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RESEARCH ARTICLE

Formation of mineral-associated organic matter in temperate soils is primarily controlled by mineral type and modified by land use and management intensity

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Abstract

Formation of mineral-associated organic matter (MAOM) supports the accumulation and stabilization of carbon (C) in soil, and thus, is a key factor in the global C cycle. Little is known about the interplay of mineral type, land use and management intensity in MAOM formation, especially on subdecadal time scales. We exposed mineral containers with goethite or illite, the most abundant iron oxide and phyllosilicate clay in temperate soils, for 5 years in topsoils of 150 forest and 150 grassland sites in three regions across Germany. Results show that irrespective of land use and management intensity, more C accumulated on goethite than illite (on average 0.23 ± 0.10 and 0.06 ± 0.03 $\mathrm{mg\,m^{-2}}$ mineral surface respectively). Carbon accumulation across regions was consistently higher in coniferous forests than in deciduous forests and grasslands. Structural equation models further showed that thinning and harvesting reduced MAOM formation in forests. Formation of MAOM in grasslands was not affected by grazing. Fertilization had opposite effects on MAOM formation, with the positive effect being mediated by enhanced plant productivity and the negative effect by reduced plant species richness. This highlights the caveat of applying fertilizers as a strategy to increase soil C stocks in temperate grasslands. Overall, we demonstrate that the rate

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and amount of MAOM formation in soil is primarily driven by mineral type, and can be modulated by land use and management intensity even on subdecadal time scales. Our results suggest that temperate soils dominated by oxides have a higher capacity to accumulate and store C than those dominated by phyllosilicate clays, even under circumneutral pH conditions. Therefore, adopting land use and management practices that increase C inputs into oxide-rich soils that are under their capacity to store C may offer great potential to enhance near-term soil C sequestration.

KEYWORDS
fertilization, forests, grasslands, grazing, iron oxides and clay minerals, soil organic matter, thinning and harvesting, tree species selection

1 | INTRODUCTION

Soils play a pivotal role in the global carbon (C) cycle as they are the largest terrestrial C pool (Georgiou et al., 2022; Paustian et al., 2016). The sorption of dissolved organic matter (DOM) onto mineral surfaces facilitates long-term stabilization of organic carbon (OC) in soils, with mineral-associated organic matter (MAOM) contributing to as much as 90% to total soil organic matter (OM) (Mikutta et al., 2019; Sokol et al., 2022). Given the importance of mineral-organic associations, there is pressing need to understand the factors controlling MAOM formation in order to predict the mitigation potential of soils and their response to global change.

The availability of reactive mineral surfaces for OM sorption is a decisive factor for the formation of MAOM (Creamer et al., 2019; Kaiser & Guggenberger, 2003; Kleber et al., 2015; Kögel-Knabner et al., 2008; Neurath et al., 2021; Sokol et al., 2022). Soil minerals are, however, not equally efficient in sorbing OM (Creamer et al., 2019; Mikutta et al., 2007; Neurath et al., 2021). Laboratory experiments demonstrated that iron (Fe) (oxyhydr)oxides (hereafter termed 'oxides') sorb more OM than phyllosilicate clay minerals (hereafter termed 'clays') (Gao et al., 2018; Han et al., 2021; Saidy et al., 2013; Tombácz et al., 2004). The higher sorption capacity of oxides is attributed to their net positive surface charge under acidic and neutral conditions and their often larger specific surface area (SSA) (Gao et al., 2018; Kaiser & Guggenberger, 2003; Saidy et al., 2013). The capability of oxides to bind OM more strongly might also play a role (Gao et al., 2018; Saidy et al., 2013). Still, it remains untested whether oxides are capable of sorbing more OM than clays under field conditions. Since oxides and clays both occur in the same particle size fraction and tend to associate with each other (Khomo et al., 2017; Kirsten et al., 2021), straightforward differentiation of their individual contributions to soil OC storage is difficult. In addition, MAOM might not only form from interaction of DOM with minerals, but also stem from residues of microorganisms that colonize the minerals (Angst et al., 2021; Cotrufo et al., 2013), with the colonization patterns varying between different mineral types (Brandt et al., 2023; Dong et al., 2022; Uroz et al., 2015). Field incubation of pristine minerals (Kandeler et al., 2019; Liebmann et al., 2022; Vieira et al., 2020) offers the opportunity to directly determine the contributions of oxides and clays to MAOM formation, but such an approach has not yet been applied along a gradient in land use and soil management intensity.

