2003). In terrestrial ecosystems the impact of stoichiometry on ecosystem processes is not easy to disentangle since many factors covary. For instance, the litter nutrient ratios (C:N, C:P, N:P) are correlated with litter C quality (lignin content) and structural traits (e.g. tissue density or surface-to-volume ratios) (Zechmeister-Boltenstern et al., 2015). However, soil properties such as texture and moisture that determine habitat conditions also contribute to soil nutrient stoichiometries (Tian et al., 2018).

The stoichiometric theory provides an excellent foundation for developing concepts of microbial ecology since microorganisms require both N and P to build up their biomass and to decompose plant detritus through extracellular enzymes (Prosser et al., 2007; Zechmeister-Boltenstern et al., 2015). For instance initial growth of microbial r-strategists after labile C (glucose) addition to soils immobilized N and promoted the growth of microbial K-strategists that in order to overcome the N limitation fed on r-strategist's necromass (Cui et al., 2020). The high investment in N- and P-acquisition relative to the more readily available energy sources (C) leads to the regulation of microbial growth and OM turnover by nutrient availability. Consequently, similar behaviour of C:N and C:P ratios compared to the N:P ratio are observed (Zhang et al., 2008; Zechmeister-Boltenstern et al., 2015). However, the stoichiometric effects are smaller compared to the direct impact of overall nutrient limitations as a driver of microbial activity and C cycling (Zechmeister-Boltenstern et al., 2015).

In forests, OM accumulates based on above- and belowground inputs. Both differ between tree species and strongly impact the microbial communities and thus C and nutrient cycling rates at all scales (Bell et al., 2014; Mooshammer et al., 2014; Buchkowski et al., 2015; Zechmeister-Boltenstern et al., 2015; Zhou et al., 2020). Litter decomposition is driven by initial N content of leaves (Parton et al., 2007; Manzoni et al., 2008), the C:N ratio, pH values and tree species identity (Prescott and Grayston, 2013; Zhou et al., 2019).

Reportedly, litter of coniferous trees is decomposed at slower rates than litter of broadleaved trees (Kögel-Knabner, 2018; Prescott and Grayston, 2013). The fate of N and P in litter is further determined by the C use efficiency (CUE) of microorganisms which in turn is governed by C to nutrient (N, P) ratios (Manzoni et al., 2010; Sinsabaugh et al., 2013). High initial C:N and C:P ratios result in lower CUE which then increases as C to nutrient ratios decrease. Viceversa, low C:N and C:P ratios result in C limitations and thus low N and P use efficiency (Zechmeister-Boltenstern et al., 2015). In temperate and boreal ecosystems, modelling suggests that nutrient immobilization is more efficient through incorporation into microbial biomass compared to the tropics (Manzoni et al., 2010).

Similarly to leaf litter, root exudates were shown to be of paramount importance in SOC decomposition processes. In analogy to leaf litter, the stoichiometry of rhizodeposits is also of high importance for microbial activity and thus nutrient cycling (Jones et al., 2009; Bardgett et al., 2014; Finzi et al., 2015; Meier et al., 2017). For instance, low N root exudates reinforce N limitation of microorganisms which in turn constrains microbial activity (Drake et al., 2013; Wild et al., 2017).

2.3 Extracellular enzyme activity

2.3.1 Enzyme function and regulation

Microorganisms and plants produce intra- and extracellular enzymes that are mediators of biochemical transformations of organic compounds which in turn provide energy for the microbial metabolism (Burns, 1977; Rao et al., 2014, 2017). Intracellular enzymes occur in living and dead microbial biomass and are responsible for the lysis of small molecules to sustain the metabolism of organisms (Rao et al., 2014). To cleave molecules to a size that allows for the passing of the cell wall, microorganisms produce and excrete extracellular enzymes that cleave larger macromolecules.

We distinguish oxidative and hydrolytic enzymes. Oxidative enzymes (e.g. phenol oxidases, peroxidases, dehydrogenases) are involved in the breakdown of lignin (also ligninases) (Burns

et al., 2013; Rao et al., 2017). Fungi and their enzymatic products, fungal laccases, are the main responsible organisms in the breakdown of lignin compounds at least at early decomposition stages (Baldrian, 2006; Baldrian et al., 2010). Oxidative enzyme activities, however, vary considerably over space and time (Sinsabaugh, 2010) but may play a key role as they facilitate the accessibility of hydrolytic enzymes to polysaccharides (Talbot et al., 2012). Hydrolytic enzymes comprise a broad range of enzymes that cleave different organic compounds (Rao et al., 2017). Hydrolytic enzymes therefore play an important role in the acquisition of nutrients (N and P) for microorganisms. For instance, they cleave chitin (from insect and fungal cell walls) via N-acetyl-β-Glucosaminidase which is a key source of N for microorganisms. Further, acid and alkaline phosphatase contribute to P acquisition (Eivazi and Tabatabai, 1977; Shi, 2011).

Why microorganisms invest 1-5 % of the assimilated C and N (Schimel and Weintraub (2003) calculated a minimum of 2 % to sustain microbial biomass) in the production of extracellular enzymes was extensively discussed in the scientific community (Frankena et al., 1988; Burns et al., 2013). To date, there is an emerging consensus that microorganisms release more extracellular enzymes to overcome nutrient limitations since they provide a relatively low-cost and efficient tool to cleave organic macromolecules for ingestion (Frankena et al., 1988; Sinsabaugh and Moorhead, 1994; Allison et al., 2010; Burns et al., 2013). Conversely, as microorganisms strive to maximize the cost-benefit balance, resources are mostly allocated to nutrients that are not available instead of investing more in readily available nutrients (Tiemann and Billings, 2011). This relationship was observed in experiments on inorganic P availability (Olander and Vitousek, 2000) and on ecosystem scales as the economic principle explained the variation of enzyme activities from N- (temperate) to P-limited (tropical) ecosystems (Zhou et al., 2020). Therefore, extracellular enzyme activities (EEA) and ecoenzymatic stoichiometries (ratios of EEAs) can serve as a proxy for the nutrient availability and enable the inference on decomposition processes across different sites (Olander and Vitousek, 2000; Sinsabaugh and Moorhead, 1994).

However, overall EEAs are strongly determined by the general (organic) substrate availability (Hendriksen et al., 2016). In scarce (nutrient) environments with low OM contents, the allocation of resources to produce enzymes may be constrained (DeForest et al., 2012). The conception of economic calculations responsible for enzyme production appears valid in most circumstances. However, the long-term stabilization of enzymes on mineral surfaces might lead to legacy effects that result in high EEAs despite the demand for the specific nutrient is already

met (Allison et al., 2007a, b). An example for such a case were the generally high EEAs that were observed after the end of the vegetation period in temperate to arctic environments (Weintraub and Schimel, 2005; Wallenstein et al., 2009; Kramer et al., 2013). Thus, measurements of EEA require a careful assessment of potential factors that may bias the measurements (Nannipieri et al., 2018).

2.3.2 Enzymes on minerals

Extracellular enzymes or exoenzymes are either free or bound to soil colloids (organic or mineral surfaces) (Burns, 1977, 1982; Burns et al., 2013). When extracellular enzymes are attached to colloids, their activity and longevity is altered (Gianfreda and Bollag, 1994). The present study focussed on the impact of mineral-organic interactions on EEA that tie back to the mineralosphere concept (see Section 2.2.4). The influence of the mineralosphere on enzyme activities still requires more attention since the mineral surface type bears the potential to alter microbial community composition and thereby potentially affects nutrient and biogeochemical cycles (Uroz et al., 2012, 2015; Ahmed et al., 2017; Jilling et al., 2018).

In spite of extracellular enzymes being considered short-lived compounds, EEA were found to maintain their activity in more than 9,000 years old permafrost samples (Skujins and McLaren, 1969). The prolonged activity of enzymes is enabled due to attachment of enzymes on mineral surfaces which increase the thermal stability and longevity but may decrease the activity (Skujiņš et al., 1974; Sarkar et al., 1989; Gianfreda and Bollag, 1994; Rao et al., 2000; Allison, 2006). Allison (2006) reported slower enzyme turnover times in a 21-day incubation with added allophane and ferrihydrite minerals and an inhibitory effect after adding humic acids. The increased duration of activity can be substantial. In an incubation experiment with laccases, tyrosianse, acid phosphatase, and β-D-Glucosidase, free enzymes were inactivated within 15 days while the enzymes attached to clay minerals retained 75 to 85 % of their initial activity over the same time period (Sarkar et al., 1989). Similarly, Rao et al. (2000) reported higher residual activity of enzymes after immobilization on mineral or organic surfaces but also observed different catalytic behaviour since the activity increased when attached to OH-Al species clays (i.e. montmorillonite). Also recent publications with similar experimental evidence from laboratory measurements found a positive effect of clay and iron oxides on enzyme longevity and activity (Olagoke et al., 2019, 2020).

The attachment of enzymes on mineral surfaces can lead to conformational changes that affect the functionality and were attributed to electrostatic forces that, however, act in dependency of the pH (Quiquampoix, 1987a, b; Leprince and Quiquampoix, 1996). They found three ways of

interaction: (i) high attraction of enzyme and mineral surface can lead to a strong adsorption that may negatively affect the catalytic activity of the enzyme, (ii) regular adsorption can lead to a positive effect through protection, and (iii) similarly charged enzymes and minerals can repulse each other. This holds especially true for iron oxides such as goethite with a pH-dependent charge and less for constantly negatively charged clay minerals (e.g. illite). Further, the variable charges of enzymes need to be taken into consideration. Enzymes are negatively charged at high pH values and positive at low pH values (Leprince and Quiquampoix, 1996).

2.3.3 Limitations of enzyme activity measurements

The method of EEA measurements is not trivial and many limitations must be taken into consideration to avoid overinterpretation of measurements (Nannipieri et al., 2018). Enzyme activity measurements are frequently used to determine the rate of biogeochemical cycles. However, the measured enzymes only represent a small share of the broad range of enzymes involved in the cycling of certain macronutrients, and the measurements are not actual but potential enzyme activities (Nannipieri et al., 2012, 2018). Consequently, direct conclusions on the velocity of nutrient cycles cannot be drawn and caution must be taken when interpreting such results without complementary measurements.

Moreover, the measured potential EEAs only cover a small fraction of all microbial functions and activities present in soils. Therefore, it is misleading to state that enzyme activities equal microbial activity (Nannipieri et al., 2018). Furthermore, there is a time lag due to the preservation of enzymes on mineral surfaces that introduces a bias to the enzyme activity measurements (*abiontic enzymes*) as well as it is not possible to differentiate between intra- and extracellular enzyme activities (Nannipieri et al., 2018).

2.4 Forest management and SOM dynamics

Forest management regulates the size of the aboveground forest biomass and consequently the potential of temperate forest ecosystems to bind C from the atmosphere and to allocate it to the belowground compartments (Jandl et al., 2007; Luyssaert et al., 2007; Bellassen and Luyssaert, 2014).

2.4.1 Tree species selection

The main distinction in managed temperate forests is related to the tree species composition which can be either broadleaved or deciduous tree species (here *Fagus sylvatica*/European beech) and coniferous tree species (here *Picea abies*/Norway spruce). Broadleaved trees produce leaf litter with narrower C:N ratios that has faster turnover times compared to

coniferous needle litter (Mayer et al., 2020). Conversely, needle litter found under coniferous stands provide worse conditions for litter decomposition and favour the accumulation of forest floor C compared to broadleaved stands as they have wider C:N ratios and lower pH (Prescott and Grayston, 2013; Maes et al., 2019). The poorer litter quality further hampers the activity of the soil macrofauna thereby decreasing the incorporation rates into soils (Walmsley et al., 2019; Desie et al., 2020). Thus, mineral soil stores more C under broadleaved stands which is favoured by the faster incorporation of litter into the mineral soil (Wiesmeier et al., 2013; Boča et al., 2014; Augusto et al., 2015). Concomitant with the accumulation of C in the mineral soil and thus in MAOM, the C stability increases (Wiesmeier et al., 2013).

Still, other important factors contribute to SOC storage under specific stands. The belowground fluxes of C are still not well understood (Mayer et al., 2020). Further, larger SOC stocks were found in topsoils of tree species associated with ECM fungi, while trees associated with AM fungi had larger C stocks in 10-100 cm depth (Craig et al., 2018). Finally, the total C stocks (forest floor + mineral soil) do not differ among broadleaved and coniferous stands (Boča et al., 2014; Mayer et al., 2020). Thus, it is difficult to draw conclusions on the effect of tree species on SOC stocks when only focussing on one compartment of the C cycle (Mayer et al., 2020). The faster growth of coniferous trees (under favourable nutrient and moisture conditions) may offset increased SOC stocks under broadleaved stands (Augusto et al., 2014). Moreover, the soil- and site-specific properties may play a crucial role since tree-growth limiting nutrient conditions in soils may decrease overall C accumulation independently of the tree species (Ribbons et al., 2018).

2.4.2 Stand density and thinning

Theoretically, higher stand density and consequently higher basal area should increase litterfall and C input into soils thereby increasing SOC stocks (Mayer et al., 2020). Multiple field studies that addressed this issue mostly focused on afforested stands (Laganière et al., 2010; Zhou et al., 2013; Bravo-Oviedo et al., 2015). Regarding thinning, a recent meta-analysis found SOC stocks to increase at low thinning intensities (by 17 %), to remain stable at moderate intensities, and to decrease in intensively thinned plots (by 8 %). However, the observed increases occurred mainly in the first two years after thinning and after that no significant differences between control and thinned stands could be detected (Zhang et al., 2018). The initial increase of C stocks goes along with increased CO_2 respiration after thinning that might be a consequence of more favourable microclimatic conditions (Vesterdal et al., 1995). In general, forest floor C

was more negatively affected by thinning activities compared to mineral soil C which was only affected at intensive thinning sites (Achat et al., 2015).

The overall neutral effect of thinning activities on C stocks is likely more influential for the aboveground biomass since thinning increases the stand stability (Bravo-Oviedo et al., 2015). The selective removal of tree species may further affect the stoichiometry of litter or SOC and thus the decomposability by microorganisms (Mooshammer et al., 2014; Zechmeister-Boltenstern et al., 2015). However, it is difficult to disentangle the single aspects of forest management since many processes happen simultaneously or depend on each other and large site-specific uncertainties are associated to the isolated parameters or measures (Clarke et al., 2015). Since the fate of SOC in mineral soils interacts with multiple spheres, the results of studies assessing the effect of forest management on SOC stocks are often multidirectional and complex (Mayer et al., 2020). Therefore, despite the wealth of studies, often contradictory results prevail and clear conclusions cannot be drawn. Hence, composite measures of forest management were developed to account for the multiple co-occurring processes.

2.5 Measures of forest management intensity (SMI, ForMI)

Despite the importance of forest management on a broad range of ecosystem services (Felipe-Lucia et al., 2018), it remains elusive to quantify forest management intensity (Gossner et al., 2014). Unlike grasslands where fertilization, mowing, and grazing activities largely cover the management intensity (Blüthgen et al., 2012), the development of a similar system in forest ecosystems is more complex. Many different approaches have been developed that determined naturalness (hemeroby) (e.g. Luyssaert et al., 2011), disturbance (e.g. Seymour et al., 2002; Kohv and Liira, 2005), or management-related aspects (e.g. Zenner et al., 2006; Haberl et al., 2007; Bell et al., 2008) as determinants (see also Schall and Ammer, 2013). Still, a satisfying solution has not been found so far since often a sound ecological foundation is lacking (Luyssaert et al., 2011). One promising approach to quantify management intensity in temperate forests is discussed in greater depth.

The Silvicultural Management Intensity index (SMI) is composed of two components, namely a risk indicator (SMIr) and a density indicator (SMId) which are both derived from data on species composition, stand age, and aboveground biomass (living and dead) in relation to the forest management practices in place (Schall and Ammer, 2013). The SMIr determines the risk of a stand loss before a stand reaches a tree-species specific reference age. It uses the probability of a stand loss that was calculated for the main tree species of Central Europe (Staupendahl and Möhring, 2011; Staupendahl and Zucchini, 2011). The stand loss probability only covers

calamities (wind throw, snow break) excluding natural decay of trees. The risk component is highest for Norway spruce, followed by Scots pine, sessile and pendulate oak, and European beech. Stands with ages above 180 years obtain a SMIr of 0. Hence, a diverse tree species composition and a high stand age lowers the risk of a stand loss and decreases the SMIr (Schall and Ammer, 2013).

The SMId also builds upon the self-thinning relationship and represents the deviation of basal area G of a stand to the natural basal area (G_{nat}) that were calculated in previous studies (Assmann and Franz, 1965; Pretzsch, 2009). The assessment by Assmann and Franz (1965) however was done only for a small geographic area (Bavaria). Later assessments by Spellmann et al., (1999) and Döbbeler and Spellmann, (2002) were based on more diverse study areas and used a more sophisticated approach that estimates G_{nat} based on the relationship between dominant height of a stand, quadratic mean dbh, and stand density (Sterba, 1987). G_{nat} can then be derived using site index curves as in Pretzsch (2009). For uneven-aged stands, comparable reference sites might be used to determine G_{nat} (Schall and Ammer, 2013).

2.6 Conceptual framework

Forest soils are key components of global biogeochemical cycles as they stabilize large amounts of C in soils. The stabilization capacity of forests however is also shaped by forest management practices. This study aims to disentangle the relationship of management- and soil-related factors with the formation of mineral-associated organic matter (MAOM), nutrient cycling, and nutrient limitations (see Figure 1). For that, the present study assessed OC and TN contents, the C:N ratio, absolute and normalized (by OC content) extracellular enzyme activity (EEA_{abs} and EEA_{norm}), and ecoenzymatic stoichiometries (C:N, C:P, N:P) on bulk soil and in mineral containers that contained either a sand-goethite or a sand-illite mixture and were buried in forest topsoils under different management intensities for five years.

The study followed a three step approach. In a first step, the importance of mineral type (goethite vs. illite) for the formation of MAOM, nutrient cycling (EEA_{abs} and EEA_{norm}), and nutrient limitations (ecoenzymatic stoichiometries) was assessed relative to the bulk soil. Significantly lower OC and TN contents were expected to be stabilized in mineral containers since the mesh bags containing the sand-mineral mixtures represented a much higher share of inorganic mineral surfaces than the bulk soil. Further, important processes such as bioturbation, root deposition and aggregation were excluded in this experiment. Thus, OM input was limited to mostly DOM. This type of input was expected to be more strongly decomposed and thus have lower C:N ratios. The limited amount of SOC on minerals were expected to decrease the

EEA_{abs} in minerals relative to the surrounding soils. EEA_{norm} were expected to increase since the mineral surfaces prolong the longevity and in parts the activity of enzymes when attached to mineral surfaces. It was further expected that ecoenzymatic stoichiometries became wider since the mineralosphere (mimicked through the mineral containers) represented a C-limited environment.

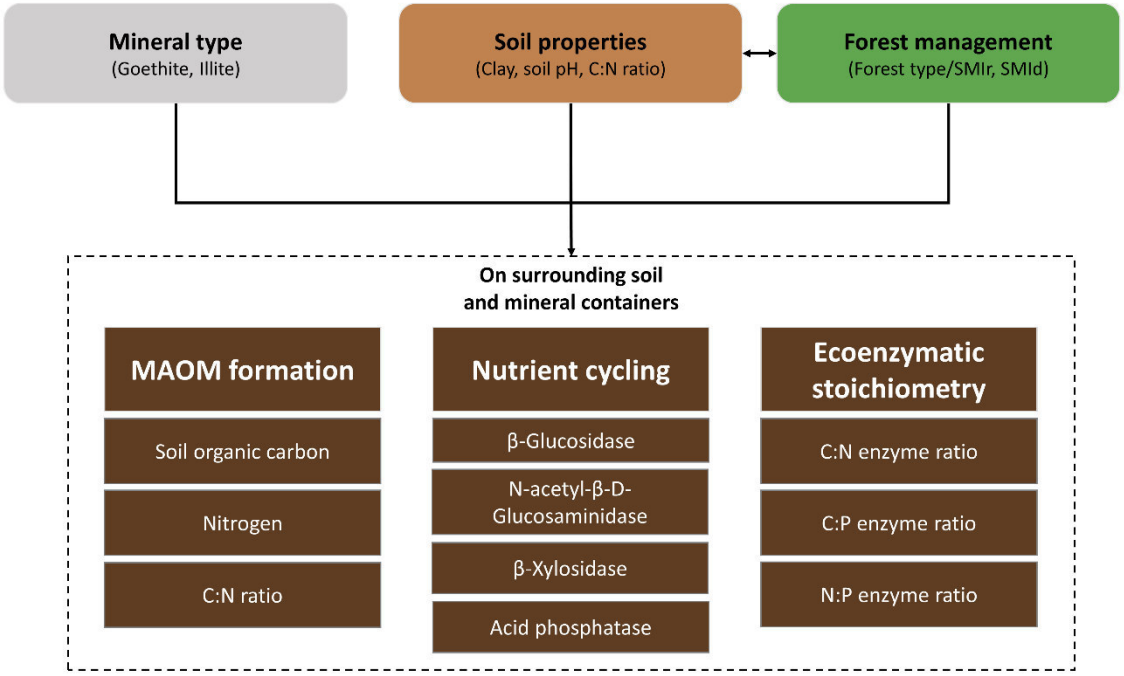

Figure 1 : Conceptual framework to explain which influences (mineral type, soil properties, and forest management) are assessed to explain differences in MAOM formation, nutrient cycling and ecoenzymatic stoichiometries on surrounding soils and mineral containers.