Land use, which is well known to shape the characteristics of the OM inputs (Bolan et al., 2011), is assumed to control the amount of MAOM formation. Temperate forest and grassland ecosystems account for about 20% of global soil OC stocks (IPCC, 2001). Therefore, understanding the controls on MAOM formation in these ecosystems has major implications for C budgeting upon global climate change. The importance of the quantity and quality of OM inputs for MAOM formation has been demonstrated in a number of laboratory experiments (Córdova et al., 2018; Cotrufo et al., 2022; Gao et al., 2018; Han et al., 2021; Kaiser & Guggenberger, 2000). Primary productivity and abundance of potentially strongly sorbing biopolymers, such as lignin derivates (Sokol et al., 2019), are generally higher in forests than grasslands (Bolan et al., 2011; Krause et al., 2022). However, this does not necessarily translate into higher MAOM-C stocks under forest vegetation (Herold et al., 2014). Indeed, studying land use effects on MAOM over short time scales remains a challenge because of the relatively slow turnover of OM in this pool (Herold et al., 2014; Schöning et al., 2013). The presence of large amounts of MAOM from previous land use could make it even more difficult to detect MAOM-C changes driven by current land use. Furthermore, the assessment of land use effects on MAOM-C stocks across a large spatial scale might be confounded by the heterogeneity in soil mineralogical characteristics and their different effects on MAOM formation (Herold et al., 2014; Keller, Borer, et al., 2022). To our knowledge, no attempt has yet been made to disentangle the effect of mineral type and land use on the efficiency of MAOM formation under field conditions. Hence, there are still open questions about the efficiency of MAOM formation under different land uses, and the relative importance of land use and mineral type for MAOM formation.

In forests, intensive thinning and harvesting can alter soil OC stocks by reducing litter inputs (Mayer et al., 2020). In a 50-year litter removal experiment, Lajtha et al. (2014) observed an overall 51% decrease in the content of MAOM. In non-experimental forests, thinning and harvesting effects on OC stocks were usually only detectable in the organic layer (Grüneberg et al., 2013; Mayer et al., 2020; Mosier et al., 2019 and references therein). Therefore, it is not yet clear whether the magnitude of MAOM formation is affected by these forest management practices. The selection of coniferous over deciduous tree species typically leads to wider soil C:N ratios and lower soil pH (Cools et al., 2014; Gan et al., 2020). This increase in soil acidity and C:N ratio decreases microbial C use efficiency, resulting in greater DOM production relative to microbial assimilation and OM oxidation (Cools et al., 2014; Córdova et al., 2018; Gan et al., 2020), and thus, potentially more MAOM formation. While OC stocks in the organic layer are typically higher in coniferous than deciduous forest, this trend is not consistent in mineral soil (Mayer et al., 2020 and references therein; Waring et al., 2022). This might be in part explained by the confounding effect of soil characteristics (e.g. texture and fertility) since these two forest types are typically established on contrasting soils (Lugato et al., 2021; Mayer et al., 2020).

In grasslands, fertilization and grazing are important management practices affecting soil OC stocks (Conant et al., 2017). While there are numerous studies on the influence of these practices on total soil OM (Conant et al., 2017; Mayer et al., 2020), their effects on MAOM formation are understudied. Moreover, the results of the few studies that exist are not always intuitive and consistent. For example, while fertilization increased plant biomass, it did not affect MAOM-C stocks (Keller, Borer, et al., 2022). Fertilization is also assumed to enhance microbial bio- and necromass production and, consequently, MAOM formation (Cotrufo et al., 2013; Poeplau et al., 2018, 2019). However, fertilizer-induced increase in microbial activity can lead to faster turnover of MAOM (Bradford et al., 2008; Stoner et al., 2021). Fertilization also reduces plant diversity (Apostolakis et al., 2022; Klaus et al., 2018), which might result in loss of MAOM since plant diversity has been found to be positively linked to soil OC storage (Anacker et al., 2021; Chen et al., 2018; Cong et al., 2014; Lange et al., 2015; Prommer et al., 2020). The higher soil OC stocks in the species-rich grasslands were mainly ascribed to the positive link between plant diversity and plant productivity. In fertilized grasslands, fertilization is likely to be a more decisive driver of plant productivity than plant diversity (Socher et al., 2012). To this end, the relationship between plant diversity and soil OC storage, and the consequences for MAOM formation needs to be investigated specifically for different fertilization levels. Grazing can increase soil OC contents (Franzluebbers & Stuedemann, 2009) but can also have no effect (Piñeiro et al., 2010) or cause significant reductions in soil OC (Paz-Kagan et al., 2016; Wright et al., 2004), depending on the intensity of grazing and interactions with vegetation, soil properties and precipitation (Eze et al., 2018; Piñeiro et al., 2010). Yet, studies that consider these interactions are rare. As the effects of grazing and fertilization are seldom assessed in combination, their relative importance for MAOM formation across a large spatial scale is still not known.