The second step focussed on the effects of forest type (deciduous vs. coniferous) on the formation of MAOM, nutrient cycling, and nutrient limitations. In deciduous forests, more C was expected to accumulate in the mineral soil since the C:N ratio of litter was more narrow and litter pH was more favourable for faster decomposition rates following enhanced microbial growth conditions. Hence, it was hypothesized that under deciduous forests, more OC and TN would be found in both mineral soil and mineral containers. The C:N ratio was expected to be narrower under deciduous forest. Concomitant with this, higher EEA_{abs} and EEA_{norm} values were expected under deciduous forests for both soils and mineral containers since nutrients (N and P) were less available. Enzyme stoichiometries were expected to be narrower under coniferous forests since the N- and P-mining gained important in the microenvironments with slow decomposition rates and consequently low nutrient release rates.

The third step assessed the influence of selected forest management-related (SMIr and SMId) in conjunction with soil-related variables (soil pH, clay, SOC, soil C:N) on the target variables.

It was expected that more intensive management (higher SMIr and SMId) negatively affected the formation of MAOM due to lower SOC and TN stocks in the surrounding mineral soil. With this, nutrient cycling and nutrient availability were expected to decrease due to wider C:N ratios. High clay content was expected to increase the formation of MAOM and EEA in bulk soil and minerals since it was linked to lower C:N ratios and higher microbial biomass. Lower soil pH was expected to positively affect the formation of MAOM on goethite, as goethite became positively charged and thus increased its binding capacity with OM. On the other hand, illite mineral surfaces were expected to be less affected by soil pH, as they had a lower variable charge and conversely depended more on overall SOC in the surrounding soil. Wider soil C:N ratios were expected to increase the formation of MAOM and thus nutrient cycling since higher DOM flow reached mineral containers. Concomitant with this, the mineral containers were expected to become more nutrient limited as the quality of the DOM decreased.

3 Methods

3.1 Study area

The study area is located in the Biosphere reserve Swabian Alb (~ 422 km²) in the state of Baden-Württemberg in Southwestern Germany and part of the long-term multidisciplinary research project "Biodiversity Exploratories" (Fischer et al., 2010). The study of Fischer et al. (2010) described the site conditions as following. Climate is cool temperate (MAT: 6-7 °C, MAP: 700-1000 mm). The 50 forest plots at the Swabian Alb are located between 460 and 860 m a.s.l. The vegetation cover differs due to forest management regimes from managed Norway spruce-dominated (Picea abies, n = 12) or European beech-dominated (Fagus sylvatica, n = 33) forest to unmanaged European beech-dominated forests (Fagus sylvatica, n = 5). The soils are clayey and developed on Jurassic shell limestone with karst phenomena. The two soil types found in the study area were classified as Leptosols (n = 35) and Cambisols (n = 15). Next to geology, inclination is an important factor. Leptosols are predominantly found at steep slopes.

3.2 Mineral container properties

The mineral containers buried within the scope of the experiment were composed of two meshes (mesh width: 50 µm) that were fixed by two steel rings. The mesh size was chosen in order to prevent the loss of material while inhibiting root in-growth. The bags were filled with a mix of calcined sea sand (sieved at 63 µm) and two types of minerals that are commonly found in (Central European) soils: goethite and illite.

Goethite (α-FeOOH, surface area: 40-90 $m^2\ g^{-1}$, charge: 0 to 0.15 $nmol_c\ g^{-1}$) is a very stable iron oxide commonly found in all soils due to its high stability (Kleber et al., 2021). Illite is a clay mineral that is among the globally most abundant minerals in soils (surface area: 20-200 $m^2\ g^{-1}$, charge: -0.16 to -0.22 $nmol_c\ g^{-1}$) (Meunier and Velde, 2004; Kleber et al., 2021). It is a 2:1 layer phyllosilicate that is characterized by K^+-ions attached at the inner surfaces between the silicate layers which results in less negative charges and inhibits the characteristic swelling observable in other 2:1 layer type minerals, such as smectite or vermiculite (Kleber et al., 2021). Both minerals differ in densities. Thus to ensure that the same volume of minerals relative to sand is contained in each mineral bag, the mixing ratio was adapted. The sand-goethite mixture was composed of 12 g of sand and 12 g of goethite. The sand-illite mixture contained 33 g of sand and 12 g of illite. In this study, no correction factors for the respective pure mineral content were employed since it cannot be ruled out that the sand fraction was not colonized by microorganisms or accumulated to a certain extent OM (Marx et al., 2005).

3.3 Experimental design

At the Swabian Alb, the Biodiversity Exploratories maintain 50 experimental plots (EPs) in forests with a size of 100 x 100 m. On these EPs, mineral containers were buried for five years (2015-2020) on 1 x 1 m patches. In total, 10 mineral containers (5 for each sand-mineral mixture) were buried at 5 cm depth and over a length of 80 cm. A distance of 50 cm was kept between the sand-goethite and sand-illite containers at each EP. In addition to the mineral containers, the immediately surrounding soil was collected for further analysis in the laboratory. Mineral containers and soil samples were stored at -20 °C.

3.4 Laboratory methods

3.4.1 Elemental analysis

The subsamples for the elemental analysis were ground prior to be measured. Freeze dried mineral samples were ground with mortar and pestle, soil samples were dried at 40 °C and ball milled at a rotation frequency of 25 rotations per second for 3 min with zirconium oxide balls in a Mixer Mill MM 400 (Retsch GmbH, Haan, Germany). The elemental analysis was done with a VarioMAX cube (Elementar Analysensysteme GmbH, Langenselbold, Germany). Total C, total N (TN), and inorganic C concentration of the samples were measured by dry combustion. Prior to measure the inorganic C, samples were burnt at 450 °C for 16 hours to remove organic C (OC). SOC was then calculated as the difference from total C and inorganic C. TC in the mineral containers was taken as SOC since the inorganic C content was negligible.

In addition, measurements were corrected for the water content of the air-dried samples by determining the dry matter content at 105 °C for 24 hours.

3.4.2 Multiplate fluorometric enzyme assays

In the present study, we followed a flurometric approach based on 4-methylumbellyferone (MUF) were developed (Pancholy and Lynd, 1972). The flurometric approach using MUF is suitable when using microplates (Marx et al., 2001; Deng et al., 2013). The MUF-based fluorometric microplate assay was used to determine the potential activity of four hydrolytic enzymes, namely β-Glucosidase (GLUC; EC 242-736-7), N-acetyl-β-D-glucosaminidase (sometimes called chitinase) (NAC; EC 253-333-0), β-Xylosidase (XYL; EC 229-784-4), and acid phosphatase (acid phosphomonoesterase) (PHOS; EC 245-325-0). Both GLUC and XYL belong to the lignocellulose degrading enzymes (Burns, 1977; Sinsabaugh, 1994). GLUC is responsible for the cleavage of the β-1,4-glucoside bonds between the glucose monomers constituting cellobiose dimers (Burns, 1977; Kögel-Knabner, 2018). In analogy, XYL cleaves the bonds linking xylose, a hemicellulose polymer (Kögel-Knabner, 2018). NAC cleaves chitin into N-acetyl-D-glucosamin monomers. Chitin is a constituent of microbial cell walls and can be used as proxy for microbial N (Rao et al., 2017; Kögel-Knabner, 2018). Finally, PHOS cleaves phosphate groups from organic molecules and produces inorganic phosphorus that can be taken up by plants and microorganisms (Burns, 1977; Rao et al., 2000).

All chemical substances for the enzyme assay were purchased at Sigma Aldrich (Sigma Aldrich GmbH, St. Louis, MO, USA). 2-(N-Morpholino)-ethanesulfonic acid hemisodium salt (MES) was mixed with autoclaved water to obtain a 0.1 M solution with an pH of 6.1. 10 mM MUF-stuck solutions were solved in 5 ml methanol, filled up to 10 ml with sterile water. Working solutions were diluted by combining 400 µl of stuck solution and 3600 µl of MES-buffer, extracting 500 µl into a 50 ml flask and filling it up with 49.5 ml MES-buffer. The substrate solutions were produced sterile. For each enzyme, 10 mM stuck solutions were prepared by weighing 1/10000 of the molar mass of the substrate in sterile PP-tubes and dissolving it in 300 µl dimethyl sulfoxide. Afterwards 9.7 ml sterile water was added. 1 mM working solutions were produced by mixing 1 ml of stuck solution with 9 ml of the MES buffer.

One gram of soil and sand-illite was used, but only 0.5 g for the sand-goethite mixture due to particularly high fluorescence therein. 50 ml of sterile water was added to the sample and solubilized at 50 J/s for 1:32 minutes using an ultrasonic disaggregator. Afterwards, aliquots of 50 µl were taken from the soil suspension and pipetted by hand on black PP-microplates with 96 wells (Greiner Bio-One GmbH, Frickenhausen, Germany). For each enzyme and sample six

analytical replicates were measured. Next, 50 µl of MES-buffer and 100 µl of substrate were automatically pipetted on the microplates by a Freedom EVO 75 (Tecan Group Ltd., Männedorf, Switzerland). Standard plates with a MUF-substrate concentration ranging from 0 to 1200 pmol were measured to ultimately quantify enzyme activity.

After that, the microplates were pre-incubated for 30 min (for soil) and 1 h (for minerals) at 30 °C. After the pre-incubation, fluorometric measurements were carried out at 0, 30, 60, 120, 180 min while keeping the microplates at a constant temperature of 30 °C. Since overall enzyme activity was low on minerals two additional measurements at 240 and 300 min were taken. Fluorescence was measured with a microplate reader (Infinite 200 Pro, Tecan Group Ltd., Männedorf, Switzerland) at an excitation of 360 nm and 460 nm emission.

To calculate potential enzyme activities, the fluorescence measurements were checked for outliers and removed individually and carefully by comparing the coefficient of variance among the analytical replicates. The increase in fluorescence over time (slope) in each well was calculated. In addition, the slope across the wells of the standard plates with increasing MUF concentration was calculated. Both slopes were then divided resulting in the fluorescence F in pmol * well^{-1} * min^{-1} per sample.

$$(1)\ nmol * g^{-1}DM * h^{-1} = \frac{F*60*EV*100}{1000*A*SW*DM}$$

The fluorescence F was then inserted in Eq. (1), multiplied with the extraction volume (EV), factor 60 to convert minutes to hours, and divided by the product of 1000 (conversion from pmol to nmol), the aliquot of the soil suspension (A), the sample weight (SW), and the dry matter content (DM). Finally, the fluorescence in nmol per g dry matter per hour was obtained and could be used for further analysis as absolute extracellular enzyme activity (EEA_{abs}). The EEA_{abs} values were normalized by SOC content (EEA_{norm}).

3.4.4 Calculation of ecoenzymatic stoichiometries

Ecoenzymatic stoichiometries were calculated to assess changes in acquisition strategies of microorganisms and as indicators of nutrient or C-limitations. All ratios were calculated with the natural logarithm of the individual enzyme activities to avoid artifacts generated by the different ranges of absolute values (Sinsabaugh et al., 2009; Zhou et al., 2020). The ratio of C- to N-acquiring enzyme activities was calculated as the ratio of the sum of GLUC and XYL divided by the NAC enzyme activities (see Eq. 2-4):

$$(2)\ Enzyme\ C:N\ ratio = \frac{ln(GLUC+XYL)}{\ln(NAC)}$$

Similarly, the C:P ratio was obtained as following:

$$(3)\ Enzyme\ C{:}P\ ratio = \frac{ln(GLUC+XYL)}{\ln(PHOS)}$$

The N:P ratio was calculated as:

$$(4)\ Enzyme\ N{:}P\ ratio = \frac{\ln(NAC)}{\ln(PHOS)}$$

3.5 Data sources

3.5.1 Data from the Biodiversity Exploratories Information System

Since the establishment of the EP between 2006 and 2008, a large collection of datasets has accumulated covering a broad spectrum of topics (Fischer et al., 2010). This study made extensive use of these data to complement the laboratory measurements. The basic information on location and soil type of each EP was obtained from BExIS. Forest inventory (e.g. species diversity) and stand structural attributes (e.g. dbh, stand density, basal area) were taken from Schall and Ammer (2017, 2018). The forest type classification determined by the management regime was obtained from Schall and Ammer (2018). Further information on the forest management intensity were taken from the SMI dataset for the years 2008-2014 (Schall and Ammer, 2014). Aboveground litter weights as well as C, N, and S content of the litter were measured by the MinSoil project for the years 2015 to 2018 (Schöning et al., 2021a,b). We further used different datasets on important soil properties. Mean soil pH values were taken from Schöning et al. (2017) and soil texture from Schöning et al. (2012).

3.5.2 Data description of BEmins project

100 mineral samples were collected and measured from the 50 EPs. There were 50 sand-goethite mixtures and 50 sand-illite mixtures. Also, 100 samples were collected from the surrounding soil of which 98 samples were measured within the scope of this study. 49 soil samples were from the proximities of the sand-goethite containers and 49 from the surroundings of the sand-illite containers. Since they were sampled in close proximity to each other and did not show significant differences, they were considered as duplicates and averaged for the statistical analysis (n = 49).

3.6 Statistical analysis

All statistical analyses were carried out in R version 4.1.2 (R Core Team, 2021). The significance levels reported in this study are $p < 0.001$ denoted as (***), $p < 0.01$ as (**), and $p < 0.05$ (*). To perform mean comparisons the estimated marginal means (EMMEANS) were

computed (Lenth, 2022). Estimated marginal means (or least-squares means) are usually employed to calculate means between levels of categorical variables in models that contain more than one categorical variable and/or continuous variables. However, they also provide a user-friendly and transparent way to calculate one-way analysis of variance (ANOVA) with only one categorical variable. The mean of each response variable was quantified across mineral type (soil, goethite and illite) and forest type (beech vs. spruce). The response variables were SOC and TN content, the C:N ratio, absolute and normalized GLUC, NAC, XYL, and PHOS activity, as well as the enzyme ratios of C:N, C:P and N:P acquiring enzymes. Pairwise comparisons using the Tukey Honest Significant Difference method were calculated to identify significant differences across groups.

Table 2 : Overview of the explanatory variables that were used for each response variable group depending on the compartment (soil or mineral container).

Response variable	**Compartment**	**Explanatory variables**	
		Forest management	**Soil related**
SOM	soils	SMIr, SMId	soil pH, clay
	mineral containers	SMIr, SMId	soil C:N, soil pH, clay
Enzyme activities	soils & mineral containers	SMIr, SMId	SOC, C:N, soil pH, clay
Ecoenzymatic stoichiometry	soils & mineral containers	SMIr, SMId	SOC, C:N, soil pH, clay

In a second step, multiple linear least-squares regression models were formulated to relate the response variables with forest management intensity and relevant soil properties. The variable selection was based on an extensive previous literature review which was consolidated in a conceptual framework (see Figure 1). Taking all available variables could have led to the selection of variables that represent statistical artifcats instead of providing scientifically meaningful explanations (James et al., 2013). An overview of the explanatory variables selected for each group of response variables (SOM, EEA, ecoenzymatic stoichiometries) is provided in Table 2. The models did not include non-linear (quadratic) effects or interaction terms among the explanatory variables and no variable transformation (i.e. log-transformation) was done. The linear model equation was as follows (James et al., 2013):

$$(5)\ Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \cdots + \beta_p X_p + \epsilon$$

The relationship between the predictor variables X_p is estimated based on p model parameters β (see Eq. 5). The intercept term β_0 represents the value Y takes when X is 0. The model parameters β_p in turn determine the slope of the regression line depending on their individual

relationship between each predictor variable with the response variable. Finally, ϵ reflects the error term of the estimated relationship between Y and X (James et al., 2013).

The linear models were visually checked to comply with the model assumptions. This included the assessment whether the relationship between predictors and response variable was linear by checking the residual plot for homoscedasticity, which means that the variances of the residuals are constant, and the existence of high-leverage points (outliers) (James et al., 2013). Indeed, some points with high-leverage were identified. Still, the nature of enzyme activity measurements induces high variability and therefore no high-leverage points were removed.

Further, predictor variables were controlled for multicollinearity among each other by means of the variance inflation factor (vif) with the car package (Kuhn, 2021). The vif is calculated as follows:

$$(6)\ VIF(\hat{\beta}_j) = \frac{1}{1 - R^2 X_j | X_{-j}}$$

High collinearity exists, if the model fits equally well to one of the predictor variables and consequently achieves a high R^2. The vif calculates the R^2 that is achieved when fitting a response variable to the formulated linear model. If it achieves high R^2 values, the denominator becomes smaller and thereby increases the vif (see Eq. 6). Values above 5 are considered to be problematic and therefore predictor variables with vifs > 5 would have been excluded from the linear model (James et al., 2013). However, in the present case all vifs were below < 2.

To statistically assess whether the formulated linear models appropriately explained the variation of the response variables, F-tests were calculated (see Eq. 7). The F-statistic informs whether all model parameters equal to 0 (null hypothesis). This means that if the null hypothesis is rejected, the model parameters are unequal to 0 and thus releated to the response variable since they significantly affect the regression slope. In this case, at least one model parameters is related to the predictor variable. The F-statistic is calculated as follows (see James et al., 2013):

$$(7)\ F = \frac{(TSS - RSS)/p}{RSS/DF}$$

The F-value is calculated as the difference between total sum of squares (TSS) and residual sum of squares (RSS) that is divided by the number of model parameters and then divided by the quotient of the RSS and the degrees of freedom (DF) (see Eq. 7). In general, higher F values indicate a closer relationship between predictor and response variable. However, this strongly depends on the sample size. Thus, in this study we assess the relationship between model

predictors and response variable through the p-level of the F-test. Significance levels below $p < 0.05$ indicate that the model is suited to explain the variance of the response variable.

Several methods exist to evaluate the variable importance of individual model parameters (Grömping, 2015). In this study, the t-values of each parameter were used in combination with the p-values. The t-value is the quotient of the parameter estimate β_p and the standard error of estimation and can be used as indicator of how much each model parameter contributes to the regression slope that estimates the relationship between response variable and predictors (Kuhn, 2021). The information of how the regression slope is affected by each model parameter is complemented by the significance level of each model parameter (Bring, 1996).

4 Results

The manipulative experiment underlying this study aims to shed light on the question of how minerals and OM associate to form MAOM and how in turn nutrient cycling and ecoenzymatic stoichiometries are affected. To this end, (i) overall differences in SOM accumulation and EEA activities, and differences in enzyme stoichiometry between bulk soil and mineral types (goethite and illite), and (ii) differences in each compartment related to the forest type (beech vs. spruce) are discussed. Finally, (iii) the influence of soil properties and forest management intensity indicators are assessed by means of linear models.

4.1 Influence of mineral type

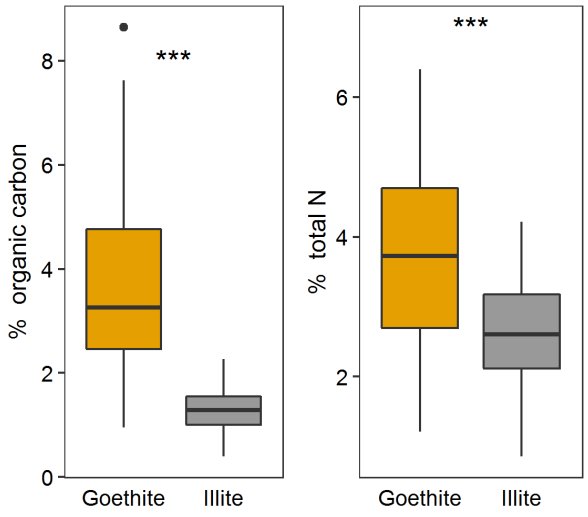

Figure 2 : Relative share of organic carbon, total nitrogen that was retained on either goethite or illite containers relative to the bulk soil. Significant differences at the $p < 0.001$ level between the minerals are indicated by ***.

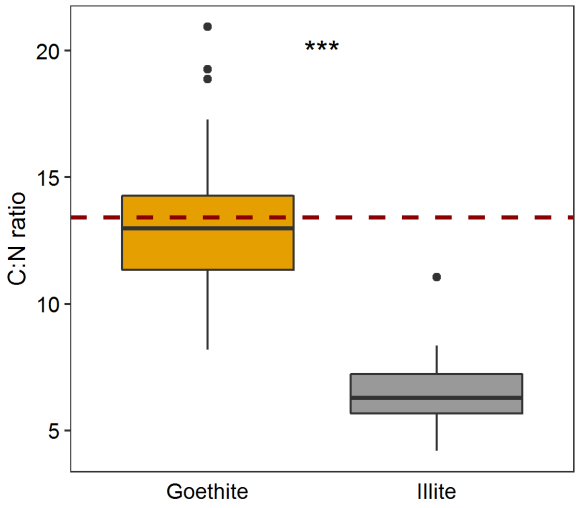

Figure 3 : The C:N ratio in each mineral container. The red dashed line indicates the mean soil C:N ratio found in soils. The differences between goethite and illite are significant on the $p < 0.001$ level (***).

Overall, SOM accumulation and thus formation of MAOM differed significantly between soil, goethite and illite (see Table 3). The mean SOC in forest soils was 68.0 ± 2.0 g kg^{-1} (mean ± SE) and differed significantly from the OC accumulated on goethite (2.3 ± 0.1 g kg^{-1}) and illite (0.8 ± 0.1 g kg^{-1}) which also differed significantly from each other ($p < 0.001$). Similarly, TN was significantly higher in bulk soil compared to goethite containers and illite (see Table 3). The differences of TN accumulation across goethite and illite were also significant ($p < 0.001$). The relative shares of OC and TN on each mineral relative to the bulk soil illustrate the higher retention of OC and TN on goethite (see Figure 2). The C:N ratio did not differ between soil (13.4 ± 0.3) and goethite (13.2 ± 0.3) but was significantly lower in the illite containers (6.5 ± 0.3) ($p < 0.001$) (see Figure 3).

Table 3 : Overview of the mean and standard error (SE) to assess differences between bulk soil, goethite and illite containers. The uppercase letters indicate significant differences at the $p < 0.05$ level between groups.

Response variable	**Soil**	**Goethite**	**Illite**
Soil organic C [g kg^{-1}]	68.0 ± 2.0 ^{A}	2.3 ± 0.1 ^{B}	0.8 ± 0.1 ^{C}
Total N [g kg^{-1}]	5.1 ± 0.2 ^{A}	0.2 ± 0.0 ^{B}	0.1 ± 0.0 ^{C}
C:N ratio	13.4 ± 0.3 ^{A}	13.2 ± 0.3 ^{A}	6.5 ± 0.3 ^{B}
$GLUC_{abs}$ [nmol g^{-1} DM h^{-1}]	262.2 ± 15.5 ^{A}	37.4 ± 2.0 ^{B}	12.6 ± 2.0 ^{C}
NAC_{abs} [nmol g^{-1} DM h^{-1}]	239.2 ± 15.1 ^{A}	56.9 ± 3.4 ^{B}	15.6 ± 3.4 ^{C}
XYL_{abs} [nmol g^{-1} DM h^{-1}]	64.1 ± 3.1 ^{A}	21.8 ± 1.1 ^{B}	2.6 ± 1.1 ^{C}
$PHOS_{abs}$ [nmol g^{-1} DM h^{-1}]	1188.1 ± 54.2 ^{A}	581.8 ± 23.7 ^{B}	60.4 ± 23.7 ^{C}
$GLUC_{norm}$	3.9 ± 1.0 ^{B}	16.6 ± 1.2 ^{A}	16.1 ± 1.2 ^{A}
NAC_{norm}	3.7 ± 1.3 ^{C}	25.1 ± 1.5 ^{A}	20.1 ± 1.5 ^{B}
XYL_{norm}	1.0 ± 0.5 ^{C}	9.7 ± 0.6 ^{A}	3.4 ± 0.6 ^{B}
$PHOS_{norm}$	19.7 ± 9.1 ^{C}	263.4 ± 11.0 ^{A}	78.1 ± 11.0 ^{B}
C:N enzymes	1.1 ± 0.0 ^{A}	1.0 ± 0.0 ^{B}	1.0 ± 0.0 ^{B}
C:P enzymes	0.8 ± 0.0 ^{A}	0.6 ± 0.0 ^{B}	0.7 ± 0.0 ^{B}
N:P enzymes	0.8 ± 0.0 ^{A}	0.6 ± 0.0 ^{B}	0.7 ± 0.0 ^{C}

A similar pattern as for OC and TN was found for the EEA_{abs} that were highest in soil, followed by goethite and lowest on illite (see Table 3). All decreases in EEA_{abs} from the surrounding soil to goethite to illite were highly significant ($p < 0.001$) and followed the overall decrease in OC (see Table 3). Highest EEA_{abs} for both mineral containers were measured for $PHOS_{abs}$. The relative shares of EEA_{abs} relative to the ones in the bulk soil are shown in Figure 4.

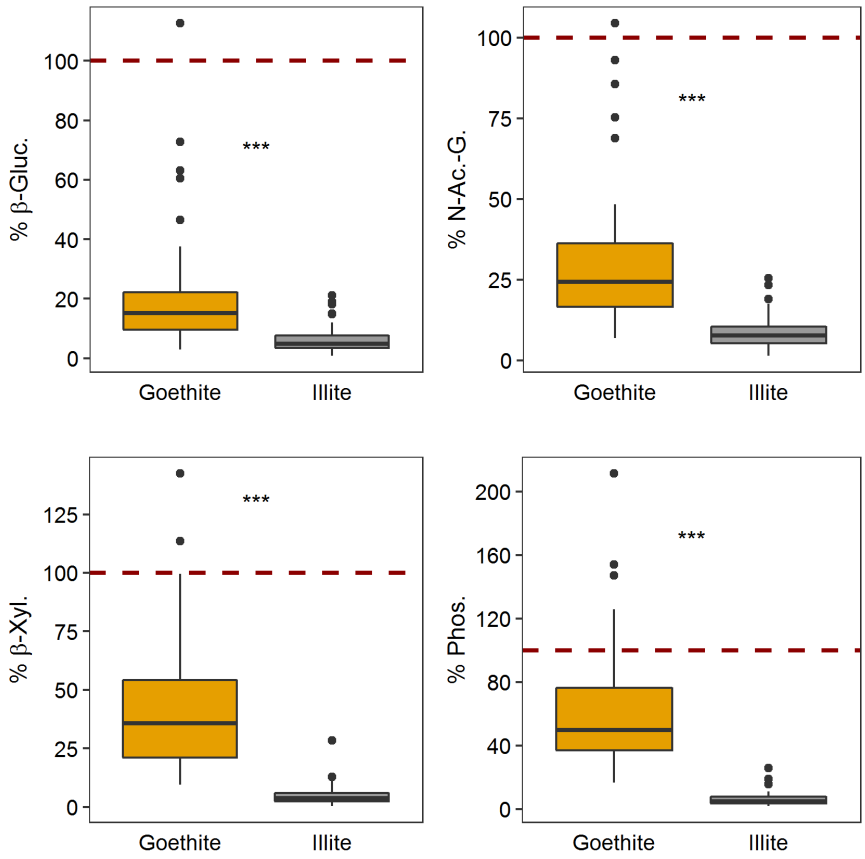

Figure 4 : Relative share of absolute extracellular enzyme activities (EEA_{abs}) for GLUC, NAC, XYL, and PHOS that was retained on either goethite or illite containers relative to the bulk soil. The red dashed line indicates the level at which the mean would be equal to bulk soil. Significant differences between the minerals are indicated by the asterisks ($p < 0.001$ = ***).

Complementary to the EEA_{abs}, EEA were normalized by the OC content (EEA_{norm}) to identify changes in EEA that were not related to the strongly differing availability of SOC. The EEA_{norm} increased from the surrounding soil to the mineral containers (see Table 3). The general pattern showed highest values on goethite, followed by illite and soil. The $GLUC_{norm}$ activity was lowest on soils (3.9 ± 1.0) and significantly increased in both minerals. On goethite, the $GLUC_{norm}$ activity reached 16.6 ± 1.2 which was not significantly different from the one on illite (16.1 ± 1.2) ($p = 0.76$). The NAC_{norm} activity was 3.7 ± 1.3 on soils, 25.1 ± 1.5 on goethite and 20.1 ± 1.5 on illite. Soil, goethite, and illite were all significantly different from each other (soil-mineral differences on $p < 0.001$, goethite – illite on $p < 0.05$). XYL_{norm} activities were lowest on soil (1.0 ± 0.5) followed by illite (3.4 ± 0.6) and goethite (9.7 ± 0.6). $PHOS_{norm}$

activities were lowest on soil (19.7 ± 9.1) followed by illite (78.1 ± 11.0) and goethite (263.4 ± 11.0). The patterns also persisted when looking at the relative shares of EEA_{norm} retained on each mineral surface compared to the bulk soil (see Figure 5).

The ecoenzymatic stoichiometries (see Chapter 3.4.4) reflect the relative allocation of ressources to enzymes that acquire certain nutrients and thus may yield information on nutrient limitation. Therefore, changes in C- to N-, C- to P-, and N- to P-acquiring EEA ratios were assessed. The C:N enzyme stoichiometry decreased from 1.1 ± 0.0 in the surrounding soil to 1.0 ± 0.0 on goethite but was not significantly different. The C:N enzyme stoichiometry on illite then differed significantly from soil but not from goethite (1.0 ± 0.0) (see Table 3). The C:P enzyme ratio decreased significantly from 0.8 ± 0.0 to 0.6 ± 0.0 on goethite and respective 0.7 ± 0.0 on illite ($p < 0.001$). The N:P enzyme ratio was highest on soil (0.8 ± 0.0) followed by illite (0.7 ± 0.0) and goethite (0.6 ± 0.0) which were all significantly different from each other (see Table 3).

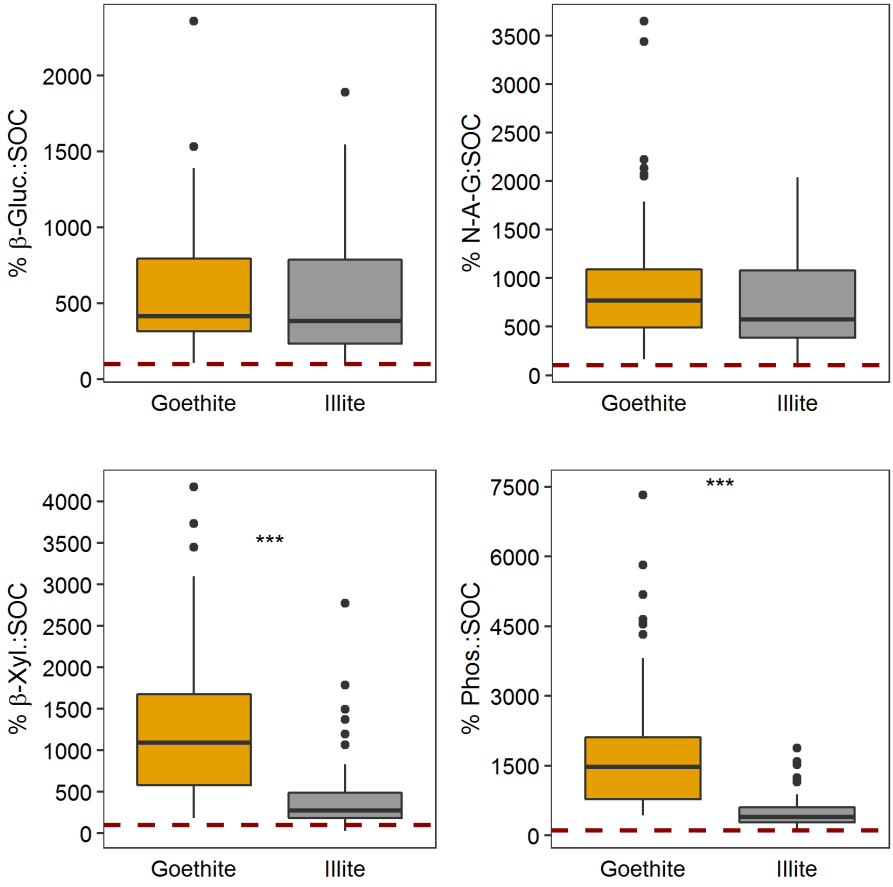

Figure 5 : Relative share of normalized extracellular enzyme activities (EEA_{norm}) for GLUC, NAC, XYL, and PHOS that was retained on either goethite or illite containers relative to the bulk soil. The red dashed line indicates the level at which the values would be equal to the mean bulk soil values. Significant differences between the minerals are indicated by the asterisks ($p < 0.001$ = ***).

4.2 Influence of forest type

Estimated marginal means were calculated to determine to what extent MAOM is affected by the forest types (beech vs. spruce stands). For that, significant differences were assessed related to SOM accumulation, the EEA_{abs} and EEA_{norm}, and ecoenzymatic stoichiometries in soil, goethite and illite containers.

4.2.1 Soil

In the surrounding soils, mostly no significant differences were found when comparing the differences related to forest type in the surrounding soils. There was no significant difference regarding the SOC and TN contents across forest types (see Table 4). However, significant differences were found for the C:N ratio. The C:N ratio was significantly higher under spruce stands (14.1 ± 0.4) compared to beech stands (13.2 ± 0.2) ($p < 0.05$). Further, $GLUC_{abs}$, NAC_{abs}, and XYL_{abs} activities did not differ significantly across deciduous to coniferous forest ecosystems but beech stands showed a lower $PHOS_{abs}$ activity (1013.9 ± 88.7 nmol g^{-1} DM h^{-1}) compared to spruce (1725.3 ± 155.7 nmol g^{-1} DM h^{-1}) ($p < 0.001$). A similar pattern was observed for the EEA_{norm} activities. Only $PHOS_{norm}$ activity was higher under spruce (27.9 ± 3.3) compared to beech stands (17.1 ± 27.9) ($p < 0.01$). All enzyme stoichiometries did not differ across forest types in the soil.

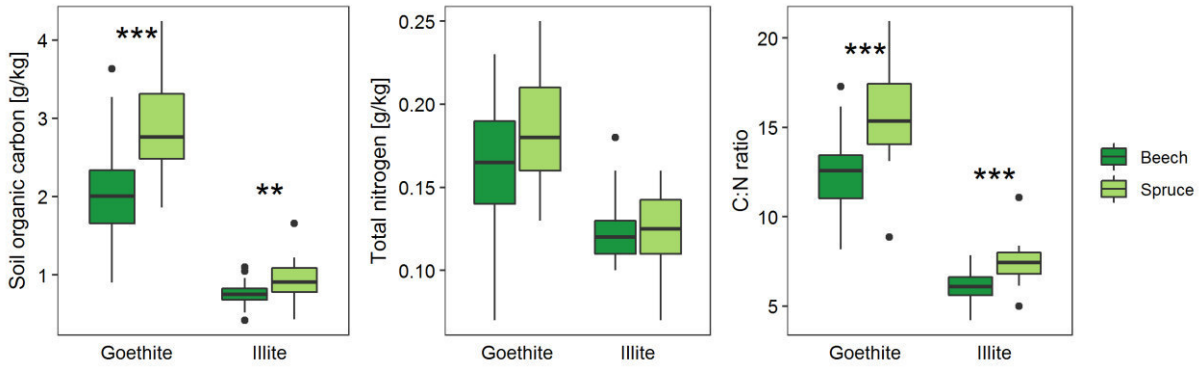

Figure 6 : MAOM formation per mineral bag and forest type (dark green = beech dominated forest, light green = spruce dominated forest). Significance levels of $p < 0.01$ were denoted as **, and $p < 0.001$ as ***.

Table 4 : Overview of the mean and standard error (SE) to assess differences across forest type in soil, goethite containers, and illlite containers. The uppercase letters indicate significant differences at the $p < 0.05$ level between forest type.

Response variables	Compartment	Beech	Spruce
Soil organic C [g kg^{-1}]	Soil	68.2 ± 4.1 ^{A}	67.4 ± 7.3 ^{A}
	Goethite	2.1 ± 0.1 ^{B}	2.9 ± 0.2 ^{A}
	Illite	0.8 ± 0.0 ^{B}	0.9 ± 0.1 ^{A}
Total N [g kg^{-1}]	Soil	5.2 ± 0.3 ^{A}	4.7 ± 0.5 ^{A}
	Goethite	0.2 ± 0.0 ^{A}	0.2 ± 0.0 ^{A}
	Illite	0.1 ± 0.0 ^{A}	0.1 ± 0.0 ^{A}
C:N ratio	Soil	13.2 ± 0.2 ^{B}	14.1 ± 0.4 ^{A}
	Goethite	12.5 ± 0.4 ^{B}	15.6 ± 0.7 ^{A}
	Illite	6.1 ± 0.2 ^{B}	7.5 ± 0.3 ^{A}
$GLUC_{abs}$ [nmol g^{-1} DM h^{-1}]	Soil	262.6 ± 31.3 ^{A}	260.9 ± 54.9 ^{A}
	Goethite	34.0 ± 2.8 ^{B}	48.0 ± 5.0 ^{A}
	Illite	13.4 ± 1.3 ^{A}	10.1 ± 2.3 ^{A}
NAC_{abs} [nmol g^{-1} DM h^{-1}]	Soil	239.0 ± 30.1 ^{A}	239.8 ± 52.9 ^{A}
	Goethite	55.0 ± 5.3 ^{A}	63.1 ± 9.5 ^{A}
	Illite	16.2 ± 1.4 ^{A}	13.4 ± 2.4 ^{A}
XYL_{abs} [nmol g^{-1} DM h^{-1}]	Soil	58.7 ± 5.8 ^{B}	80.6 ± 10.1 ^{A}
	Goethite	19.4 ± 1.7 ^{B}	29.4 ± 3.0 ^{A}
	Illite	2.8 ± 0.5 ^{A}	2.2 ± 0.8 ^{A}
$PHOS_{abs}$ [nmol g^{-1} DM h^{-1}]	Soil	1013.9 ± 88.7 ^{B}	1725.3 ± 155.7
	Goethite	542.6 ± 36.6 ^{B}	706.0 ± 65.2 ^{A}
	Illite	59.9 ± 6.0 ^{A}	62.0 ± 10.6 ^{A}
$GLUC_{norm}$	Soil	3.8 ± 0.4 ^{A}	3.9 ± 0.6 ^{A}
	Goethite	16.4 ± 1.1 ^{A}	17.38 ± 2.0 ^{A}
	Illite	17.4 ± 1.5 ^{A}	12.1 ± 2.6 ^{A}
NAC_{norm}	Soil	3.7 ± 0.5 ^{A}	3.6 ± 0.9 ^{A}
	Goethite	25.8 ± 1.8 ^{A}	22.6 ± 3.2 ^{A}
	Illite	21.4 ± 1.7 ^{A}	16.0 ± 3.0 ^{A}
XYL_{norm}	Soil	1.0 ± 0.1 ^{A}	1.3 ± 0.2 ^{A}
	Goethite	9.3 ± 0.7 ^{A}	10.7 ± 1.2 ^{A}
	Illite	3.6 ± 0.6 ^{A}	2.7 ± 1.0 ^{A}
$PHOS_{norm}$	Soil	17.1 ± 1.9 ^{B}	27.9 ± 3.3 ^{A}
	Goethite	267.4 ± 15.9 ^{A}	250.5 ± 28.3 ^{A}
	Illite	79.9 ± 8.2 ^{A}	72.4 ± 14.6 ^{A}
C:N enzymes	Soil	1.1 ± 0.0 ^{A}	1.1 ± 0.0 ^{A}
	Goethite	1.0 ± 0.0 ^{A}	1.1 ± 0.0 ^{A}
	Illite	1.0 ± 0.0 ^{A}	1.0 ± 0.1 ^{A}
C:P enzymes	Soil	0.8 ± 0.0 ^{A}	0.8 ± 0.0 ^{A}
	Goethite	0.6 ± 0.0 ^{B}	0.7 ± 0.0 ^{A}
	Illite	0.7 ± 0.0 ^{A}	0.6 ± 0.0 ^{A}
N:P enzymes	Soil	0.8 ± 0.0 ^{A}	0.7 ± 0.0 ^{A}
	Goethite	0.6 ± 0.0 ^{A}	0.6 ± 0.0 ^{A}
	Illite	0.7 ± 0.0 ^{A}	0.6 ± 0.0 ^{A}

4.2.2 Goethite

In contrast to soils, in goethite containers more differences across forest types could be observed (see Table 4). OC content was significantly higher under spruce stands (2.88 ± 0.2 g kg^{-1}) compared to 2.1 ± 0.1 g kg^{-1} under beech ($p < 0.001$) (see Figure 6). The same trend was observed for TN but the differences between beech and spruce were not significant ($p = 0.1$) (see Figure 6). The C:N ratio was significantly higher under spruce (15.6 ± 0.7) compared to beech stands (12.5 ± 0.4) ($p < 0.001$) (see Figure 6).

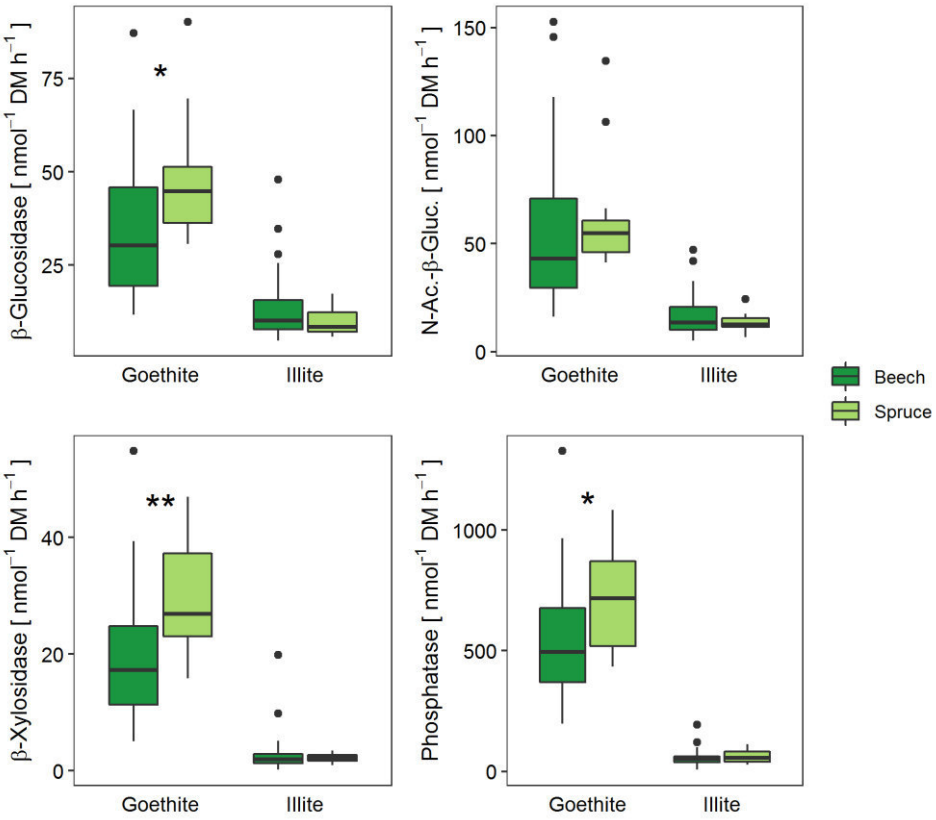

Figure 7 : Absolute extracellular enzyme activities (EEA) per mineral bag and forest type (dark green = beech dominated forest, light green = spruce dominated forest). Significance level of $p < 0.05$ was denoted as *, $p < 0.01$ as **, and $p < 0.001$ as ***.