The main objective of this study was to quantify the efficiency of MAOM formation for goethite and illite, the most abundant iron oxide and clay in temperate soils (Cornell & Schwertmann, 2003; Ito & Wagai, 2017; Journet et al., 2014), when placed in the same soil environment. To quantify effects of different land use types and management intensities as well, we exposed containers filled with pristine minerals for 5 years to ambient conditions at 5 cm depth in the mineral soil of 150 forest and 150 grassland sites across three regions in Germany. By exposing pristine minerals over a 5-year period, we were able to study the formation of MAOM as a consequence of current land use regimes. Our setup enables the first-time assessment of the relative importance of mineral type, site conditions (soil and climatic factors), land use (forest vs. grassland) and management practices (thinning and harvesting, and tree species selection in forests; fertilization and grazing in grasslands) on the formation of MAOM. We hypothesized that the amount of MAOM formed (i) depends on mineral type, being higher for goethite than illite, (ii) is higher in forests, especially in coniferous forests than in grasslands and (iii) is controlled by management intensity in both, forests and grasslands.

2 | MATERIALS AND METHODS

2.1 | Study region and management

The study was conducted in the *Biodiversity Exploratories* (BE), which is a large-scale and long-term research platform established in 2006 for studying the effects of forest and grassland management on biodiversity and ecosystem processes (Fischer et al., 2010). The BE comprise a set of standardized field plots located in three regions of Germany: the Schwäbische Alb, Hainich-Dün and Schorfheide-Chorin. The study regions are defined by distinct climatic, geological and soil conditions (Table 1), thereby enabling the assessment of the influence of these factors on ecosystem processes. Each study region includes 50 forest plots and 50 grassland plots, resulting in a total of 300 study sites across regions and land uses.

Each forest plot covers an area of 100 m × 100 m within the larger forest (Fischer et al., 2010). The forests are dominated by European beech (*Fagus sylvatica*), oak (*Quercus robur* and *Quercus petraea*), Norway spruce (*Picea abies*) or Scots pine (*Pinus sylvestris*), and consist of either unmanaged (for at least 60 years), even-aged or uneven-aged stands (Schall et al., 2018). We categorized each plot as coniferous or deciduous forest based on the dominant tree species to assess the effect of these two tree functional types on MAOM formation. As an additional measure of the effect of forest management, we used the silvicultural management intensity index (SMI) developed by Schall and Ammer (2013). The SMI is the additive effect of two components: the risk of stand loss (SMIr) and the stand density (SMId). The SMIr reflects the effects of tree species identity and stand age on the probability of stand loss and is calculated as the probability of a stand to be lost before reaching the age of 180 years (i.e. a reference age for an old growth forest). The SMIr is highest for Norway spruce, followed by Scots pine, oak and European beech and decreases nonlinearly with stand age. Since there is a greater risk of coniferous than deciduous forest stands to break down, SMIr is strongly positively correlated with per cent conifer share (Supporting Information S1). The SMId quantifies the difference between the actual stand stocking (i.e. the actual basal area of a stand at a specific site) and the carrying capacity of that site (i.e. the maximum natural basal area), thus reflecting the forest developmental stage (i.e. lower stocking in young stands) and the intensity of thinning and harvesting.

TABLE 1 Overview on climatic conditions, soil and land use management in the three study regions Schwäbische Alb, Hainich-Dün and Schorfheide-Chorin (mean values across the plots with standard deviation). conif., plots in coniferous forest, $n=37$; decid., plots in deciduous forest, $n=112$; $\mathrm{Fe_d}$ and $\mathrm{Al_d}$, dithionite-extractable Fe and Al; $\mathrm{Fe_o}$ and $\mathrm{Al_o}$, oxalate-extractable Fe and Al; grass, grassland plots; MAP, mean annual precipitation in the years 2016–2020; MAT, mean annual air temperature in the years 2016–2020; min. grass, Schorfheide-Chorin grassland plots with mineral soil, $n=22$; org. grass, Schorfheide-Chorin grassland plots with organic soil, i.e., Histosols and Gleysols, $n=27$; SMId, density component of the silvicultural management index (Schall & Ammer, 2013), which reflects the thinning and harvesting intensity; SMIr, risk component of the silvicultural management index, which reflects conifer share; WEOC, water-extractable OC. For SMId, SMIr, fertilization, grazing, aboveground biomass and plant species richness an average over the years 2016–2020 was taken. For the litter C input and litter C:N ratio, an average of the years 2015–2019 was taken. For more information on the measurement of the variables see Supporting Information S4.

	Study region		
Parameter	**Schwäbische Alb**	**Hainich-Dün**	**Schorfheide-Chorin**
Elevation (m a.s.l.)	460–860	258–500	3–140
MAT (°C)	8.2±0.7	9.2±0.7	9.7±0.6
MAP (mm)	902±49	485±48	581±29
Typical soils	Leptosols, Cambisols	Cambisols, Stagnosols, Luvisols	Histo-, Gley- and Luvisols in grasslands; Cambi-, Areno- and Podsols in forests
Clay (g kg $^{-1}$)	53.6±13.3 (grass)	42.3±13.0 (grass)	12.9±4.5 (org. grass)
			21.2±9.6 (min. grass)
	49.3±9.6 (conif.)	29.6±9.6 (conif.)	5.4±1.9 (conif.)
	50.6±12.8 (decid.)	37.1±14.4 (decid.)	3.4±1.1 (decid.)
Sand (g kg $^{-1}$)	5.7±4.5 (grass)	5.8±2.3 (grass)	65.0±10.7 (org. grass)
			28.6±13.5 (min. grass)
	3.4±1.3 (conif.)	5.4±1.3 (conif.)	90.0±4.6 (conif.)
	6.8±4.9 (decid.)	5.8±1.7 (decid.)	84.8±6.1 (decid.)
Soil OC (g kg $^{-1}$)	71.0±17.1 (grass)	47.2±12.5 (grass)	188.4±107.9 (org. grass)
			27.1±6.2 (min. grass)
	67.4±25.9 (conif.)	37.4±9.6 (conif.)	28.3±12.2 (conif.)
	67.7±25.2 (decid.)	42.2±16.9 (decid.)	29.9±17.0 (decid.)
Soil C:N ratio	10.6±1.3 (grass.)	10.1±0.45(grass)	10.7±1.4(org. grass)
			10.6±0.6 (min. grass)
	14.1±1.9 (conif.)	13.8±2.0 (conif.)	20.6±2.2 (conif.)
	13.2±1.2 (decid.)	13.3±1.8 (decid.)	17.3±1.8 (decid.)
Soil pH	6.3±0.6 (grass)	6.9±0.5 (grass)	7.0±0.8 (org. grass)
			5.9±0.7 (min. grass)
	5.0±1.0 (conif.)	6.0±0.8 (conif.)	3.5±0.1 (conif.)
	5.7±0.7 (decid.)	4.9±0.8 (decid.)	3.6±0.1 (decid.)
Root biomass (g cm $^{-3}$)	259.9±119.4 (grass)	275.4±94.2 (grass)	348.0±196.2 (org. grass)
			502.9±211.7 (min. grass)
	113.3±80.6 (conif.)	104.3±19.0 (conif.)	50.6±25.5 (conif.)
	106.6±57.2 (decid.)	124.6±62.5 (decid.)	68.1±25.9 (decid.)
WEOC (mg kg $^{-1}$)	72.1±23.0 (grass)	73.5±28.3 (grass.)	112.5±37.0 (org. grass)
			58.9±21.2 (min. grass)
	186.6±67.5 (conif.)	96.9±21.6 (conif.)	106.0±47.0 (conif.)
	180.3±75.9 (decid.)	109.4±47.3 (decid.)	91.6±33.5 (decid.)
$\mathrm{Fe_o}$ (g kg $^{-1}$)	3.0±1.4 (grass)	2.1±0.6 (grass)	10.1±7.1 (org. grass)
			1.4±0.4 (min. grass)
	2.9±0.9 (conif.)	2.8±0.7 (conif.)	1.2±0.3 (conif.)
	2.6±1.0 (decid.)	3.1±0.7 (decid.)	1.2±0.3 (decid.)
$\mathrm{Al_o}$ (g kg $^{-1}$)	0.6±0.7 (grass)	0.4±0.2 (grass)	0.02±0.04 (org. grass)
			0.3±0.2 (min. grass)
	0.4±0.3 (conif.)	0.3±0.1 (conif.)	0.6±0.2 (conif.)
	0.6±0.4 (decid.)	0.2±0.1 (decid.)	0.5±0.1 (decid.)