Concomitant with the higher OC accumulation, the $GLUC_{abs}$ activity was higher under spruce (48.0 ± 5.0 nmol g^{-1} DM h^{-1}) compared to beech stands (34.0 ± 2.8 nmol g^{-1} DM h^{-1}) ($p < 0.05$) (see Figure 7). However, this did not hold for NAC_{abs} activity which did not differ across forest types. The pattern of higher values under spruce stands continued for XYL_{abs} ($p < 0.01$) and $PHOS_{abs}$ (see Figure 7). The $PHOS_{abs}$ activity was significantly higher in spruce stands (706.0 ± 65.2 nmol g^{-1} DM h^{-1}) compared to spruce stands (542.6 ± 36.6 nmol g^{-1} DM h^{-1}) ($p < 0.05$) (see Figure 7). In contrast to the EEA_{abs} activities, the EEA_{norm} acitivities did not differ significantly between forest types (see Table 4). There was only a marginally significant difference between C:N enzymes that showed higher values under spruce (1.1 ± 0.0) compared

to beech stands (1.0 ± 0.0) (p = 0.09). The C:P ratio showed significantly higher values under spruce (0.7 ± 0.0) compared to beech stands (0.6 ± 0.0) (p < 0.05) (see Figure 8). The N:P enzyme ratio did not differ between forest types on goethite containers.

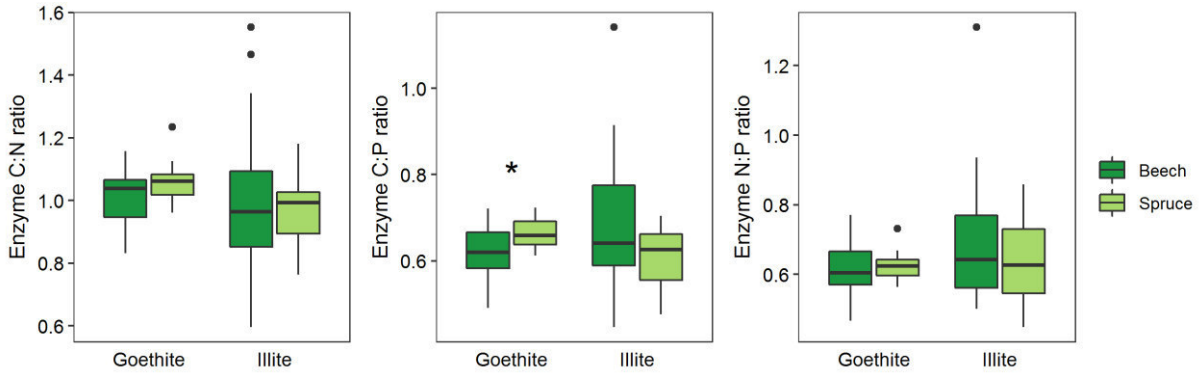

Figure 8 : Ecoenzymatic stoichiometries per mineral bag and forest type (dark green = beech dominated forest, light green = spruce dominated forest). Significance level of p < 0.05 was denoted as *.

4.2.3 Illite

OC accumulation was significantly higher under spruce stands (0.9 ± 0.1 g kg^{-1}) compared to beech stands (0.8 ± 0.0 g kg^{-1}) (p < 0.05) (see Figure 6). However, there were no differences in N accumulation across forest types (see Table 4). The C:N ratio was significantly higher under spruce (7.5 ± 0.3) compared to beech stands (6.1 ± 0.2) (p < 0.001). In contrast to goethite containers, there were no significant differences for EEA_{abs} and EEA_{norm} between coniferous and deciduous forests (see Table 4 and Figure 7). There were also no significant differences between ecoenzymatic stoichiometries (C:N, C:P, and N:P) (see Figure 8).

4.3 Disentangling the influence of forest management intensity and soil properties

This study showed that there were significant differences between soil, goethite, and illite. This section clarifies to what extent the significant differences of OC, total N, C:N ratio, EEA_{abs} and EEA_{norm}, and enzyme stoichiometries occurred as a function of mineral type (goethite vs. illite) and forest type (beech vs. spruce). By means of linear models, the importance of key factors to explain the observed differences and similarities can be achieved.

Table 5 : Overview of the linear regression output for each response variable in soils. The response variables are found in columns. As model metrics, the R^2 value and the p-value of the F-statistic are shown. Below are the variable importance coefficients calculated with the respective significance level of each model parameter. The p-values are denoted with *** for $p < 0.001$, ** for $p < 0.01$, and * for $p < 0.05$. The linear regressions were based on $n = 49$.

	SOC	TN	C:N ratio	$GLUC_{abs}$	NAC_{abs}	XYL_{abs}	$PHOS_{abs}$	$GLUC_{norm}$	NAC_{norm}	XYL_{norm}	$PHOS_{norm}$	Enzyme C:N	Enzyme C:P	Enzyme N:P
R^2	0.06	0.1	0.08	0.33	0.15	0.13	0.34	0.10	0.10	0.22	0.46	0.27	0.54	0.48
F-statistic (p-value)	0.591	0.312	0.416	0.007	0.287	0.411	0.005	0.609	0.619	0.085	0.000	0.031	0.000	0.000
SOC				3.72***	1.12	0.8	-1.22	0.27	-1.51	-2.14*	-4.22***	1.39	5.53***	3.38**
soil C:N				-1.11	1.57	0.15	2.02*	-1.17	1.66	-0.3	0.89	-3.42**	-2.04*	1.29
pH	-0.08	-0.16	0.3	0.46	0.6	-1.38	-1.43	0.84	0.68	-1.37	-1.51	-0.89	2.09*	2.65*
Clay	1.57	1.87	-0.69	0.87	0.24	0.12	0.79	0.67	0.12	-0.22	0.53	-0.96	-1.02	-0.04
SMIr	-0.31	-1.01	1.73	0.89	-0.4	1.06	1.43	0.92	-0.53	0.65	1.12	1.07	0.12	-0.93
SMId	0.14	-0.09	1.01	1.51	-0.8	0.55	-1.89	1.16	-0.74	0.3	-1.88	2.03*	2.69**	0.6

4.3.1 Soil

Most linear models on soils had a poor fit and the regression models were not significant (see Table 5). Therefore, in the following only the models with significant F-test were described in more detail. The model on $GLUC_{abs}$ activity was significant ($F_{42,6} = 3.52$, $p < 0.01$) and explained 33 % of the variance. The SOC content was the only significant model parameter and increased the $GLUC_{abs}$ activity with increasing SOC content (see Table 5). Further, the model on $PHOS_{abs}$ activity was significant ($F_{42,6} = 3.68$, $p < 0.01$) and explained 34 % of the variance. The soil C:N ratio was the most important variable indicating an increase of $PHOS_{abs}$ with increasing soil C:N ratio (see Table 5). Similarly, the model on $PHOS_{norm}$ activity was significant ($F_{42,6} = 6.02$, $p < 0.001$) and explained 46 % of the variance. The most important model parameter was the SOC content that negatively affected the $PHOS_{norm}$ activity.

All linear models on the enzyme ratios were significant. The model on the C:N enzyme ratio ($F_{42,6} = 6.02$, $p < 0.05$) explained 27 % of the variance. The most important model parameters were the soil C:N ratio which had a negative impact on the regression slope. Conversely, higher SMId which represent more dense forest stands led to wider C:N enzyme ratios. The models with C:P and N:P enzyme ratio as response variables were also highly significant. The model on the C:P enzyme ratio ($F_{42,6} = 8.29$, $p < 0.001$) explained 54 % of the variance. The SOC content, the SMId, and the soil pH had a positive impact on the C:P ratio while the soil C:N ratio had a negative impact. The model on N:P enzyme ratio ($F_{42,6} = 6.36$, $p < 0.001$) explained 48 % of the variance. The two significant and most important predictor variables were the SOC content and the soil pH. Higher SOC and soil pH values both increased the N:P enzyme ratio (see Table 5).

4.3.2 Goethite

In contrast to the models that explained the response variables in soil, the models explaining the variance on goethite minerals were more significant. The model explaining OC accumulation on goethite containers was significant ($F_{43,5} = 6.27$, $p < 0.001$) and explained 42 % of the variance. The significant model parameters were soil C:N ratio and soil pH. Wider C:N ratios increased OC accumulation and higher pH values led to decreasing OC accumulation in goethite containers (see Table 6). The model explaining TN accumulation was also significant ($F_{43,5} = 3.53$, $p < 0.01$) and explained 29 % of the variance. Similarly to the model on OC accumulation, increasing soil pH had a negative impact on TN accumulation. In addition, higher clay contents in the surrounding soils increased the TN accumulation on goethite containers.

Table 6 : Overview of the linear regression output for each response variable in goethite containers. The response variables are found in columns. As model metrics, the R^2 value and the p-value of the F-statistic are shown. Below are the variable importance coefficients calculated with the respective significance level of each model parameter. The p-values are denoted with *** for $p < 0.001$, ** for $p < 0.01$, and * for $p < 0.05$. The linear regressions were based on $n = 50$.

	OC	TN	C:N ratio	$GLUC_{abs}$	NAC_{abs}	XYL_{abs}	$PHOS_{abs}$	$GLUC_{norm}$	NAC_{norm}	XYL_{norm}	$PHOS_{norm}$	Enzyme C:N	Enzyme C:P	Enzyme N:P
R^2	0.42	0.29	0.51	0.35	0.32	0.28	0.23	0.18	0.23	0.26	0.02	0.15	0.26	0.20
F-statistic (p-value)	0.000	0.009	0.000	0.005	0.011	0.028	0.071	0.197	0.070	0.039	0.986	0.290	0.042	0.132
SOC				0.88	0.08	0.22	-0.38	2.38*	1.77	1.73	0.78	0.13	1.44	0.96
soil C:N	2.5*	-0.23	4.52***	2.35*	3.27*	1.78	1.84	0.21	1.52	0.01	-0.36	-1.36	1.37	2.13*
pH	-3.11**	-3.41**	-1.02	-1.94	-0.8	0.6	-1.84	-0.21	0.67	2.74**	0.58	0.33	-0.38	-0.54
Clay	1.08	2.31*	-0.95	-0.22	-0.54	-0.87	0.96	-1.06	-1.06	-1.8	-0.26	-0.14	-0.93	-0.56
SMIr	1.25	-0.09	2.4*	1.01	-1.02	2.41*	0.75	0.8	-1.11	2.63*	0.3	2.43*	1.75	-0.80
SMId	-1	-0.64	-0.42	-0.43	-2.38*	-0.49	-0.4	0.36	-1.56	0.63	0.11	1.50	0.25	-1.22

Table 7 : Overview of the linear regression output for each response variable in illite containers. The response variables are found in columns. As model metrics, the R^2 value and the p-value of the F-statistic are shown. Below are the variable importance coefficients calculated with the respective significance level of each model parameter. The p-values are denoted with *** for $p < 0.001$, ** for $p < 0.01$, and * for $p < 0.05$. The linear regressions were based on $n = 50$.

	OC	TN	C:N ratio	$GLUC_{abs}$	NAC_{abs}	XYL_{abs}	$PHOS_{abs}$	$GLUC_{norm}$	NAC_{norm}	XYL_{norm}	$PHOS_{norm}$	Enzyme C:N	Enzyme C:P	Enzyme N:P
R^2	0.24	0.05	0.35	0.17	0.23	0.10	0.18	0.18	0.21	0.11	0.18	0.12	0.26	0.22
F-statistic (p-value)	0.032	0.839	0.002	0.218	0.072	0.579	0.179	0.189	0.119	0.551	0.190	0.458	0.040	0.093
SOC				1.64	1.2	1.18	-1.27	1.92	1.48	1.44	-1.23	0.54	3.43**	2.61*
soil C:N	1.76	0.37	1.76	-0.7	0.54	-1.26	-0.15	-1.25	0	-1.56	-0.68	-1.59	-1.85	-0.27
pH	-1.31	-0.55	-1.23	-1.71	0.13	-1.39	-2.66	-1.44	0.39	-1.05	-2.21*	-0.66	0.06	1.06
Clay	1.73	1.21	1.38	0.92	1.22	0.4	1.12*	0.08	0.24	-0.11	0.27	-0.46	-0.73	-0.29
SMIr	1.13	-0.84	2.6*	-1.29	-1.74	-0.41	-1.11	-1.37	-1.82	-0.41	-1.24	0.42	-0.41	-0.64
SMId	-0.75	-0.39	-0.44	0.84	-2.15*	0.68	-0.04	0.78	-1.94	0.6	0.04	1.81	0.86	-0.96

The model on the C:N ratio was also significant ($F_{43,5} = 8.98$, $p < 0.001$) and explained 51 % of the variance. The most important model parameter was the soil C:N ratio and the SMIr indicator, which informs about the risk of a stand loss which is in turn linked to tree species composition and stand age (composition). Wider C:N ratios of the surrounding soil led to higher C:N ratios in the goethite containers. Higher SMIr which indicate a higher share of spruce and more homogeneous stands increased the C:N ratio according to the linear model (see Table 6).

Similarly to the SOM variables (OC, total N, and the C:N ratio), linear models were formulated to explain the variation of EEA_{abs} and EEA_{norm} as well as ecoenzymatic stoichiometries. For these models the SOC content and the C:N ratio of the surrounding soil were included as additional explanatory variables since we expected a correlation of SOM quantity and quality with nutrient mining.

The model on $GLUC_{abs}$ activities was significant ($F_{42,6} = 3.75$, $p < 0.01$) and explained 35 % of the variance. The soil C:N ratio significantly contributed to the regression slope indicating higher $GLUC_{abs}$ activities in mineral containers with higher C:N ratio of the surrounding soil (see Table 6). The model on the NAC_{abs} activity was significant ($F_{42,6} = 3.22$, $p < 0.01$) and explained 32 % of the variance. The most important and significant model parameters were the soil C:N ratio, and the SMId (see Table 6). NAC_{abs} activity on goethite minerals was lower in more dense stands (SMId) and it increased as the C:N ratio of the surrouding soils widened. The model on absolute XYL activity was significant ($F_{42,6} = 2.66$, $p < 0.05$) and had an R^2 of 28 %. The most important model parameters was the SMIr that indicated higher XYL_{abs} values in stands with higher risk of stand loss (more coniferous trees, more homogeneous age structure) (see Table 6). The model on $PHOS_{abs}$ activity in goethite containers was only marginally significant ($F_{42,6} = 2.12$, $p < 0.1$) and explained 23 % of the variance. However, no single model parameter was significant (see Table 6).

The models that explained the EEA_{norm} in goethite containers had worse model fits than the EEA_{abs} models. The linear model on the $GLUC_{norm}$ activity was not significant ($F_{42,6} = 1.51$, $p = 0.198$) and explained 18 % of the variance. The most important significant variable was SOC which positively influenced the $GLUC_{norm}$ activity. The model on NAC_{norm} activity was not significant ($F_{42,6} = 2.13$, $p = 0.07$) and explained 23 % of the variance. The significant model parameters were the soil C:N ratio and the SMId indicator which indicated that NAC_{norm} activity increased with increasing soil C:N ratio and decreased with increasing stand density. The model on XYL_{norm} activity was significant ($F_{42,6} = 2.46$, $p < 0.05$) and explained 26 % of the variance. The only significant model parameter was the SMIr indicator that showed an increase of

XYL_{norm} activity with increasing SMIr. The model on $PHOS_{norm}$ activity was not significant (see Table 6).

The linear models explaining the ecoenzymatic ratios of C- to N-, C- to P-, and N- to P-acquiring enzymes on goethite containers were not significant except for the model on the C:P enzyme ratio ($F_{42,6} = 2.43$, $p < 0.05$). It accounted for 26 % of the variance. Still, the model contained no parameter with significant contributions to the regression slope (see Table 6).

4.3.3 Illite

In the following, the results of the linear models that were formulated to explain the variation of SOM, EEA_{abs} and EEA_{norm}, and ecoenzymatic stoichiometries in illite containers are described. Overall, the significance of the models and the explained variance decreased compared to the ones formulated for goethite containers.

The linear model on OC content was significant ($F_{43,5} = 2.71$, $p < 0.05$) and explained 24 % of the variance. None of the model parameters was significant (see Table 7). The model on N content was highly insignificant ($F_{43,5} = 0.41$, $p = 0.83$) and explained only 5 % of the variance. Consequently, there was no significant model parameter. In contrast, the C:N ratio was significantly explained by the model ($F_{43,5} = 4.65$, $p < 0.01$) and accounted for 35 % of the variance. The most important and significant model parameter was the SMIr indicator that indicated wider C:N ratios on illite containers with increasing SMIr (see Table 7).

Out of the models explaining the EEA_{abs} in illite containers, only the one explaining NAC_{abs} activity was marginally significant ($F_{42,6} = 2.11$, $p < 0.1$) (see Table 7). It explained 23 % of the variance and had as most important and significant model parameters the SMId which indicated a negative impact of stand density on NAC_{abs} activity. Similarly, the models on EEA_{norm} in illite containers were not significantly explained by the linear models. The models explained between 11 % (XYL_{norm} activity) and 21 % (NAC_{norm} activity) of the variance (see Table 7). The linear models fitted to the enzyme ratios found in illite containers were not significant except for the C:P enzyme ratio ($F_{42,6} = 2.45$, $p < 0.05$). The model explained 26 % of the variance and had the SOC content of the surrounding soil as most important and significant model parameter that positively affected the regression slope.

5 Discussion

This study investigated the dynamics of mineral-associated OM (MAOM) formation and nutrient cycling at pristine mineral surfaces in a manipulative experiment. To this end, mineral containers filled with either a sand-goethite or a sand-illite mixture were buried in topsoils of

temperate forests with different management regimes for five years and then analysed regarding how much SOM was bound at mineral surfaces (formation of MAOM as indicated by OC and TN content), how SOM decomposition and nutrient cycling (indicated by EEA_{abs} and EEA_{norm}) were affected, and whether certain nutrient limitations (C, N, P) were detectable via EEA ratios (ecoenzymatic stoichiometries).

5.1 Dynamics on goethite and illite relative to soil

5.1.1 MAOM formation and SOM quality

In comparison to the SOM content of the surrounding soil, the fraction that accumulated in the mineral containers was very low (see Table 3). This decrease was expected since several factors limited SOM accrual on mineral containers that came almost exclusively from dissolved organic matter (DOM). Input from roots, fungal hyphae, and via bioturbation were strongly limited or excluded due to the very fine mesh size surrounding the minerals (50 µm) (Müller et al., 2020). Consequently, the inflow of OM into the mineral containers was limited to DOM that originated mostly from aboveground litter and potential contributions of root exudates and root litter decomposition. Still, as the mineral containers were not only open on the top but also on the bottom, potential outflow of DOM with downward waterfluxes may have occurred and corroborates that OM found in mineral containers was immobilized by the formation of MAOM.

Previous studies suggested that goethite enhanced the stabilization of OM as for instance rhizodeposits were increasingly stabilized following the addition of goethite to soils (Jeewani et al., 2020). The goethite-OM association also enhanced aggregation processes that further increased the stabilization of OM (Liu et al., 2014). Since the OM input in mineral containers was mainly originating from litter-derived and root-derived DOM, the higher share of OM accumulation on goethite minerals corroborates the high potential of goethite mineral surfaces to stabilize OM relative to illite. The diverging formation of MAOM may also be driven by the type of interaction between OM and goethite/illite. Illite has a permanent negative charge while the sorption capacity of goethite increases with low pH values (Liu et al., 2014). At low pH of the soil solution the probability for ligand exchanges with OM increases for variably charged iron oxides (Kleber et al., 2021). Since the increasing soil pH of the surrounding soil had a negative impact on OC accumulation on goethite, this study confirms the pH-dependent binding capacity of goethite.

Lower C:N ratios were expected on mineral surfaces due to the higher degree of decomposition of DOM that accumulated in the mineral containers and potentially led to a higher share of

microbial biomass since microbial colonization of inorganic surfaces in forest ecosystems was observed in previous studies (Uroz et al., 2015). However, significantly lower C:N ratios were only measured in illite containers. The similar C:N ratio between soil and goethite suggests that predominantly OM from decomposed plant materials accumulated in the goethite-filled containers since the C:N signature was not as low as expected for microbial biomass (C:N < 10) (Kögel-Knabner, 2018). This is in line with previous studies that found a preferential adsorption of plant-derived OM with narrow C:N on mineral surfaces (Kopittke et al., 2020; Kleber et al., 2021). Moreover, the DOM that reached the mineral soils was likely composed of low-molecular weight compounds that are dominant DOM of temperate forests soils (Kaiser et al., 2002). The very low C:N ratio in illite-filled containers, in turn, is likely driven by ammonium which is present in the interlayer of illite minerals. Thus, the low C:N ratios do not stand for higher microbial biomass which would usually be expected at such low C:N ratios.