TABLE 1 (Continued)

Parameter	Study region		
	Schwäbische Alb	Hainich-Dün	Schorfheide-Chorin
Fe$_d$ (g kg^{-1})	23.4 ± 5.4 (grass)	14.0 ± 2.6 (grass)	24.1 ± 14.7 (org. grass)
			4.7 ± 1.6 (min. grass)
	23.9 ± 9.7 (conif.)	14.7 ± 0.9 (conif.)	2.5 ± 0.8 (conif.)
	25.8 ± 5.9 (decid.)	11.5 ± 3.9 (decid.)	2.5 ± 0.8 (decid.)
Al$_d$ (g kg^{-1})	69 ± 3.4 (grass)	5.3 ± 1.9 (grass)	0.7 ± 0.4 (org. grass)
			0.8 ± 0.3 (min. grass)
	10.8 ± 6.0 (conif.)	6.8 ± 1.7 (conif.)	0.8 ± 0.3 (conif.)
	10.0 ± 3.7 (decid.)	3.9 ± 1.5 (decid.)	0.6 ± 0.2 (decid.)
Forest parameters			
Dominant forest type	(Mixed) beech forests, spruce forests	European (mixed) beech forests	Pine—durmast oak forests, (mixed) beech forests
SMId	0.27 ± 0.10 (conif.)	0.12 ± 0.03 (conif.)	0.30 ± 0.14 (conif.)
	0.37 ± 0.16 (decid.)	0.27 ± 0.21 (decid.)	0.31 ± 0.19 (decid.)
SMIr	0.77 ± 0.02 (conif.)	0.65 ± 0.09 (conif.)	0.22 ± 0.06 (conif.)
	0.09 ± 0.10 (decid.)	0.03 ± 0.03 (decid.)	0.06 ± 0.03 (decid.)
Litter C input (g m^2)	227.0 ± 38.7 (conif.)	201.4 ± 21.4 (conif.)	247.3 ± 53.7 (conif.)
	257.7 ± 44.8 (decid.)	264.2 ± 44.1 (decid.)	257.5 ± 46.3 (decid.)
Litter C:N ratio	47.9 ± 2.9 (conif.)	46.5 ± 4.3 (conif.)	63.8 ± 2.9 (conif.)
	40.2 ± 4.8 (decid.)	41.8 ± 4.6 (decid.)	43.0 ± 5.1 (decid.)
C stock of organic layer (kg m^{-2})	1.33 ± 0.42 (conif.)	0.66 ± 0.32 (conif.)	2.92 ± 1.16 (conif.)
	0.84 ± 0.39 (decid.)	0.59 ± 0.16 (decid.)	1.01 ± 0.45 (decid.)
Grassland parameters			
Grazing (livestock units days ha^{-1} year^{-1})	76.9 ± 105.7	112.4 ± 199.3	120.5 ± 149.9 (org. grass)
			244.9 ± 219.2 (min. grass)
Fertilization (kg N ha^{-1} year^{-1})	55.6 ± 74.1	42.9 ± 52.3	2.2 ± 4.1 (org. grass)
			11.1 ± 22.1 (min. grass)
Aboveground biomass (g m^{-2})	142.7 ± 72.9	123.6 ± 62.6	208.8 ± 70.7 (org. grass)
			257.8 ± 78.3 (min. grass)
Species richness (count of plant species per 16 m^2)	32.6 ± 8.4	37.2 ± 11.8	19.6 ± 3.0 (org. grass)
			30.2 ± 3.2 (min. grass)