5.1.2 Nutrient cycling

Nutrient cycling (EEA_{abs} and EEA_{norm}) was consistent with the pattern found for MAOM formation. Highest EEA_{abs} were found on soil followed by goethite and illite. However, the EEA normalized to the SOC content (EEA_{norm}) showed the inverse relationship with highest values on goethite followed by illite and soils. This finding is in line with meta-analyses on EEA_{abs} that found the allocation of resources to extracellular enzyme production to depend upon the availability of energy sources (i.e. SOM content) (Sinsabaugh et al., 2008; Hendriksen et al., 2016).

At second instance, the production of specific enzymes is then driven by nutrient limitations (Allison et al., 2010). Hence, increased production of an enzyme indicates either the scarcity of a certain nutrient or the increased presence of nutrients that makes the investment of an organism in extracellular enzyme production advantageous. However, in regards to the EEA_{abs} no clear conclusions regarding nutrient limitations can be derived since the overriding effect of SOM content on EEA_{abs} masks potential effects driven by nutrient limitations. This effect was consistent for all four hydrolytic enzymes measured in this study and thus supports the importance of SOM content on EEA_{abs}.

Since the EEA_{abs} was strongly influenced by the differing SOM content, the EEA_{norm} yielded more information on potential nutrient limitations and overall nutrient cycling rates. The EEA_{norm} was higher on minerals (goethite > illite) compared to soils (see Table 3). This pattern can be explained in two ways.

On one hand, the scarce microenvironment in the mineralosphere may foster the relative allocation of energy to the enzyme production to enhance nutrient availability (Sinsabaugh and Moorhead, 1994; Allison et al., 2010). This follows the "Microbial Enzyme Allocation during Decomposition" (MEAD) model that coupled the extracellular enzyme production to substrate quality (Schimel and Weintraub, 2003). Thus, the lack of nutrients might be perceived by microorganisms via mechanisms, such as quorum sensing (Burns et al., 2013). Quorum sensing was first observed in aquatic environments and recently shown to regulate the synthesis of extracellular enzymes (McBride and Strickland, 2019).

On the other hand, the mineral surfaces may increase the longevity and activity of enzymes that accumulated in the mineral containers due to immobilization of enzymes on mineral surfaces (Quiquampoix and Burns, 2007; Olagoke et al., 2020). These enzymes would then represent "abiontic" enzymes that are decoupled from the emitting microorganism but remain active following stabilization, e.g. on mineral surfaces (Skujiņš et al., 1974; Nannipieri et al., 2018). Hence, it remains unclear to what extent the EEA_{abs} and EEA_{norm} in mineral containers are driven by abiontic enzymes that are of particular importance in the organo-mineral interactions. For instance, the relatively high phosphatase activity in goethite corresponds well with previous studies that found high phosphatase activities in irradiated soils (McLaren et al., 1956). The specific nature of goethite further facilitates aggregation that may enhance the existence of abiontic enzymes (Nannipieri et al., 2018). Still, the significantly higher EEA_{norm} in goethite containers compared to illite (except for $GLUC_{norm}$ activity) indicates that a minimum amount of SOM needs to be present so that the synthesis of EEA takes off. This is in line with previous studies that found acid phosphatase activity to be affected by initially bioavailable P contents (DeForest et al., 2012).

The EEA_{norm} did not follow a similarly consistent pattern compared to EEA_{abs}. This is likely due to the overriding importance of OC concentration. $GLUC_{norm}$ activity did not differ between goethite and illite. Furthermore, the fact that GLUC, which cleaves cellobiose into glucose monomers, may have a particularly stable presence in both mineral containers since the main input source in the experiment was DOM mostly from aboveground litter sources. Thus, the cleavage of cellobiose as a component of litter DOM may have been enhanced independently of the mineral surface type (Xu et al., 2021).

5.1.3 Ecoenzymatic stoichiometries

Ecoenzymatic stoichiometries serve as indicator of microbial nutrient acquisition rates and indicate nutrient limitations (Luo et al., 2017). In this study, econzymatic stoichiometries

showed significantly higher values in soils compared to mineral containers (except for the C:N enzyme ratio, see Table 3). The stoichiometries however only differed significantly between mineral types for the N:P enzyme ratio. This suggests that nutrients became increasingly limited in mineral containers and thus thereby fostered the production of especially P-cleaving enzymes (Schimel and Weintraub, 2003; Zechmeister-Boltenstern et al., 2015). This contrasts the hypothesis that the mineralosphere is more C-limited whereas bulk soils more nutrient-limited.

The reason why the C-limited nature of mineral surfaces is not reflected in the ecoenzymatic stoichiometries of this study may originate from the fact that the DOM flow into the mineral containers did not differ too strongly from the one in bulk soil. That indicates an overall nutrient limitation as the ecoenzymatic ratios were also for soils mostly below or at 1 (Luo et al., 2017; Thieme et al., 2019).

Further, PHOS activities may have a particular role since $PHOS_{norm}$ values on mineral containers were very high (see Figure 3). The reason for the increased investment in P-acquiring enzymes, particularly on goethite, may be a result of the high phosphate binding capacity of goethite minerals (Liu et al., 2014). This may foster the excretion of acid phosphatase enzymes and might mask the C-limitation of the mineralosphere. The particular role of PHOS activity is further sustained as the cleavage of phosphates is less complex compared to N- or C-cycling enzymes (Olander and Vitousek, 2000; Luo et al., 2017). For instance, does the continuous cleavage of C also increase N availability and thus decouples the N-acquisition from the mere cleaving of chitin. Similarly, the cellobiose cleavage indicated by GLUC activities only represents one specific pathway of C acquisition.

5.2 Dynamics between forest type (beech vs. spruce)

5.2.1 Differences in MAOM formation

The MAOM formation (as expressed by the OC and TN content) of goethite and illite were assessed in relation to the SOM content of the bulk soil. Unexpectedly, the SOM content of the surrounding soils did not differ between forest types despite the fact that in deciduous forest stands generally more SOM accumulates in the mineral soil while coniferous stands accumulate SOM in the forest floor (Schulp et al., 2008). In general, the impact of forest type on bulk soil were insignificant except for the C:N ratio which widened under spruce-dominated stands as the litter has a wider C:N ratio (Albers et al., 2004).

Interestingly, the MAOM formation in mineral containers was more clearly affected by the forest type than the surrounding soil. There was more C and N (significant only for goethite)

accumulation under spruce stands than beech stands (see Table 4). The MAOM formation in mineral containers might be more strongly affected by forest type since the importance and quantity of DOM is higher under coniferous forests.

Further, the observed differences in C:N ratios might have affected microbial community composition and thus microbial activity as for instance the share of soluble N increased in soils under deciduous forests (Xing et al., 2010; Wang et al., 2016). Higher C allocation through root exudates of coniferous trees may have enhanced the accumulation of C in mineral containers (Rog et al., 2021). Finally, the lower soil pH under spruce stands may have corroborated the stabilization capacity particularly on goethite as it increased the adsorption capacity of the mineral (Liu et al., 2014).

5.2.2 Differences in nutrient cycling

The bulk soil showed higher nutrient cycling under spruce for XYL_{abs} and $PHOS_{abs}$ activities but not for the EEA_{norm} (see Table 4). Thus, C- and N-acquiring EEAs were less affected by the forest type and the most consistent effect was observed for PHOS. In the case of the mineral containers, the EEA_{abs} were significantly higher under spruce on goethite containers (except for NAC), the EEA_{abs} on illite did not differ between forest type (see Table 5 and 6). Similarly, the EEA_{norm} did not indicate that specific differences in nutrient cycling occur across forest types. This is unexpected since the wider C:N ratio under spruce stands supposedly leads to nutrient limitations and thus induces changes in EEA_{norm}.

In spite of lacking evidence for shifts in SOM quality that would reflect in the EEA_{norm} between the two different forest types in each mineral container, the soil C:N ratio still indicates significantly wider ratios under spruce (see Table 4). Hence, this study does not show any differences between forest types with regards to OM quality but it highlights the mediating role of mineral surfaces in conjunction with DOM quality for the nutrient cycling in forest soils.

It is known that more DOM is produced in coniferous stands and that the soil solution has a lower soil pH. This explains why goethite containers showed significant differences while illite containers did not. The lower pH of the soil solution under spruce likely increased the adsorption capacity of goethite and thus stabilized more SOM and potentially enzymes (Quiquampoix et al., 1987a; 1987b). Consequently, the EEA_{abs} increased reflecting the higher overall SOM content in the goethite containers. This development did not occur in illite containers. There, the stable negative charge of the clay minerals did not lead to fluctuation in the stabilization capacity. Still, the overall very low OM concentrations on illite likely contributed to the insignificant results.

Hence, the mineral type played a mediating role in how much of the higher DOM flow under spruce could actually be stabilized. Conversely, this suggests that the quality of the incoming DOM does not matter in terms of components since the overall low SOM content on mineral surfaces was already found to be the overriding factor (Hendriksen et al., 2016).

5.2.3 Differences in ecoenzymatic stoichiometries

Ecoenzymatic stoichiometries narrowed in the bulk soil and illite containers under spruce. However, goethite containers showed the opposite pattern (significantly higher under spruce for C:P enzyme ratio). Still, most differences were not significant (see Table 4, 5, and 6). The wider C:N ratios found under spruce led to narrower ecoenzymatic stoichiometries on soils and illite, whereas on goethite the wider ratios on spruce indicated a more C-limited environment but may also reflect a shift towards a fungi-dominated community composition (Zechmeister-Boltenstern et al., 2015).

Mineral surfaces are known to associate predominantly with SOM that has a lower C:N ratio (Kalbitz et al., 2000; Kaiser et al., 2002). Hence, the increases in ecoenzymatic stoichiometries under spruce for goethite indicate that C-acquiring enzymes become relatively more important in a C-limited environment. Since the spruce DOM is expected to have wider C:N ratios, the wider ecoenzymatic stoichiometries under spruce indicated that higher C availability might have led to slight increases in C acquisition through GLUC enzymes. Still, the overall enzyme ratios are narrow and thus indicative for a nutrient limited environment (Luo et al., 2017).

To conclude, the ecoenzymatic stoichiometries did not differ significantly across forest types in the different compartments. Further studies are needed to clarify how SOM composition affects the allocation of microorganisms to enzyme synthesis and how this affects ecoenzymatic stoichiometries. Most likely the strong transformation of DOM, especially within the soil matrix, homogenizes the chemical composition of DOM that is still much more pronounced in the forest floor (Thieme et al., 2019).

5.3 Joint influence of soil properties and forest management intensity

5.3.1 Linear models on MAOM formation

The linear models showed that the stabilization of OC via the formation of MAOM on goethite was clearly driven by the C:N ratio of the surrounding soil and the soil pH. In contrast, the linear models on illite had a worse model fit and thus the model parameters were not significant. Still, the coefficients indicated similar weighting of the C:N ratio and SMIr as most important variables. These findings are in line with the previously formulated hypotheses. Wider C:N

ratios increase the flux of DOM and are likely to occur in forest stands with a high SMIr that corresponds to a high or even pure coniferous stand in the study area (Schall and Ammer, 2014). In line with that, the MAOM formation appeared to be more strongly affected on goethite compared to illite. This suggests that the DOM quality which has a lower soil pH under coniferous stands had played a central role in increasing goethite sorptive capacity. In turn, the constant negative charge of illite surfaces was less affected by the fluctuation in the pH of the DOM.

Next to the stronger effect on goethite containers, it is noteworthy that TN contents were less explained by the models and more affected by clay and the SMIr management indicator than by the soil C:N ratio. However, the relationship between TN content in the mineral containers and soil pH contrasts findings that indicate increasing microbial biomass with increasing soil pH (Friedel et al., 2006; Kara et al., 2008). Thus, it is unlikely that higher TN values on mineral containers indicate microbial biomass but rather reflect overall increases in SOM. This also explains the positive effect of more clayey surrounding soils that enhanced the TN content in mineral containers.

5.3.2 Linear models on nutrient cycling

In general, the linear models that showed the response of EEA_{abs} and thus nutrient cycling based on surrounding soil properties and forest management intensity were not significant except for goethite. The nutrient cycling activity as indicated by EEA_{abs} was more strongly influenced by the C:N ratio on goethite but tended to be similarly influenced by OC concentrations on illite (not significant) (see Table 6 and 7). Hence, wider soil C:N ratios that are also closely related to management aspects significantly contributed to increasing EEA_{abs} on goethite. This is consistent with all previously discussed findings that point towards a central role of DOM flow for MAOM formation, enhanced stabilization capacity of goethite, and increasing enzyme activities.

However, the lower model fits especially for EEA_{norm} also suggest that other factors such as inherent differences between mineral types or factors related to the microbial community composition might govern the allocation of resources to EEAs. In light of the diverging microhabitat conditions at different mineral surfaces and consequential shifts in microbial communities investigating this further may be rewarding (Carson et al., 2007; Vieira et al., 2020a).

5.3.3 Linear models on ecoenzymatic stoichiometries

The ecoenzymatic stoichiometries on soils were all significant. They increased with higher SOC content and decreased with wider soil C:N ratios. Further, soil pH and SMId contributed significantly to the model. However, this effect was not visible on minerals except for the C:P enzyme ratio in goethite and illite containers. Again, the SOC and the soil C:N ratio of the surrounding soil were most important (see Tables 5-7).

Nutrient limitations in the bulk soil were coupled to overall SOC content and SOM quality. This holds especially true for N availability which can be a by-product of SOC decomposition (Zechmeister-Boltenstern et al., 2015). P limitation (indicated by lower C:P and N:P enzyme ratios) in turn increased with soil pH. This is in line with very recent studies that experimentally tested the pH-mediated availability of plant-available P (Barrow et al., 2020)

The patterns of nutrient limitations in soils as indicated by the ecoenzymatic stoichiometries did not continue in mineral containers. Thus, despite some correlation with regards to the C:P and N:P enzyme ratio, no clear conclusions can be drawn with respect to the drivers on mineral surfaces. Hence, the overall decrease from soil ecoenzymatic stoichiometries to mineral containers discussed in Section 5.1.3 might be rather linked to properties of the microbiome that were not covered in this study. Mineral type-specific processes such as the previously mentioned goethite-phosphate binding mechanisms may be less relevant since the models were similar for goethite and illite. Illite surfaces may have shown more clear trends due to the very low MAOM formation which likely limited the availability of key nutrients even more.

5.4 Strengths and limitations of the study

The study provides strong evidence that the properties of mineral surfaces are central for SOM dynamics in managed temperate forests. The more intensive management practices that resulted in coniferous forest stands in the study area increased the flow of DOM concomitant with lower pH values. These properties were crucial to significantly enhance the capacity of goethite surfaces to form MAOM, and enhance nutrient cycling through increased EEAs and narrower ecoenzymatic stoichiometries.

The evidence presented in this study is convincing but some peculiarities of the approach need to be highlighted. Most importantly, this study assessed the MAOM formation in a sand-mineral mixture and not in pure mineral containers for practical reasons that ensured similar volumes in both containers. With this, the actual mineral content in the mineral containers differed between goethite and illite (see Chapter 3.2). Usually, microbial activity and MAOM formation

on sand fractions are low which would speak in favour of correcting for the pure mineral content. However, in the present study this correction was not done since it cannot be ultimately ruled out that the sand fraction in the mineral containers did not contribute at all to the values reported here. Studies that investigated the retention of OM and EEAs on sand-sized particles found low values that still were too high to simply ignore them (Marx et al., 2005). Moreover, it was shown that the sand fraction can also increase SOM content following additional fertilizer input (Ling et al., 2014). Thus, sand-sized particles can develop a certain dynamic and therefore may have contributed to the stabilization of OM within the mineral containers.

Further, it is noteworthy that broadening the array of methods employed in the study context would greatly enhance the ability to draw a more mechanistic understanding from the experiment. The investigation of the chemical composition of SOM found in soils and on mineral containers would be of great value. This is recommendable due to the fact that C- and N-cyles are more complex and involve many different enzymes. Finally, a deepened understanding of the microbial community composition on soils, goethite and illite containers would increase the capacity to describe ecological processes that occur on mineral surfaces.

This study was limited to 50 experimental plots located on the Swabian Alb and provides sound evidence for the processes shaping the SOM dynamics on pristine mineral surfaces in the context of contrasting management regimes in the study area. Yet, the relatively small sample size hampered the use of more sophisticated statistical methods such as structural equation modelling. Expanding the study area therefore means that these methods could be used and increase the ability to disentangle soil- and management-related contributions since central soil properties such as the soil C:N ratio or the soil pH are also influenced by forest management.

6 Conclusion

This study supports the notion that mineral surfaces are a central component of C dynamics in forest soils. Irrespective of the mineral type, MAOM formed and EEA_{norm} were many times higher than in bulk soil. Still, the MAOM formation and the EEA_{abs} were significantly higher in goethite containers. This was mediated by the forest management regime since coniferous stands exhibit not only higher DOM flows but also contribute to a more acidic soil environment. This study suggests that these effects, together with the widened C:N ratio were crucial for increasing the effectiveness of goethite minerals to foster the stabilization capacity in comparison to illite containers. The present experiment is a promising attempt to disentangle soil-related and forest management-related factors on C dynamics on mineral surfaces.

Exploring the specific mechanisms between mineral and organic phase in order to increase the understanding of C and nutrient dynamics in soils may be an interesting area for future research.

References

Achat, D. L., Fortin, M., Landmann, G., Ringeval, B., and Augusto, L.: Forest soil carbon is threatened by intensive biomass harvesting, Sci. Rep., 5, 1–10, https://doi.org/10.1038/srep15991, 2015.

Ahmed, E., Hugerth, L. W., Logue, J. B., Brüchert, V., Andersson, A. F., and Holmström, S. J. M.: Mineral Type Structures Soil Microbial Communities, Geomicrobiol. J., 34, 538–545, https://doi.org/10.1080/01490451.2016.1225868, 2017.

Albers, D., Migge, S., Schaefer, M., and Scheu, S.: Decomposition of beech leaves (Fagus sylvatica) and spruce needles (Picea abies) in pure and mixed stands of beech and spruce, Soil Biol. Biochem., 36, 155–164, https://doi.org/10.1016/j.soilbio.2003.09.002, 2004.

Allison, S. D.: Soil minerals and humic acids alter enzyme stability: Implications for ecosystem processes, Biogeochemistry, 81, 361–373, https://doi.org/10.1007/s10533-006-9046-2, 2006.

Allison, S. D., Gartner, T. B., Holland, K., Weintraub, M., and Sinsabaugh, R. L.: Soil Enzymes : Linking Proteomics and Ecological Processes, in: Manual of Environmental Microbiology, edited by: Hurst, C., Crawford, R., Garland, J., Lipson, D., Mills, A., and Stetzenbach, L., ASM, Washington DC, 704–711, 2007a.

Allison, S. D., Weintraub, M. N., Gartner, T. B., and Waldrop, M. P.: Evolutionary-Economic Principles as Regulators of Soil Enzyme Production and Ecosystem Function, 229–243, https://doi.org/10.1007/978-3-642-14225-3_12, 2010.

Allison, V. J., Condron, L. M., Peltzer, D. A., Richardson, S. J., and Turner, B. L.: Changes in enzyme activities and soil microbial community composition along carbon and nutrient gradients at the Franz Josef chronosequence, New Zealand, Soil Biol. Biochem., 39, 1770–1781, https://doi.org/10.1016/j.soilbio.2007.02.006, 2007b.

Assmann, E. and Franz, F.: Vorläufige Fichten-Ertragstafel für Bayern, Forstwissenschaftliches Cent., 84, 13–43, https://doi.org/10.1007/BF01872794, 1965.

Augusto, L., Davies, T. J., Delzon, S., and de Schrijver, A.: The enigma of the rise of angiosperms: Can we untie the knot?, Ecol. Lett., 17, 1326–1338, https://doi.org/10.1111/ele.12323, 2014.

Augusto, L., De Schrijver, A., Vesterdal, L., Smolander, A., Prescott, C., and Ranger, J.: Influences of evergreen gymnosperm and deciduous angiosperm tree species on the functioning of temperate and boreal forests, Biol. Rev., 90, 444–466, https://doi.org/10.1111/brv.12119, 2015.

Aznar-Sánchez, J. A., Belmonte-Ureña, L. J., López-Serrano, M. J., and Velasco-Muñoz, J. F.: Forest ecosystem services: An analysis of worldwide research, 9, https://doi.org/10.3390/f9080453, 2018.

Baisden, W. T., Amundson, R., Brenner, D. L., Cook, A. C., Kendall, C., and Harden, J. W.: A multiisotope C and N modeling analysis of soil organic matter turnover and transport as a function of soil depth in a California annual grassland soil chronosequence, Global Biogeochem. Cycles, 16, 82-1-82–26, https://doi.org/10.1029/2001gb001823, 2002.

Baldrian, P.: Fungal laccases-occurrence and properties, FEMS Microbiol. Rev., 30, 215–242, https://doi.org/10.1111/j.1574-4976.2005.00010.x, 2006.