The grassland plots are 50 m × 50 m in size and include meadows that are fertilized and mown; pastures that are fertilized, mown and grazed; and pastures that are grazed but not mown or fertilized (Fischer et al., 2010). We calculated the intensity of fertilization (kg N ha^{-1} year^{-1}) and grazing (livestock units days ha^{-1} year^{-1}) according to Blüthgen et al. (2012), using the calculation tool of Ostrowski et al. (2020) implemented in the Biodiversity Exploratories Information System (BExIS). As plots that are fertilized are also commonly mown, we excluded mowing from our analyses to avoid issues with collinearity.

2.2 | Experimental design

A total of 3648 mineral containers were installed at all 300 sites between November 2015 and January 2016. The mineral containers had a surface area of 35 cm^2 and consisted of a plastic ring that framed a 50-µm mesh which served to prevent root ingrowth and mineral losses but allowed for water passage and microbial colonization (Figure 1a; Brandt et al., 2023). Given the container design, translocation of OM into the containers can result from: (i) transport of DOM from soil OM decomposition or root exudates via the soil solution, (ii) transport of small (<50 µm) particulate material and microbes by percolating soil water and (iii) ingrowth of fungi followed by transport of OM and bacteria via fungal hyphae (see Frey et al., 2003; See et al., 2022). The containers were filled with either a mixture of 12 g of synthetic goethite (Bayferrox® 920 Z, CAS-No. 51274-00-1, Lanxess AG, Cologne, Germany) and 12 g of washed and annealed sea sand (VWR, CAS-No. 14808-60-7; >63 µm) or 12 g of natural illite (Inter-ILI. Engineering Co. Ltd., Kosd, Hungary) and 33 g of sea sand. Selected chemical, physical and mineralogical properties of the minerals and sea sand can be found in Table 2. Information on their DOM sorption capacity is presented in Supporting Information S2. The addition of the sand to the containers ensured that drainage was not impeded. More sand was mixed with illite to standardize the volume of sample material in the containers.

Five replicates of mineral containers containing either goethite or illite were placed at 5 cm soil depth in a horizontal slit in the

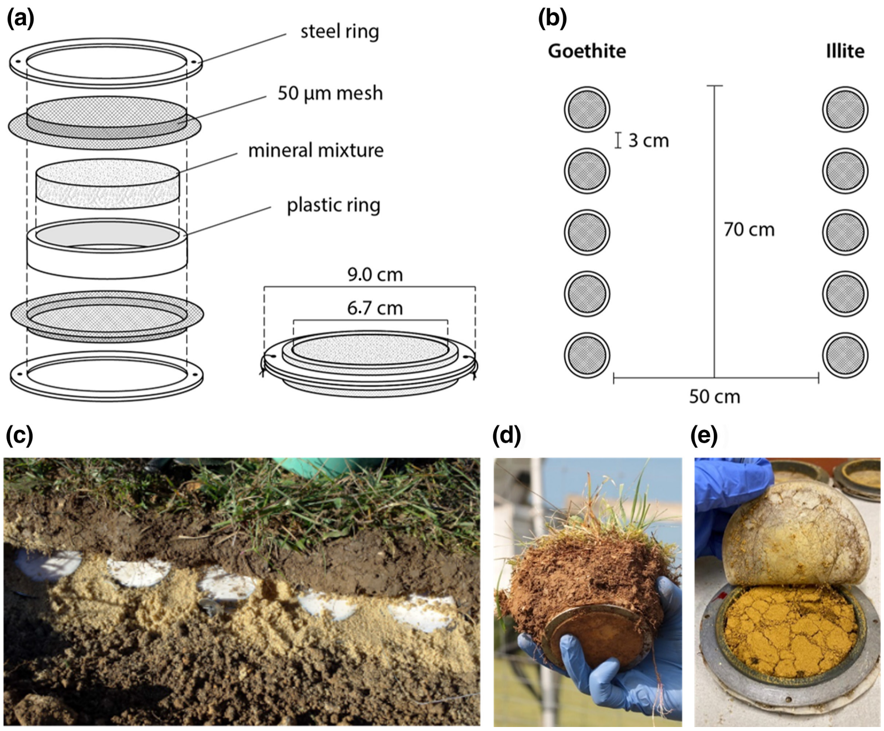

FIGURE 1 (a) Setup and dimensions of a mineral container; (b) schematic top view of the mineral container placement in 5 cm soil depth; (c) photo of a row of minerals container on a sand bed during installation in 2015; (d) photo of sampling a mineral container and the surrounding soil; (e) photo of an opened mineral container (reprinted from Brandt et al., 2023 with the permission from Elsevier).