Baldrian, P.: Forest microbiome: Diversity, complexity and dynamics, FEMS Microbiol. Rev., 41, 109–130, https://doi.org/10.1093/femsre/fuw040, 2017.

Baldrian, P., Merhautová, V., Cajthaml, T., Petránková, M., and Šnajdr, J.: Small-scale distribution of extracellular enzymes, fungal, and bacterial biomass in Quercus petraea forest topsoil, Biol. Fertil. Soils, 46, 717–726, https://doi.org/10.1007/s00374-010-0478-4, 2010.

Bardgett, R. D., Mommer, L., and De Vries, F. T.: Going underground: Root traits as drivers of ecosystem processes, Trends Ecol. Evol., 29, 692–699, https://doi.org/10.1016/j.tree.2014.10.006, 2014.

Barré, P., Fernandez-Ugalde, O., Virto, I., Velde, B., and Chenu, C.: Impact of phyllosilicate mineralogy on organic carbon stabilization in soils: Incomplete knowledge and exciting prospects, Geoderma, 235–236, 382–395, https://doi.org/10.1016/j.geoderma.2014.07.029, 2014.

Barré, P., Plante, A. F., Cécillon, L., Lutfalla, S., Baudin, F., Bernard, S., Christensen, B. T., Eglin, T., Fernandez,

J. M., Houot, S., Kätterer, T., Le Guillou, C., Macdonald, A., van Oort, F., and Chenu, C.: The energetic and chemical signatures of persistent soil organic matter, Biogeochemistry, 130, 1–12, https://doi.org/10.1007/s10533-016-0246-0, 2016.

Barrow, N. J., Debnath, A., and Sen, A.: Measurement of the effects of pH on phosphate availability, Plant Soil, 454, 217–224, https://doi.org/10.1007/s11104-020-04647-5, 2020.

Basile-Doelsch, I., Amundson, R., Stone, W. E. E., Masiello, C. A., Bottero, J. Y., Colin, F., Masin, F., Borschneck, D., and Meunier, J. D.: Mineralogical control of organic carbon dynamics in a volcanic ash soil on La Réunion, Eur. J. Soil Sci., 56, 689–703, https://doi.org/10.1111/j.1365-2389.2005.00703.x, 2005.

Batjes, N. H.: Total carbon and nitrogen in the soils of the world, Eur. J. Soil Sci., 47, 151–163, https://doi.org/10.1111/j.1365-2389.1996.tb01386.x, 1996.

Bell, C., Carrillo, Y., Boot, C. M., Rocca, J. D., Pendall, E., and Wallenstein, M. D.: Rhizosphere stoichiometry: Are C : N : P ratios of plants, soils, and enzymes conserved at the plant species-level?, New Phytol., 201, 505–517, https://doi.org/10.1111/nph.12531, 2014.

Bell, F. W., Parton, J., Stocker, N., Joyce, D., Reid, D., Wester, M., Stinson, A., Kayahara, G., and Towill, B.: Developing a silvicultural framework and definitions for use in forest management planning and practice, For. Chron., 84, 678–693, https://doi.org/10.5558/tfc84678-5, 2008.

Bellassen, V. and Luyssaert, S.: Carbon sequestration: managing forests in uncertain times., Nature, 506, 153–155, https://doi.org/10.1038/506153a, 2014.

Blüthgen, N., Dormann, C. F., Prati, D., Klaus, V. H., Kleinebecker, T., Hölzel, N., Alt, F., Boch, S., Gockel, S., Hemp, A., Müller, J., Nieschulze, J., Renner, S. C., Schöning, I., Schumacher, U., Socher, S. A., Wells, K., Birkhofer, K., Buscot, F., Oelmann, Y., Rothenwöhrer, C., Scherber, C., Tscharntke, T., Weiner, C. N., Fischer, M., Kalko, E. K. V., Linsenmair, K. E., Schulze, E. D., and Weisser, W. W.: A quantitative index of land-use intensity in grasslands: Integrating mowing, grazing and fertilization, Basic Appl. Ecol., 13, 207–220, https://doi.org/10.1016/j.baae.2012.04.001, 2012.

Boča, A., Van Miegroet, H., and Gruselle, M.-C.: Forest Overstory Effect on Soil Organic Carbon Storage: A Meta-analysis, Soil Sci. Soc. Am. J., 78, S35–S47, https://doi.org/10.2136/sssaj2013.08.0332nafsc, 2014.

Bonan, G. B.: Forests and climate change: Forcings, feedbacks, and the climate benefits of forests, Science (80-.)., 320, 1444–1449, https://doi.org/10.1126/science.1155121, 2008.

Bowden, R. D., Deem, L., Plante, A. F., Peltre, C., Nadelhoffer, K., and Lajtha, K.: Litter Input Controls on Soil Carbon in a Temperate Deciduous Forest, Soil Sci. Soc. Am. J., 78, https://doi.org/10.2136/sssaj2013.09.0413nafsc, 2014.

Bradford, J. B., Jensen, N. R., Domke, G. M., and Amato, A. W. D.: Forest Ecology and Management Potential increases in natural disturbance rates could offset forest management impacts on ecosystem carbon stocks, For. Ecol. Manage., 308, 178–187, https://doi.org/10.1016/j.foreco.2013.07.042, 2013.

Bravo-Oviedo, A., Ruiz-Peinado, R., Modrego, P., Alonso, R., and Montero, G.: Forest thinning impact on carbon stock and soil condition in Southern European populations of P. sylvestris L., For. Ecol. Manage., 357, 259–267, https://doi.org/10.1016/j.foreco.2015.08.005, 2015.

Bring, J.: A Geometric Approach to Compare Variables in a Regression Model, Am. Stat., 50, 57–62, 1996.

Buchkowski, R. W., Schmitz, O. J., and Bradford, M. A.: Microbial stoichiometry overrides biomass as a regulator of soil carbon and nitrogen cycling, Ecology, 96, 1139–1149, https://doi.org/10.1890/14-1327.1, 2015.

Burns, R. G.: Soil enzymology., Sci. Prog., 64, 275–285, 1977.

Burns, R. G.: Enzyme activity in soil: Location and a possible role in microbial ecology, Soil Biol. Biochem., 14, 423–427, https://doi.org/10.1016/0038-0717(82)90099-2, 1982.

Burns, R. G., DeForest, J. L., Marxsen, J., Sinsabaugh, R. L., Stromberger, M. E., Wallenstein, M. D., Weintraub, M. N., and Zoppini, A.: Soil enzymes in a changing environment: Current knowledge and future directions, Soil Biol. Biochem., 58, 216–234, https://doi.org/10.1016/j.soilbio.2012.11.009, 2013.

Carson, J. K., Rooney, D., Gleeson, D. B., and Clipson, N.: Altering the mineral composition of soil causes a shift in microbial community structure, FEMS Microbiol. Ecol., 61, 414–423, https://doi.org/10.1111/j.1574-6941.2007.00361.x, 2007.

Chenu, C. and Stotzky, G.: Interactions Between Microorganisms and Soil Particles: An Overview, in: Fundamentals of Soil Particle-Microorganism Interaction, edited by: Huang, P. M., Bollag, J.-M., and Senesi, N.,

John Wiley & Sons, New York, 4–40, 2002.

Cotrufo, M. F., Soong, J. L., Horton, A. J., Campbell, E. E., Haddix, M. L., Wall, D. H., and Parton, W. J.: Formation of soil organic matter via biochemical and physical pathways of litter mass loss, Nat. Geosci., 8, 776–779, https://doi.org/10.1038/ngeo2520, 2015.

Craig, M. E., Turner, B. L., Liang, C., Clay, K., Johnson, D. J., and Phillips, R. P.: Tree mycorrhizal type predicts within-site variability in the storage and distribution of soil organic matter, Glob. Chang. Biol., 24, 3317–3330, https://doi.org/10.1111/gcb.14132, 2018.

Cui, J., Zhu, Z., Xu, X., Liu, S., Jones, D. L., Kuzyakov, Y., Shibistova, O., Wu, J., and Ge, T.: Carbon and nitrogen recycling from microbial necromass to cope with C:N stoichiometric imbalance by priming, Soil Biol. Biochem., 142, 107720, https://doi.org/10.1016/j.soilbio.2020.107720, 2020.

Davidson, E. A. and Janssens, I. A.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, Nature, 440, 165–173, https://doi.org/10.1038/nature04514, 2006.

DeForest, J. L., Smemo, K. A., Burke, D. J., Elliott, H. L., and Becker, J. C.: Soil microbial responses to elevated phosphorus and pH in acidic temperate deciduous forests, Biogeochemistry, 109, 189–202, 2012.

Deng, S., Popova, I. E., Dick, L., and Dick, R.: Bench scale and microplate format assay of soil enzyme activities using spectroscopic and fluorometric approaches, Appl. Soil Ecol., 64, 84–90, https://doi.org/10.1016/j.apsoil.2012.11.002, 2013.

Desie, E., Van Meerbeek, K., De Wandeler, H., Bruelheide, H., Domisch, T., Jaroszewicz, B., Joly, F. X., Vancampenhout, K., Vesterdal, L., and Muys, B.: Positive feedback loop between earthworms, humus form and soil pH reinforces earthworm abundance in European forests, Funct. Ecol., 34, 2598–2610, https://doi.org/10.1111/1365-2435.13668, 2020.

Döbbeler, H. and Spellmann, H. J.: Methodological approach to simulate and evaluate silvicultural treatments under climate change, Forstwissenschaftliches Cent., 121, 52–69, 2002.

Doetterl, S., Berhe, A. A., Arnold, C., Bodé, S., Fiener, P., Finke, P., Fuchslueger, L., Griepentrog, M., Harden, J. W., Nadeu, E., Schnecker, J., Six, J., Trumbore, S., Van Oost, K., Vogel, C., and Boeckx, P.: Links among warming, carbon and microbial dynamics mediated by soil mineral weathering, Nat. Geosci., 11, 589–593, https://doi.org/10.1038/s41561-018-0168-7, 2018.

Drake, J. E., Darby, B. A., Giasson, M. A., Kramer, M. A., Phillips, R. P., and Finzi, A. C.: Stoichiometry constrains microbial response to root exudation-insights from a model and a field experiment in a temperate forest, 10, 821–838, https://doi.org/10.5194/bg-10-821-2013, 2013.

Eivazi, F. and Tabatabai, M. A.: Phosphates in soils, Soil Biol. Biochem., 9, 167–172, 1977.

FAO and UNEP: The state of the World's forests 2020. Forest biodiversity and people, FAO, Rome, https://doi.org/https://doi.org/10.4060/ca8642en, 2020.

Felipe-Lucia, M. R., Soliveres, S., Penone, C., Manning, P., van der Plas, F., Boch, S., Prati, D., Ammer, C., Schall, P., Gossner, M. M., Bauhus, J., Buscot, F., Blaser, S., Blüthgen, N., de Frutos, A., Ehbrecht, M., Frank, K., Goldmann, K., Hänsel, F., Jung, K., Kahl, T., Nauss, T., Oelmann, Y., Pena, R., Polle, A., Renner, S., Schloter, M., Schöning, I., Schrumpf, M., Schulze, E. D., Solly, E., Sorkau, E., Stempfhuber, B., Tschapka, M., Weisser, W. W., Wubet, T., Fischer, M., and Allan, E.: Multiple forest attributes underpin the supply of multiple ecosystem services, Nat. Commun., 9, https://doi.org/10.1038/s41467-018-07082-4, 2018.

Finzi, A. C., Abramoff, R. Z., Spiller, K. S., Brzostek, E. R., Darby, B. A., Kramer, M. A., and Phillips, R. P.: Rhizosphere processes are quantitatively important components of terrestrial carbon and nutrient cycles, Glob. Chang. Biol., 21, 2082–2094, https://doi.org/10.1111/gcb.12816, 2015.

Fischer, M., Bossdorf, O., Gockel, S., Hänsel, F., Hemp, A., Hessenmöller, D., Korte, G., Nieschulze, J., Pfeiffer, S., Prati, D., Renner, S., Schöning, I., Schumacher, U., Wells, K., Buscot, F., Kalko, E. K. V., Linsenmair, K. E., Schulze, E. D., and Weisser, W. W.: Implementing large-scale and long-term functional biodiversity research: The Biodiversity Exploratories, Basic Appl. Ecol., 11, 473–485, https://doi.org/10.1016/j.baae.2010.07.009, 2010.

Frankena, J., Van Verseveld, H. W., and Stouthamer, A. H.: Substrate and energy costs of the production of exocellular enzymes by Bacillus licheniformis, Biotechnol. Bioeng., 32, 803–812, https://doi.org/10.1002/bit.260320612, 1988.

Friedel, J. K., Ehrmann, O., Pfeffers, M., Stemmer, M., Vollmer, T., and Sommer, M.: Soil microbial biomass and activity: The effect of site characteristics in humid temperate forest ecosystems, J. Plant Nutr. Soil Sci., 169, 175–184, https://doi.org/10.1002/jpln.200521763, 2006.

Gartzia-Bengoetxea, N., Virto, I., Arias-González, A., Enrique, A., Fernández-Ugalde, O., and Barré, P.: Mineral control of organic carbon storage in acid temperate forest soils in the Basque Country, Geoderma, 358, 113998, https://doi.org/10.1016/j.geoderma.2019.113998, 2020.

Gaudinski, J., Trumbore, S., and Davidson, E.: Soil carbon cycling in a temperate forest: radiocarbon-based estimates of residence times, …, Biogeochemistry, 51, 33–69, 2000.

Gianfreda, L. and Bollag, J.-M.: Effect of Soils on the Behavior of Immobilized Enzymes, Soil Sci. Soc. Am. J., 58, 1672, https://doi.org/10.2136/sssaj1994.03615995005800060014x, 1994.

Goodale, C. L., Apps, M. J., Birdsey, R. A., Field, C. B., Heath, L. S., Houghton, R. A., Jenkins, J. C., Kohlmaier, G. H., Kurz, W., Liu, S., Nabuurs, G. J., Nilsson, S., and Shvidenko, A. Z.: Forest carbon sinks in the Northern Hemisphere, Ecol. Appl., 12, 891–899, https://doi.org/10.1890/1051-0761(2002)012[0891:FCSITN]2.0.CO;2, 2002.

Gossner, M. M., Schall, P., Ammer, C., Ammer, U., Engel, K., Schubert, H., Simon, U., Utschick, H., and Weisser, W. W.: Forest management intensity measures as alternative to stand properties for quantifying effects on biodiversity, 5, 1–111, https://doi.org/10.1890/ES14-00177.1, 2014.

Grömping, U.: Variable importance in regression models, Wiley Interdiscip. Rev. Comput. Stat., 7, 137–152, https://doi.org/10.1002/wics.1346, 2015.

Gu, B., Schmitt, J., Chen, Z., Liang, L., and McCarthy, J. F.: Adsorption and Desorption of Natural Organic Matter on Iron Oxide: Mechanisms and Models, Environ. Sci. Technol., 28, 38–46, https://doi.org/10.1021/es00050a007, 1994.

Haberl, H., Erb, K. H., Krausmann, F., Gaube, V., Bondeau, A., Plutzar, C., Gingrich, S., Lucht, W., and Fischer-Kowalski, M.: Quantifying and mapping the human appropriation of net primary production in earth's terrestrial ecosystems, Proc. Natl. Acad. Sci. U. S. A., 104, 12942–12947, https://doi.org/10.1073/pnas.0704243104, 2007.

Han, L., Sun, K., Jin, J., and Xing, B.: Some concepts of soil organic carbon characteristics and mineral interaction from a review of literature, Soil Biol. Biochem., 94, 107–121, https://doi.org/10.1016/j.soilbio.2015.11.023, 2016.

Hari, P., Heliövaara, K., and Kulmala, L.: Physical and Physiological Forest Ecology, Springer, Dordrecht, Heidelberg, New York, London, https://doi.org/10.1007/978-94-007-5603-8, 2013.

Hassink, J.: A Model of the Physical Protection of Organic Matter in Soils The capacity of soils to preserve organic C and N by their association with clay and silt particles, Plant Soil, 191, 77–87, 1997.

Hendriksen, N. B., Creamer, R. E., Stone, D., and Winding, A.: Soil exo-enzyme activities across Europe-The influence of climate, land-use and soil properties, Appl. Soil Ecol., 97, 44–48, https://doi.org/10.1016/j.apsoil.2015.08.012, 2016.

Jackson, R. B., Lajtha, K., Crow, S. E., Hugelius, G., Kramer, M. G., and Piñeiro, G.: The Ecology of Soil Carbon: Pools, Vulnerabilities, and Biotic and Abiotic Controls, Annu. Rev. Ecol. Evol. Syst., 48, 419–445, https://doi.org/10.1146/annurev-ecolsys-112414-054234, 2017.

James, G., Witten, D., Hastie, T., and Tibshirani, R.: An Introduction to Statistical Learning with Applications in R, Springer, New York, 618 pp., 2013.

Jandl, R., Lindner, M., Vesterdal, L., Bauwens, B., Baritz, R., Hagedorn, F., Johnson, D. W., Minkkinen, K., and Byrne, K. A.: How strongly can forest management influence soil carbon sequestration ?, 137, 253–268, https://doi.org/10.1016/j.geoderma.2006.09.003, 2007.

Jeewani, P. H., Gunina, A., Tao, L., Zhu, Z., Kuzyakov, Y., Van Zwieten, L., Guggenberger, G., Shen, C., Yu, G., Singh, B. P., Pan, S., Luo, Y., and Xu, J.: Rusty sink of rhizodeposits and associated keystone microbiomes, Soil Biol. Biochem., 147, 107840, https://doi.org/10.1016/j.soilbio.2020.107840, 2020.

Jeewani, P. H., Luo, Y., Yu, G., Fu, Y., He, X., Van Zwieten, L., Liang, C., Kumar, A., He, Y., Kuzyakov, Y., Qin, H., Guggenberger, G., and Xu, J.: Arbuscular mycorrhizal fungi and goethite promote carbon sequestration via hyphal-aggregate mineral interactions, Soil Biol. Biochem., 162, 108417, https://doi.org/10.1016/j.soilbio.2021.108417, 2021.

Jilling, A., Keiluweit, M., Contosta, A. R., Frey, S., Schimel, J., Schnecker, J., Smith, R. G., Tiemann, L., and Grandy, A. S.: Minerals in the rhizosphere: overlooked mediators of soil nitrogen availability to plants and microbes, Biogeochemistry, 139, 103–122, https://doi.org/10.1007/s10533-018-0459-5, 2018.

Jobbágy, E. G. and Jackson, R. B.: The vertical distribution of soil organic carbon and its relation to climate and vegetation, Ecol. Appl., 10, 423–436, https://doi.org/10.1890/1051-0761(2000)010[0423:TVDOSO]2.0.CO;2, 2000.

Jones, D. L., Nguyen, C., and Finlay, R. D.: Carbon flow in the rhizosphere: Carbon trading at the soil-root interface, Plant Soil, 321, 5–33, https://doi.org/10.1007/s11104-009-9925-0, 2009.

Kahle, M., Kleber, M., and Jahn, R.: Retention of dissolved organic matter by illitic soils and clay fractions: Influence of mineral phase properties, J. Plant Nutr. Soil Sci., 166, 737–741, https://doi.org/10.1002/jpln.200321125, 2003.

Kaiser, K. and Guggenberger, G.: Mineral surfaces and soil organic matter, Eur. J. Soil Sci., 54, 219–236, https://doi.org/10.1046/j.1365-2389.2003.00544.x, 2003.

Kaiser, K., Guggenberger, G., Haumaier, L., and Zech, W.: The composition of dissolved organic matter in forest soil solutions: Changes induced by seasons and passage through the mineral soil, Org. Geochem., 33, 307–318, https://doi.org/10.1016/S0146-6380(01)00162-0, 2002.

Kaiser, M., Zederer, D. P., Ellerbrock, R. H., Sommer, M., and Ludwig, B.: Effects of mineral characteristics on content, composition, and stability of organic matter fractions separated from seven forest topsoils of different pedogenesis, Geoderma, 263, 1–7, https://doi.org/10.1016/j.geoderma.2015.08.029, 2016.

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., and Matzner, E.: Controls on the dynamics of dissolved organic matter in soils. A review, Soi Sci., 165, 277–304, 2000.

Kalbitz, K., Schwesig, D., Rethemeyer, J., and Matzner, E.: Stabilization of dissolved organic matter by sorption to the mineral soil, Soil Biol. Biochem., 37, 1319–1331, https://doi.org/10.1016/j.soilbio.2004.11.028, 2005.

Kandeler, E., Gebala, A., Boeddinghaus, R. S., Müller, K., Rennert, T., Soares, M., Rousk, J., and Marhan, S.: The mineralo-sphere – Succession and physiology of bacteria and fungi colonising pristine minerals in grassland soils under different land-use intensities, Soil Biol. Biochem., 136, https://doi.org/10.1016/j.soilbio.2019.107534, 2019.

Kara, Ö., Bolat, I., Çakiroğlu, K., and Öztürk, M.: Plant canopy effects on litter accumulation and soil microbial biomass in two temperate forests, Biol. Fertil. Soils, 45, 193–198, https://doi.org/10.1007/s00374-008-0327-x, 2008.

Keiluweit, M., Bougoure, J. J., Nico, P. S., Pett-Ridge, J., Weber, P. K., and Kleber, M.: Mineral protection of soil carbon counteracted by root exudates, Nat. Clim. Chang., 5, 588–595, https://doi.org/10.1038/nclimate2580, 2015.