TABLE 2 Selected properties of pristine minerals goethite, illite and sea sand: (a) Reaction (pH in $CaCl_2$ solution); oxalate- and dithionite–citrate–bicarbonate (DCB)-extractable Al, Fe and Mn (Al_o, Fe_o, Mn_o and Al_d, Fe_d, Mn_d respectively), no oxalate-soluble Si and Mn detectable; specific surface area (SSA); point of zero charge (PZC); (b) Element concentration (C:N analyser; X-ray fluorescence spectrometry), since no inorganic carbon was detectable, C represents organic C; (c) Cation exchange capacity (CEC) and exchangeable cations; n.a., not analysed; n.d., not detectable.

Sample	pH ($CaCl_2$)	Al_o g kg^{-1}	Fe_o g kg^{-1}	Al_d g kg^{-1}	Fe_d g kg^{-1}	Mn_d g kg^{-1}	SSA (N_2-BET) m^2 g^{-1}	PZC
(a)								
Goethite	7.3	0.17	1.82	1.36	614.52	0.28	20.4	7.8
Illite	7.0	0.26	0.12	n.d.	0.25	n.d.	40.7	n.a.
Sea sand	6.7	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	n.a.

Sample	C g kg^{-1}	N g kg^{-1}	C:N	Fe g kg^{-1}	Mn g kg^{-1}	Al g kg^{-1}	Si g kg^{-1}	K g kg^{-1}	Mg g kg^{-1}	Ca g kg^{-1}	P g kg^{-1}
(b)											
Goethite	0.40	0.19	2.1	613.49	0.46	2.15	0.24	1.00	0.28	0.36	0.12
Illite	0.42	0.38	1.1	4.07	0.07	149.33	265.58	70.24	7.50	2.31	0.21
Sea sand	0.10	0.04	2.5	n.d.	0.02	5.02	460.59	1.24	0.56	0.29	0.03

Sample	CEC (pH 7) mmol$_c$ kg^{-1}	Al^{3+} mmol$_c$ kg^{-1}	Fe^{3+} mmol$_c$ kg^{-1}	Ca^{2+} mmol$_c$ kg^{-1}	Mg^{2+} mmol$_c$ kg^{-1}	K^+ mmol$_c$ kg^{-1}	Na^+ mmol$_c$ kg^{-1}	NH_4^+ mmol$_c$ kg^{-1}	Ca, Mg, K, Na saturation of CEC (pH 7) %
(c)									
Goethite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Illite	165.5	<0.01	3.7	110.4	33.2	14.5	2.6	0.03	>97
Sea sand	4.8	n.d.	n.d.	3.5	0.4	0.5	0.4	n.d.	100

Note: Details on the methods can be found in Supporting Information S2.

soil. The two types of mineral containers were positioned directly opposite to each other at a distance of 50 cm (Figure 1b). We filled the space created in the soil by placing sand above and below the mineral containers (Figure 1c) to prevent holes and to standardize the physical conditions under which the containers were exposed.

2.3 | Collection, preparation and analysis of mineral and soil samples

Three of the five replicated mineral containers of each type were extracted from the field in August 2020 after ca. 5 years of exposure to natural soil conditions. The soil overlying the mineral containers was also taken and a composite sample was created for each mineral type (Figure 1d). All samples were transported to the laboratory in coolers. The mineral containers were opened (Figure 1e) and, if necessary, visible fine roots and hyphae were removed with a tweezer. We also weighed the contents of the mineral cylinders to account for potential losses during the 5-year field exposure. We did not observe any difference in the dry mass of the minerals in the containers during the experimental period. This suggests that there were no significant losses. Nevertheless, as we aimed at determining elemental concentrations and not stocks or fluxes, potential small losses of minerals are not relevant to the objectives our study. The mineral replicates were combined, thoroughly homogenized, freeze-dried and finely ground. Soil samples were air-dried, sieved to <4 mm, and a portion was ground for elemental analysis. The moisture content of the air-dried soil samples was determined by drying a 2-g aliquot at 105°C for 24 h.