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., and Nico, P. S.: Mineral-Organic Associations: Formation, Properties, and Relevance in Soil Environments, Elsevier Ltd, 1–140 pp., https://doi.org/10.1016/bs.agron.2014.10.005, 2015.

Kleber, M., Bourg, I. C., Coward, E. K., Hansel, C. M., Myneni, S. C. B., and Nunan, N.: Dynamic interactions at the mineral–organic matter interface, Nat. Rev. Earth Environ., 2, 402–421, https://doi.org/10.1038/s43017-021-00162-y, 2021.

Kögel-Knabner, I.: Organische Bodensubstanz, in: Scheffer/Schachtschabel - Lehrbuch der Bodenkunde, edited by: Amelung, W., Blume, H.-P., Fleige, H., Horn, R., Kandeler, E., Kögel-Knabner, I., Kretzschmar, R., Stahr, K., and Wilke, B.-M., Springer, Heidelberg, 63–102, 2018.

Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., Eusterhues, K., and Leinweber, P.: Organo-mineral associations in temperate soils: Integrating biology, mineralogy, and organic matter chemistry, J. Plant Nutr. Soil Sci., 171, 61–82, https://doi.org/10.1002/jpln.200700048, 2008.

Kohv, K. and Liira, J.: Anthropogenic effects on vegetation structure of the boreal forest in Estonia, Scand. J. For. Res., 20, 122–134, https://doi.org/10.1080/14004080510041011, 2005.

Kopittke, P. M., Dalal, R. C., Hoeschen, C., Li, C., Menzies, N. W., and Mueller, C. W.: Soil organic matter is stabilized by organo-mineral associations through two key processes: The role of the carbon to nitrogen ratio, Geoderma, 357, 113974, https://doi.org/10.1016/j.geoderma.2019.113974, 2020.

Kramer, M. G. and Chadwick, O. A.: Climate-driven thresholds in reactive mineral retention of soil carbon at the global scale, Nat. Clim. Chang., 8, 1104–1108, https://doi.org/10.1038/s41558-018-0341-4, 2018.

Kramer, M. G., Sanderman, J., Chadwick, O. A., Chorover, J., and Vitousek, P. M.: Long-term carbon storage through retention of dissolved aromatic acids by reactive particles in soil, Glob. Chang. Biol., 18, 2594–2605, https://doi.org/10.1111/j.1365-2486.2012.02681.x, 2012.

Kramer, S., Marhan, S., Haslwimmer, H., Ruess, L., and Kandeler, E.: Temporal variation in surface and subsoil abundance and function of the soil microbial community in an arable soil, Soil Biol. Biochem., 61, 76–85, https://doi.org/10.1016/j.soilbio.2013.02.006, 2013.

Kuhn, M.: caret: Classification and Regression Training, https://cran.r-project.org/package=caret, 2021.

Laganière, J., Angers, D. A., and Paré, D.: Carbon accumulation in agricultural soils after afforestation: A meta-analysis, Glob. Chang. Biol., 16, 439–453, https://doi.org/10.1111/j.1365-2486.2009.01930.x, 2010.

Lehmann, J. and Kleber, M.: The contentious nature of soil organic matter, Nature, 528, 60–68, https://doi.org/10.1038/nature16069, 2015.

Lenth, R. v.: emmeans: Estimated Marginal Means, aka Least-Squares Means., https://cran.r-project.org/package=emmeans, 2022.

Leprince, F. and Quiquampoix, H.: Extracellular enzyme activity in soil: Effect of pH and ionic strength on the interaction with montmorillonite of two acid phosphatases secreted by the ectomycorrhizal fungus Hebeloma cylindrosporum, Eur. J. Soil Sci., 47, 511–522, https://doi.org/10.1111/j.1365-2389.1996.tb01851.x, 1996.

Li, J., Nie, M., and Pendall, E.: Soil physico-chemical properties are more important than microbial diversity and enzyme activity in controlling carbon and nitrogen stocks near Sydney, Australia, Geoderma, 366, 114201, https://doi.org/10.1016/j.geoderma.2020.114201, 2020.

Liebmann, P., Mikutta, R., Kalbitz, K., Wordell-Dietrich, P., Leinemann, T., Preusser, S., Mewes, O., Perrin, E., Bachmann, J., Don, A., Kandeler, E., Marschner, B., Schaarschmidt, F., and Guggenberger, G.: Biogeochemical limitations of carbon stabilization in forest subsoils, J. Plant Nutr. Soil Sci., 185, 35–43, https://doi.org/10.1002/jpln.202100295, 2022.

Ling, N., Sun, Y., Ma, J., Guo, J., Zhu, P., Peng, C., Yu, G., Ran, W., Guo, S., and Shen, Q.: Response of the bacterial diversity and soil enzyme activity in particle-size fractions of Mollisol after different fertilization in a long-term experiment, Biol. Fertil. Soils, 50, 901–911, https://doi.org/10.1007/s00374-014-0911-1, 2014.

Liski, J., Perruchoud, D., and Karjalainen, T.: Increasing carbon stocks in the forest soils of western Europe, For. Ecol. Manage., 169, 159–175, https://doi.org/10.1016/S0378-1127(02)00306-7, 2002.

Liu, H., Chen, T., and Frost, R. L.: An overview of the role of goethite surfaces in the environment, Chemosphere, 103, 1–11, https://doi.org/10.1016/j.chemosphere.2013.11.065, 2014.

Luo, L., Meng, H., and Gu, J. D.: Microbial extracellular enzymes in biogeochemical cycling of ecosystems, J. Environ. Manage., 197, 539–549, https://doi.org/10.1016/j.jenvman.2017.04.023, 2017.

Von Lützow, M., Kögel-Knabner, I., Ludwig, B., Matzner, E., Flessa, H., Ekschmitt, K., Guggenberger, G., Marschner, B., and Kalbitz, K.: Stabilization mechanisms of organic matter in four temperate soils: Development and application of a conceptual model, J. Plant Nutr. Soil Sci., 171, 111–124, https://doi.org/10.1002/jpln.200700047, 2008.

Luyssaert, S., Inglima, I., Jung, M., Richardson, A. D., Reichstein, M., Papale, D., Piao, S. L., Schulze, E. D., Wingate, L., Matteucci, G., Aragao, L., Aubinet, M., Beer, C., Bernhofer, C., Black, K. G., Bonal, D., Bonnefond, J. M., Chambers, J., Ciais, P., Cook, B., Davis, K. J., Dolman, A. J., Gielen, B., Goulden, M., Grace, J., Granier, A., Grelle, A., Griffis, T., Grünwald, T., Guidolotti, G., Hanson, P. J., Harding, R., Hollinger, D. Y., Hutyra, L. R., Kolari, P., Kruijt, B., Kutsch, W., Lagergren, F., Laurila, T., Law, B. E., Le Maire, G., Lindroth, A., Loustau, D., Malhi, Y., Mateus, J., Migliavacca, M., Misson, L., Montagnani, L., Moncrieff, J., Moors, E., Munger, J. W., Nikinmaa, E., Ollinger, S. V., Pita, G., Rebmann, C., Roupsard, O., Saigusa, N., Sanz, M. J., Seufert, G., Sierra, C., Smith, M. L., Tang, J., Valentini, R., Vesala, T., and Janssens, I. A.: CO2 balance of boreal, temperate, and tropical forests derived from a global database, Glob. Chang. Biol., 13, 2509–2537, https://doi.org/10.1111/j.1365-2486.2007.01439.x, 2007.

Luyssaert, S., Hessenmöller, D., Von Lüpke, N., Kaiser, S., and Schulze, E. D.: Quantifying land use and disturbance intensity in forestry, based on the self-thinning relationship, Ecol. Appl., 21, 3272–3284, https://doi.org/10.1890/10-2395.1, 2011.

Maes, S. L., Blondeel, H., Perring, M. P., Depauw, L., Brūmelis, G., Brunet, J., Decocq, G., den Ouden, J., Härdtle, W., Hédl, R., Heinken, T., Heinrichs, S., Jaroszewicz, B., Kirby, K., Kopecký, M., Máliš, F., Wulf, M., and Verheyen, K.: Litter quality, land-use history, and nitrogen deposition effects on topsoil conditions across European temperate deciduous forests, For. Ecol. Manage., 433, 405–418, https://doi.org/10.1016/j.foreco.2018.10.056, 2019.

Magnani, F., Mencuccini, M., Borghetti, M., Berbigier, P., Berninger, F., Delzon, S., Grelle, A., Hari, P., Jarvis, P. G., Kolari, P., Kowalski, A. S., Lankreijer, H., Law, B. E., Lindroth, A., Loustau, D., Manca, G., Moncrieff, J. B., Rayment, M., Tedeschi, V., Valentini, R., and Grace, J.: The human footprint in the carbon cycle of temperate and boreal forests, Nature, 447, 848–850, https://doi.org/10.1038/nature05847, 2007.

Manzoni, S., Jackson, R. B., Trofymow, J. A., and Porporato, A.: The global stoichiometry of litter nitrogen mineralization, Science (80-.)., 321, 684–686, https://doi.org/10.1126/science.1159792, 2008.

Manzoni, S., Trofymow, J. A., Jackson, R. B., and Porporato, A.: Stoichiometric controls on carbon, nitrogen, and phosphorus dynamics in decomposing litter, Ecol. Monogr., 80, 89–106, https://doi.org/10.1890/09-0179.1, 2010.

Marx, M. C., Wood, M., and Jarvis, S. C.: A microplate fluorimetric assay for the study of enzyme diversity in soils, Soil Biol. Biochem., 33, 1633–1640, https://doi.org/10.1016/S0038-0717(01)00079-7, 2001.

Marx, M. C., Kandeler, E., Wood, M., Wermbter, N., and Jarvis, S. C.: Exploring the enzymatic landscape: Distribution and kinetics of hydrolytic enzymes in soil particle-size fractions, Soil Biol. Biochem., 37, 35–48, https://doi.org/10.1016/j.soilbio.2004.05.024, 2005.

Mayer, M., Prescott, C. E., Abaker, W. E. A., Augusto, L., Cécillon, L., Ferreira, G. W. D., James, J., Jandl, R., Katzensteiner, K., Laclau, J. P., Laganière, J., Nouvellon, Y., Paré, D., Stanturf, J. A., Vanguelova, E. I., and Vesterdal, L.: Influence of forest management activities on soil organic carbon stocks: A knowledge synthesis, For. Ecol. Manage., 466, https://doi.org/10.1016/j.foreco.2020.118127, 2020.

McBride, S. G. and Strickland, M. S.: Quorum sensing modulates microbial efficiency by regulating bacterial investment in nutrient acquisition enzymes, Soil Biol. Biochem., 136, 107514, https://doi.org/10.1016/j.soilbio.2019.06.010, 2019.

McLaren, A. D., Reshetko, L., and Huber, W.: Sterilization of soil by irradiation with an electron beam and some observations on enzyme activity, Soil Sci., 83, 497–502, 1956.

Meier, I. C., Finzi, A. C., and Phillips, R. P.: Root exudates increase N availability by stimulating microbial turnover of fast-cycling N pools, Soil Biol. Biochem., 106, 119–128, https://doi.org/10.1016/j.soilbio.2016.12.004, 2017.

Meunier, A. and Velde, B.: Illite. Origins, Evolution and Metamorphism, Springer, Berlin, 2004.

Mikutta, R., Schaumann, G. E., Gildemeister, D., Bonneville, S., Kramer, M. G., Chorover, J., Chadwick, O. A., and Guggenberger, G.: Biogeochemistry of mineral-organic associations across a long-term mineralogical soil gradient (0.3-4100 kyr), Hawaiian Islands, Geochim. Cosmochim. Acta, 73, 2034–2060, https://doi.org/10.1016/j.gca.2008.12.028, 2009.

Mokany, K., Raison, R. J., and Prokushkin, A. S.: Critical analysis of root: Shoot ratios in terrestrial biomes, Glob. Chang. Biol., 12, 84–96, https://doi.org/10.1111/j.1365-2486.2005.001043.x, 2006.

Mooshammer, M., Wanek, W., Zechmeister-Boltenstern, S., and Richter, A.: Stoichiometric imbalances between terrestrial decomposer communities and their resources: Mechanisms and implications of microbial adaptations to their resources, Front. Microbiol., 5, 1–10, https://doi.org/10.3389/fmicb.2014.00022, 2014.

Müller, K., Kubsch, N., Marhan, S., Mayer-Gruner, P., Nassal, P., Schneider, D., Daniel, R., Piepho, H. P., Polle, A., and Kandeler, E.: Saprotrophic and Ectomycorrhizal Fungi Contribute Differentially to Organic P Mobilization in Beech-Dominated Forest Ecosystems, Front. For. Glob. Chang., 3, https://doi.org/10.3389/ffgc.2020.00047, 2020.

Nannipieri, P., Giagnoni, L., Renella, G., Puglisi, E., Ceccanti, B., Masciandaro, G., Fornasier, F., Moscatelli, M. C., and Marinari, S.: Soil enzymology: Classical and molecular approaches, Biol. Fertil. Soils, 48, 743–762, https://doi.org/10.1007/s00374-012-0723-0, 2012.

Nannipieri, P., Trasar-Cepeda, C., and Dick, R. P.: Soil enzyme activity: a brief history and biochemistry as a basis for appropriate interpretations and meta-analysis, Biol. Fertil. Soils, 54, 11–19, https://doi.org/10.1007/s00374-017-1245-6, 2018.

Olagoke, F. K., Kalbitz, K., and Vogel, C.: Control of soil extracellular enzyme activities by clay minerals—perspectives on microbial responses, Soil Syst., 3, 1–16, https://doi.org/10.3390/soilsystems3040064, 2019.

Olagoke, F. K., Kaiser, K., Mikutta, R., Kalbitz, K., and Vogel, C.: Persistent activities of extracellular enzymes adsorbed to soil minerals, 8, 1–15, https://doi.org/10.3390/microorganisms8111796, 2020.

Olander, L. P. and Vitousek, P. M.: Regulation of soil phosphatase and chitinase activity by N and P availability, Biogeochemistry, 49, 175–190, https://doi.org/10.1023/A:1006316117817, 2000.

Olson, J. S.: Energy storage and the balance of producers and decomposers in ecological systems, Ecology, 44, 322–331, 1963.

Pan, Y., Birdsey, R. A., Fang, J., Houghton, R., Kauppi, P. E., Kurz, W. A., Phillips, O. L., Shvidenko, A., Lewis, S. L., Canadell, J. G., Ciais, P., Jackson, R. B., Pacala, S. W., McGuire, A. D., Piao, S., Rautiainen, A., Sitch, S., and Hayes, D.: A large and persistent carbon sink in the world's forests, Science (80-.)., 333, 988–993, https://doi.org/10.1126/science.1201609, 2011.

Pancholy, S. K. and Lynd, J. Q.: Quantitative fluorescence analysis of soil lipase activity, Soil Biol. Biochem., 4, 257–259, 1972.

Parton, W., Silver, W. L., Burke, I. C., Grassens, L., Harmon, M. E., Currie, W. S., King, J. Y., Adair, E. C., Brandt, L. A., Hart, S. C., and Fasth, B.: Long-Term Decomposition, 5064, 2007.

Pérez-Cruzado, C., Mansilla-Salinero, P., Rodríguez-Soalleiro, R., and Merino, A.: Influence of tree species on carbon sequestration in afforested pastures in a humid temperate region, Plant Soil, 353, 333–353, https://doi.org/10.1007/s11104-011-1035-0, 2012.

Prescott, C. E. and Grayston, S. J.: Tree species influence on microbial communities in litter and soil: Current knowledge and research needs, For. Ecol. Manage., 309, 19–27, https://doi.org/10.1016/j.foreco.2013.02.034, 2013.

Pretzsch, H.: Forest Dynamics, Growth and Yield, https://doi.org/10.1007/978-3-540-88307-4, 2009.

Prosser, J. I., Bohannan, B. J. M., Curtis, T. P., Ellis, R. J., Firestone, M. K., Freckleton, R. P., Green, J. L., Green, L. E., Killham, K., Lennon, J. J., Osborn, A. M., Solan, M., Van Der Gast, C. J., and Young, J. P. W.: The role of ecological theory in microbial ecology, Nat. Rev. Microbiol., 5, 384–392, 2007.

Purahong, W., Kapturska, D., Pecyna, M. J., Schulz, E., Schloter, M., Buscot, F., Hofrichter, M., and Kruğer, D.: Influence of different forest system management practices on leaf litter decomposition rates, nutrient dynamics and the activity of ligninolytic enzymes: A case study from Central European forests, PLoS One, 9, 1–11, https://doi.org/10.1371/journal.pone.0093700, 2014.

Le Quéré, C., Peters, G. P., Andres, R. J., Andrew, R. M., Boden, T. A., Ciais, P., Friedlingstein, P., Houghton, R. A., Marland, G., Moriarty, R., Sitch, S., Tans, P., Arneth, A., Arvanitis, A., Bakker, D. C. E., Bopp, L., Canadell, J. G., Chini, L. P., Doney, S. C., Harper, A., Harris, I., House, J. I., Jain, A. K., Jones, S. D., Kato, E., Keeling, R. F., Klein Goldewijk, K., Körtzinger, A., Koven, C., Lefèvre, N., Maignan, F., Omar, A., Ono, T., Park, G. H., Pfeil, B., Poulter, B., Raupach, M. R., Regnier, P., Rödenbeck, C., Saito, S., Schwinger, J., Segschneider, J., Stocker, B. D., Takahashi, T., Tilbrook, B., Van Heuven, S., Viovy, N., Wanninkhof, R., Wiltshire, A., and Zaehle, S.: Global carbon budget 2013, Earth Syst. Sci. Data, 6, 235–263, https://doi.org/10.5194/essd-6-235-2014, 2014.

Quideau, S. A., Chadwick, O. A., Benesi, A., Graham, R. C., and Anderson, M. A.: A direct link between forest vegetation type and soil organic matter composition, Geoderma, 104, 41–60, https://doi.org/10.1016/S0016-7061(01)00055-6, 2001.

Quiquampoix, H.: A stepwise approach to the understanding of extracellular enzyme activity in soil I. Effect of electrostatic interactions on the conformation of a β-d-glucosidase adsorbed on different mineral surfaces, Biochimie, 69, 753–763, https://doi.org/10.1016/0300-9084(87)90196-9, 1987a.

Quiquampoix, H.: A stepwise approach to the understanding of extracellular enzyme activity in soil II. Competitive effects on adsorption of a β-d-glucosidase in mixed mineral or organo-mineral systems, Biochimie, 69, 765–771, 1987b.

Quiquampoix, H. and Burns, R. G.: Interactions between proteins and soil mineral surfaces: Environmental and health consequences, 3, 401–406, https://doi.org/10.2113/GSELEMENTS.3.6.401, 2007.

R Core Team: R: A language and environment for statistical computing, https://www.r-project.org/, 2021.

Rao, C. S., Grover, M., Sumanta, K., and Desai, S.: Soil Enzymes, Encycl. Soil Sci., 2100–2107, https://doi.org/10.1081/e-ess3-120052906, 2017.

Rao, M. A., Violante, A., and Gianfreda, L.: Interaction of acid phosphatase with clays, organic molecules and organo-mineral complexes: Kinetics and stability, Soil Biol. Biochem., 32, 1007–1014, https://doi.org/10.1016/S0038-0717(00)00010-9, 2000.

Rao, M. A., Scelza, R., and Gianfreda, L.: Enzymes in Agricultural Sciences, Enzym. Agric. Sci., 1–21, 2014.

Rasse, D. P., Rumpel, C., and Dignac, M. F.: Is soil carbon mostly root carbon? Mechanisms for a specific stabilisation, Plant Soil, 269, 341–356, https://doi.org/10.1007/s11104-004-0907-y, 2005.

Redfield, A. C.: The biological control of chemical factors in the environment, Sci. Prog., 11, 150–170, 1960.

Ribbons, R. R., Kepfer-Rojas, S., Kosawang, C., Hansen, O. K., Ambus, P., McDonald, M., Grayston, S. J., Prescott, C. E., and Vesterdal, L.: Context-dependent tree species effects on soil nitrogen transformations and related microbial functional genes, Biogeochemistry, 140, 145–160, https://doi.org/10.1007/s10533-018-0480-8, 2018.

Rog, I., Jakoby, G., and Klein, T.: Carbon allocation dynamics in conifers and broadleaved tree species revealed

by pulse labeling and mass balance, For. Ecol. Manage., 493, 119258, https://doi.org/10.1016/j.foreco.2021.119258, 2021.

Saidy, A. R., Smernik, R. J., Baldock, J. A., Kaiser, K., and Sanderman, J.: The sorption of organic carbon onto differing clay minerals in the presence and absence of hydrous iron oxide, Geoderma, 209–210, 15–21, https://doi.org/10.1016/j.geoderma.2013.05.026, 2013.

Sarkar, J. M., Leonowicz, A., and Bollag, J.-M.: Immobilization of enzymes on clays and soils, Soil Biol. Biochem., 21, 223–30, 1989.

Schall, P. and Ammer, C.: How to quantify forest management intensity in Central European forests, Eur. J. For. Res., 132, 379–396, https://doi.org/10.1007/s10342-013-0681-6, 2013.

Schall, P. and Ammer, C.: SMI - Silvicultural Management Intensity Index on all forest EPs, 2008-2014. ID: 17746, 2014.

Schall, P. and Ammer, C.: Forest EP - Forest inventory, single tree data. v1.1.9. Biodiversity Exploratories Information System., 2017.

Schall, P. and Ammer, C.: New forest type classification of all forest EPs, 2008-2014. v1.2.5, 2018.

Schimel, J. P. and Weintraub, M. N.: The implications of exoenzyme activity on microbial carbon and nitrogen limitation in soil: A theoretical model, Soil Biol. Biochem., 35, 549–563, https://doi.org/10.1016/S0038-0717(03)00015-4, 2003.

Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., Lehmann, J., Manning, D. A. C., Nannipieri, P., Rasse, D. P., Kleber, M., and Ko, I.: Persistence of soil organic matter as an ecosystem property, https://doi.org/10.1038/nature10386, 2011.

Schöning, I., Klötzing, T., Solly, E., and Schrumpf, M.: MinSoil 2011 - Soil Texture. ID: 14686, 2012.

Schöning, I., Apostolakis, A., Klötzing, T., Trumbore, S., and Schrumpf, M.: MinSoil 2017 - Soil pH. ID: 17706, 2017.

Schöning, I., Klötzing, T., Heublein, J., Ferber, S., Gan, H. Y., Trumbore, S., and Schrumpf, M.: MinSoil 2015+ Aboveground Litter CNS. ID: 20127, 2021a.

Schöning, I., Klötzing, T., Ferber, S., Heublein, J., Gan, H. Y., and Schrumpf, M.: MinSoil 2015+ Aboveground Litter Weights. ID: 20126, 2021b.

Schrumpf, M., Kaiser, K., Guggenberger, G., Persson, T., Kögel-Knabner, I., and Schulze, E. D.: Storage and stability of organic carbon in soils as related to depth, occlusion within aggregates, and attachment to minerals, 10, 1675–1691, https://doi.org/10.5194/bg-10-1675-2013, 2013.

Schrumpf, M., Kaiser, K., Mayer, A., Hempel, G., and Trumbore, S.: Age distribution, extractability, and stability of mineral-bound organic carbon in central European soils, 18, 1241–1257, https://doi.org/10.5194/bg-18-1241-2021, 2021.

Schulp, C. J. E., Nabuurs, G. J., Verburg, P. H., and de Waal, R. W.: Effect of tree species on carbon stocks in forest floor and mineral soil and implications for soil carbon inventories, For. Ecol. Manage., 256, 482–490, https://doi.org/10.1016/j.foreco.2008.05.007, 2008.

Seymour, R. S., White, A. S., and DeMaynadier, P. G.: Natural disturbance regimes in northeastern North America - Evaluating silvicultural systems using natural scales and frequencies, For. Ecol. Manage., 155, 357–367, https://doi.org/10.1016/S0378-1127(01)00572-2, 2002.

Shanin, V., Komarov, A., and Mäkipä, R.: Tree species composition affects productivity and carbon dynamics of different site types in boreal forests, Eur. J. For. Res., 133, 273–286, https://doi.org/10.1007/s10342-013-0759-1, 2014.

Shi, W.: Agricultural and Ecological Significance of Soil Enzymes: Soil Carbon Sequestration and Nutrient Cycling, in: Soil Enzymology, edited by: Shukla, G. and Varma, A., Springer, Heidelberg, Dordrecht, London, New York, 43–60, 2011.

Singh, M., Sarkar, B., Sarkar, S., Churchman, J., Bolan, N., Mandal, S., Menon, M., Purakayastha, T. J., and Beerling, D. J.: Stabilization of Soil Organic Carbon as Influenced by Clay Mineralogy, 1st ed., Elsevier Inc., 33–84 pp., https://doi.org/10.1016/bs.agron.2017.11.001, 2018.

Singh, M., Sarkar, B., Bolan, N. S., Ok, Y. S., and Churchman, G. J.: Decomposition of soil organic matter as affected by clay types, pedogenic oxides and plant residue addition rates, J. Hazard. Mater., 374, 11–19, https://doi.org/10.1016/j.jhazmat.2019.03.135, 2019.

Sinsabaugh, R. L.: Phenol oxidase, peroxidase and organic matter dynamics of soil, Soil Biol. Biochem., 42, 391–404, https://doi.org/10.1016/j.soilbio.2009.10.014, 2010.

Sinsabaugh, R. L. and Moorhead, D. L.: Resource allocation to extracellular enzyme production: A model for nitrogen and phosphorus control of litter decomposition, Soil Biol. Biochem., 26, 1305–1311, https://doi.org/10.1016/0038-0717(94)90211-9, 1994.

Sinsabaugh, R. L., Lauber, C. L., Weintraub, M. N., Ahmed, B., Allison, S. D., Crenshaw, C., Contosta, A. R., Cusack, D., Frey, S., Gallo, M. E., Gartner, T. B., Hobbie, S. E., Holland, K., Keeler, B. L., Powers, J. S., Stursova, M., Takacs-Vesbach, C., Waldrop, M. P., Wallenstein, M. D., Zak, D. R., and Zeglin, L. H.: Stoichiometry of soil enzyme activity at global scale, Ecol. Lett., 11, 1252–1264, https://doi.org/10.1111/j.1461-0248.2008.01245.x, 2008.

Sinsabaugh, R. L., Hill, B. H., and Follstad Shah, J. J.: Ecoenzymatic stoichiometry of microbial organic nutrient acquisition in soil and sediment, Nature, 462, 795–798, https://doi.org/10.1038/nature08632, 2009.

Sinsabaugh, R. L., Manzoni, S., Moorhead, D. L., and Richter, A.: Carbon use efficiency of microbial communities: Stoichiometry, methodology and modelling, Ecol. Lett., 16, 930–939, https://doi.org/10.1111/ele.12113, 2013.

Sinsabaugh, R. S.: Enzymic analysis of microbial pattern and process, Biol. Fertil. Soils, 17, 69–74, https://doi.org/10.1007/BF00418675, 1994.

Six, J., Conant, R. T., Paul, E. A., and Paustian, K.: Stabilization mechanisms of soil organic matter: implications for C-saturation of soils, Plant Soil, 241, 155–176, 2002.

Skujiņš, J., Puķite, A., and McLaren, A. D.: Adsorption and activity of chitinase on kaolinite, Soil Biol. Biochem., 6, 179–182, https://doi.org/10.1016/0038-0717(74)90024-8, 1974.

Skujins, J. J. and McLaren, A. D.: Assay of urease activity using 14C-urea in stored, geologically preserved, and in irradiated soils, Soil Biol. Biochem., 1, 89–99, 1969.

Slessarev, E. W., Lin, Y., Bingham, N. L., Johnson, J. E., Dai, Y., Schimel, J. P., and Chadwick, O. A.: Water balance creates a threshold in soil pH at the global scale, Nature, 540, 567–569, https://doi.org/10.1038/nature20139, 2016.

Sokol, N. W., Kuebbing, S. E., Karlsen-Ayala, E., and Bradford, M. A.: Evidence for the primacy of living root inputs, not root or shoot litter, in forming soil organic carbon, New Phytol., 221, 233–246, https://doi.org/10.1111/nph.15361, 2019.

Spellmann, H. J., Nagel, J., and Böckmann, T.: Summarische Nutzungsplanung auf der Basis von Betriebsinventurdaten, Allg. Forst und Jagdzeitung, 170, 122–127, 1999.

Spohn, M., Diáková, K., Aburto, F., Doetterl, S., and Borovec, J.: Sorption and desorption of organic matter in soils as affected by phosphate, Geoderma, 405, https://doi.org/10.1016/j.geoderma.2021.115377, 2022.

Staupendahl, K. and Möhring, B.: Integrating natural risks into silvicultural decision models: A survival function approach, For. Policy Econ., 13, 496–502, https://doi.org/10.1016/j.forpol.2011.05.007, 2011.

Staupendahl, K. and Zucchini, W.: Estimating survival functions for the main tree species based on time series data from the forest condition survey in Rheinland-Pfalz, Germany, Allg. Forst und Jagdzeitung, 182, 129–145, 2011.

Sterba, H.: Estimating potential density from thinning experiments and inventory data, For. Sci., 33, 1022–1034, 1987.

Sterner, R. W. and Elser, J. J.: Ecological stoichiometry: The biology of elements from molecules to the biosphere, Princeton., Princeton, 2003.

Strahm, B. D. and Harrison, R. B.: Controls on the Sorption, Desorption and Mineralization of Low-Molecular-Weight Organic Acids in Variable-Charge Soils, Soil Sci. Soc. Am. J., 72, 1653–1664, https://doi.org/10.2136/sssaj2007.0318, 2008.

Strobel, B. W., Hansen, H. C. B., Borggaard, O. K., Andersen, M. K., and Raulund-Rasmussen, K.: Composition and reactivity of DOC in forest floor soil solutions in relation to tree species and soil type, Biogeochemistry, 56, 1–26, https://doi.org/10.1023/A:1011934929379, 2001.

Talbot, J. M., Yelle, D. J., Nowick, J., and Treseder, K. K.: Litter decay rates are determined by lignin chemistry, Biogeochemistry, 108, 279–295, https://doi.org/10.1007/s10533-011-9599-6, 2012.

Tefs, C. and Gleixner, G.: Importance of root derived carbon for soil organic matter storage in a temperate old-

growth beech forest - Evidence from C, N and 14C content, For. Ecol. Manage., 263, 131–137, https://doi.org/10.1016/j.foreco.2011.09.010, 2012.

Tewksbury, C. E. and Van Miegroet, H.: Soil organic carbon dynamics along a climatic gradient in a southern Appalachian spruce-fir forest, Can. J. For. Res., 37, 1161–1172, https://doi.org/10.1139/X06-317, 2007.

Thieme, L., Graeber, D., Hofmann, D., Bischoff, S., Schwarz, M. T., Steffen, B., Meyer, U. N., Kaupenjohann, M., Wilcke, W., Michalzik, B., and Siemens, J.: Dissolved organic matter characteristics of deciduous and coniferous forests with variable management: Different at the source, aligned in the soil, 16, 1411–1432, https://doi.org/10.5194/bg-16-1411-2019, 2019.

Tian, L., Zhao, L., Wu, X., Fang, H., Zhao, Y., Hu, G., Yue, G., Sheng, Y., Wu, J., Chen, J., Wang, Z., Li, W., Zou, D., Ping, C. L., Shang, W., Zhao, Y., and Zhang, G.: Soil moisture and texture primarily control the soil nutrient stoichiometry across the Tibetan grassland, Sci. Total Environ., 622–623, 192–202, https://doi.org/10.1016/j.scitotenv.2017.11.331, 2018.

Tiemann, L. K. and Billings, S. A.: Changes in variability of soil moisture alter microbial community C and N resource use, Soil Biol. Biochem., 43, 1837–1847, https://doi.org/10.1016/j.soilbio.2011.04.020, 2011.

Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M., and Hendricks, D. M.: Mineral control of soil organic carbon storage and turnover content were measured by horizon down to the depth at which, Nature, 389, 3601–3603, 1997.

Trumbore, S. E., Chadwick, O. A., and Amundson, R.: Rapid exchange between soil carbon and atmospheric carbon dioxide driven by temperature change, Science (80-.)., 272, 393–396, https://doi.org/10.1126/science.272.5260.393, 1996.

Uroz, S., Calvaruso, C., Turpault, M. P., and Frey-Klett, P.: Mineral weathering by bacteria: ecology, actors and mechanisms, Trends Microbiol., 17, 378–387, https://doi.org/10.1016/j.tim.2009.05.004, 2009.

Uroz, S., Oger, P., Lepleux, C., Collignon, C., Frey-Klett, P., and Turpault, M. P.: Bacterial weathering and its contribution to nutrient cycling in temperate forest ecosystems, Res. Microbiol., 162, 820–831, https://doi.org/10.1016/j.resmic.2011.01.013, 2011.

Uroz, S., Turpault, M. P., Delaruelle, C., Mareschal, L., Pierrat, J. C., and Frey-Klett, P.: Minerals affect the Specific Diversity of Forest Soil Bacterial Communities, Geomicrobiol. J., 29, 88–98, https://doi.org/10.1080/01490451.2010.523764, 2012.

Uroz, S., Kelly, L. C., Turpault, M. P., Lepleux, C., and Frey-Klett, P.: The Mineralosphere Concept: Mineralogical Control of the Distribution and Function of Mineral-associated Bacterial Communities, Trends Microbiol., 23, 751–762, https://doi.org/10.1016/j.tim.2015.10.004, 2015.

Uroz, S., Buée, M., Deveau, A., Mieszkin, S., and Martin, F.: Ecology of the forest microbiome: Highlights of temperate and boreal ecosystems, Soil Biol. Biochem., 103, 471–488, https://doi.org/10.1016/j.soilbio.2016.09.006, 2016.

Vesterdal, L., Dalsgaard, M., Felby, C., Raulund-Rasmussen, K., and Jørgensen, B. B.: Effects of thinning and soil properties on accumulation of carbon, nitrogen and phosphorus in the forest floor of Norway spruce stands, For. Ecol. Manage., 77, 1–10, https://doi.org/10.1016/0378-1127(95)03579-Y, 1995.

Vidal, A., Klöffel, T., Guigue, J., Angst, G., Steffens, M., Hoeschen, C., and Mueller, C. W.: Visualizing the transfer of organic matter from decaying plant residues to soil mineral surfaces controlled by microorganisms, Soil Biol. Biochem., 160, 108347, 2021.

Vieira, S., Sikorski, J., Gebala, A., Boeddinghaus, R. S., Marhan, S., Rennert, T., Kandeler, E., and Overmann, J.: Bacterial colonization of minerals in grassland soils is selective and highly dynamic, Environ. Microbiol., 22, 917–933, https://doi.org/10.1111/1462-2920.14751, 2020a.

Vieira, S., Sikorski, J., Dietz, S., Herz, K., Schrumpf, M., Bruelheide, H., Scheel, D., Friedrich, M. W., and Overmann, J.: Drivers of the composition of active rhizosphere bacterial communities in temperate grasslands, ISME J., 14, 463–475, https://doi.org/10.1038/s41396-019-0543-4, 2020b.

Vogt, K., Vogt, D. J., Brown, S., Tilley, J. P., Edmonds, R., Silver, W. L., and Siccama, T. G.: Dynamics of forest floor and soil organic matter accumulation in boreal, temperate, and tropical forests, edited by: Kimble, J. M., Levine, E. R., and Stewart, B. A., Boca Raton, 1995.

Wagai, R., Mayer, L. M., and Kitayama, K.: Nature of the “occluded” low-density fraction in soil organic matter studies: A critical review, Soil Sci. Plant Nutr., 55, 13–25, https://doi.org/10.1111/j.1747-0765.2008.00356.x, 2009.

Wallenstein, M. D., Mcmahon, S. K., and Schimel, J. P.: Seasonal variation in enzyme activities and temperature sensitivities in Arctic tundra soils, Glob. Chang. Biol., 15, 1631–1639, https://doi.org/10.1111/j.1365-2486.2008.01819.x, 2009.

Walmsley, A., Vachová, P., and Hlava, J.: Tree species identity governs the soil macrofauna community composition and soil development at reclaimed post-mining sites on calcium-rich clays, Eur. J. For. Res., 138, 753–761, https://doi.org/10.1007/s10342-019-01202-5, 2019.

Wang, H., Liu, S. R., Wang, J. X., Shi, Z. M., Xu, J., Hong, P. Z., Ming, A. G., Yu, H. L., Chen, L., Lu, L. H., and Cai, D. X.: Differential effects of conifer and broadleaf litter inputs on soil organic carbon chemical composition through altered soil microbial community composition, Sci. Rep., 6, 1–9, https://doi.org/10.1038/srep27097, 2016.

Weintraub, M. N. and Schimel, J. P.: The seasonal dynamics of amino acids and other nutrients in Alaskan Arctic tundra soils, Biogeochemistry, 73, 359–380, https://doi.org/10.1007/s10533-004-0363-z, 2005.

Wiesmeier, M., Prietzel, J., Barthold, F., Spörlein, P., Geuß, U., Hangen, E., Reischl, A., Schilling, B., von Lützow, M., and Kögel-Knabner, I.: Storage and drivers of organic carbon in forest soils of southeast Germany (Bavaria) - Implications for carbon sequestration, For. Ecol. Manage., 295, 162–172, https://doi.org/10.1016/j.foreco.2013.01.025, 2013.

Wild, B., Alaei, S., Bengtson, P., Bodé, S., Boeckx, P., Schnecker, J., Mayerhofer, W., and Rütting, T.: Short-term carbon input increases microbial nitrogen demand, but not microbial nitrogen mining, in a set of boreal forest soils, Biogeochemistry, 136, 261–278, https://doi.org/10.1007/s10533-017-0391-0, 2017.

Williams, E. K., Fogel, M. L., Berhe, A. A., and Plante, A. F.: Distinct bioenergetic signatures in particulate versus mineral-associated soil organic matter, Geoderma, 330, 107–116, https://doi.org/10.1016/j.geoderma.2018.05.024, 2018.

Winjum, J. K., Dixon, R. K., and Schroeder, P. E.: Estimating the global potential of forest and agroforest management practices to sequester carbon, Water. Air. Soil Pollut., 64, 213–227, 1992.

Wiseman, C. L. S. and Püttmann, W.: Soil organic carbon and its sorptive preservation in central Germany, Eur. J. Soil Sci., 56, 65–76, https://doi.org/10.1111/j.1351-0754.2004.00655.x, 2005.

Wu, L., Feinstein, L. M., Valverde-Barrantes, O., Kershner, M. W., Leff, L. G., and Blackwood, C. B.: Placing the Effects of Leaf Litter Diversity on Saprotrophic Microorganisms in the Context of Leaf Type and Habitat, Microb. Ecol., 61, 399–409, https://doi.org/10.1007/s00248-010-9760-0, 2011.

Xing, S., Chen, C., Zhou, B., Zhang, H., Nang, Z., and Xu, Z.: Soil soluble organic nitrogen and active microbial characteristics under adjacent coniferous and broadleaf plantation forests, J. Soils Sediments, 10, 748–757, https://doi.org/10.1007/s11368-009-0159-9, 2010.

Xu, P., Zhu, J., Wang, H., Shi, L., Zhuang, Y., Fu, Q., Chen, J., Hu, H., and Huang, Q.: Regulation of soil aggregate size under different fertilizations on dissolved organic matter, cellobiose hydrolyzing microbial community and their roles in organic matter mineralization, Sci. Total Environ., 755, 142595, https://doi.org/10.1016/j.scitotenv.2020.142595, 2021.

Ye, J., Yue, C., Hu, Y., and Ma, H.: Spatial patterns of global-scale forest root-shoot ratio and their controlling factors, Sci. Total Environ., 800, 149251, https://doi.org/10.1016/j.scitotenv.2021.149251, 2021.

Zechmeister-Boltenstern, S., Keiblinger, K. M., Mooshammer, M., Peñuelas, J., Richter, A., Sardans, J., and Wanek, W.: The application of ecological stoichiometry to plant-microbial-soil organic matter transformations, Ecol. Monogr., 85, 133–155, https://doi.org/10.1890/14-0777.1, 2015.

Zenner, E. K., Kabrick, J. M., Jensen, R. G., Peck, J. E., and Grabner, J. K.: Responses of ground flora to a gradient of harvest intensity in the Missouri Ozarks, For. Ecol. Manage., 222, 326–334, https://doi.org/10.1016/j.foreco.2005.10.027, 2006.

Zhang, D., Hui, D., Luo, Y., and Zhou, G.: Rates of litter decomposition in terrestrial ecosystems: global patterns and controlling factors, J. Plant Ecol., 1, 85–93, https://doi.org/10.1093/jpe/rtn002, 2008.

Zhang, X., Guan, D., Li, W., Sun, D., Jin, C., Yuan, F., Wang, A., and Wu, J.: The effects of forest thinning on soil carbon stocks and dynamics: A meta-analysis, For. Ecol. Manage., 429, 36–43, https://doi.org/10.1016/j.foreco.2018.06.027, 2018.

Zhou, D., Zhao, S. Q., Liu, S., and Oeding, J.: A meta-analysis on the impacts of partial cutting on forest structure and carbon storage, 10, 3691–3703, https://doi.org/10.5194/bg-10-3691-2013, 2013.

Zhou, G., Xu, S., Ciais, P., Manzoni, S., Fang, J., Yu, G., Tang, X., Zhou, P., Wang, W., Yan, J., Wang, G., Ma, K., Li, S., Du, S., Han, S., Ma, Y., Zhang, D., Liu, J., Liu, S., Chu, G., Zhang, Q., Li, Y., Huang, W., Ren, H., Lu,

X., and Chen, X.: Climate and litter C/N ratio constrain soil organic carbon accumulation, Natl. Sci. Rev., 6, 746–757, https://doi.org/10.1093/nsr/nwz045, 2019.

Zhou, L., Liu, S., Shen, H., Zhao, M., Xu, L., Xing, A., and Fang, J.: Soil extracellular enzyme activity and stoichiometry in China's forests, Funct. Ecol., 34, 1461–1471, https://doi.org/10.1111/1365-2435.13555, 2020.

Zhu, D., Zhang, M., Chen, J., Mortimer, M., Wu, Y., Liu, J., Huang, Q., and Cai, P.: Synergism between goethite size and extracellular polymeric substances (EPS) in the formation of mineral–mineral and organo-mineral complexes of soil microaggregates, Geoderma, 410, 115650, https://doi.org/10.1016/j.geoderma.2021.115650, 2022.