Total C (TC) and total nitrogen (TN) concentration of the field-exposed mineral and soil samples were determined by dry combustion at 1100°C using a varioMAX Cube elemental analyser (Analysensysteme GmbH, Langenselbold, Germany). The inorganic C (IC) concentration of the soils was determined with the same analyser after removal of OC by heating the samples to 450°C for 16 h. The OC concentration was calculated as the difference between TC and IC. As we anticipated very low IC concentrations in the mineral samples, they were analysed for IC by suspending 200 mg of sample material in 50 mL 2 M HCl at 50°C and subsequent detection of released CO_2 (soliTIC module interfaced to the varioMAX Cube elemental analyser). Since IC concentrations on the minerals were negligible, TC equates OC. Given the twofold difference in SSA of goethite ($20.4\,m^2\,g^{-1}$) and illite ($40.7\,m^2\,g^{-1}$), we express the amount of accumulated OC per m^2 of pristine mineral. Note, although the mineral containers contained different ratios of sand to pristine mineral, the very low SSA and negligible OM sorption capacity of quartz implies that the accumulated OC can be solely ascribed to the contained reactive minerals (Table 2; Supporting Information S2).

2.4 | Additional soil and plant properties

For examining the influence of land use and management intensity on the MAOM-C accumulation, further soil and plant variables (soil texture, soil pH, OC stock of the soil organic layer, litter C and C:N ratio, water-extractable OC (WEOC), aboveground plant biomass and plant species richness) were used. For information on sampling and measurement of these variables see Supporting Information S4.

2.5 | Data analysis

All data were analysed using R (version 4.2.0, R Core Team, 2022). Student's *t*-test was used to test the effect of mineral type on MAOM-C accumulation. We used histograms and Q–Q plots to check that the data were normally distributed. We did the same before performing an analysis of variance (ANOVA). Levene's test was used to verify that the assumption of homogenous variances was not violated. For each mineral type, we assessed the effect of vegetation type separately for each study region using one-way ANOVA and Tukey's honest significant difference tests. The same statistical analyses were used to assess the effect of study region on MAOM-C accumulation in beech forests separately for goethite and illite. The relationship between MAOM-C accumulation and the OC concentration in the overlying soil material in mineral soils and organic grassland soils were assessed by linear regression analysis.

To explore management effects in forests and grasslands on the MAOM-C accumulation, individual piecewise structural equation models (SEMs; Lefcheck, 2016) were constructed for each mineral. The SEMs were developed from the conceptual models presented in Figure 2. Besides the management variables, the conceptual models contained water regime-related variables that might have an effect on MAOM formation by influencing DOM fluxes. Plant and soil properties were incorporated as mediating variables that might link the management variables to MAOM formation. The SEMs were performed with the *piecewiseSEM* 2.1 R package (Lefcheck, 2016). In all SEMs, study region was included as random factor. This allowed us to determine how much of the explained variance in MAOM-C accumulation was due to fixed (management, water regime, plant and soil properties) and random effects (study region). The variance explained solely by the fixed factors in our models is denoted as the R^2_{marginal} (R^2_m), while that explained both by the fixed and random effects is denoted as the $R^2_{\text{conditional}}$ (R^2_c). *PiecewiseSEM* uses tests for directed separation to evaluate the relevance of missing paths (i.e. not based on priori hypothesis) in the model. Only when we could ascribe them to cause and effect relations, these additional effects were included as paths in the models. Otherwise, they were considered as covariances. We applied log transformation to all explanatory variables that were not normally distributed (SMIr, $C{:}N_{\text{litter}}$, OC $\text{stock}_{\text{soil organic layer}}$ and $C{:}N_{\text{soil}}$ in forests, and fertilization and grazing intensity in grasslands). Models with *p* values ≥.05 were considered valid. The overall fit of these models was assessed with Fisher's C statistic and Akaike information criterion (AIC). Variables (except for management indices, and OC concentration and C:N ratio of the overlying soil) and paths that were not significant ($p > .1$) for either mineral were excluded from the final models.

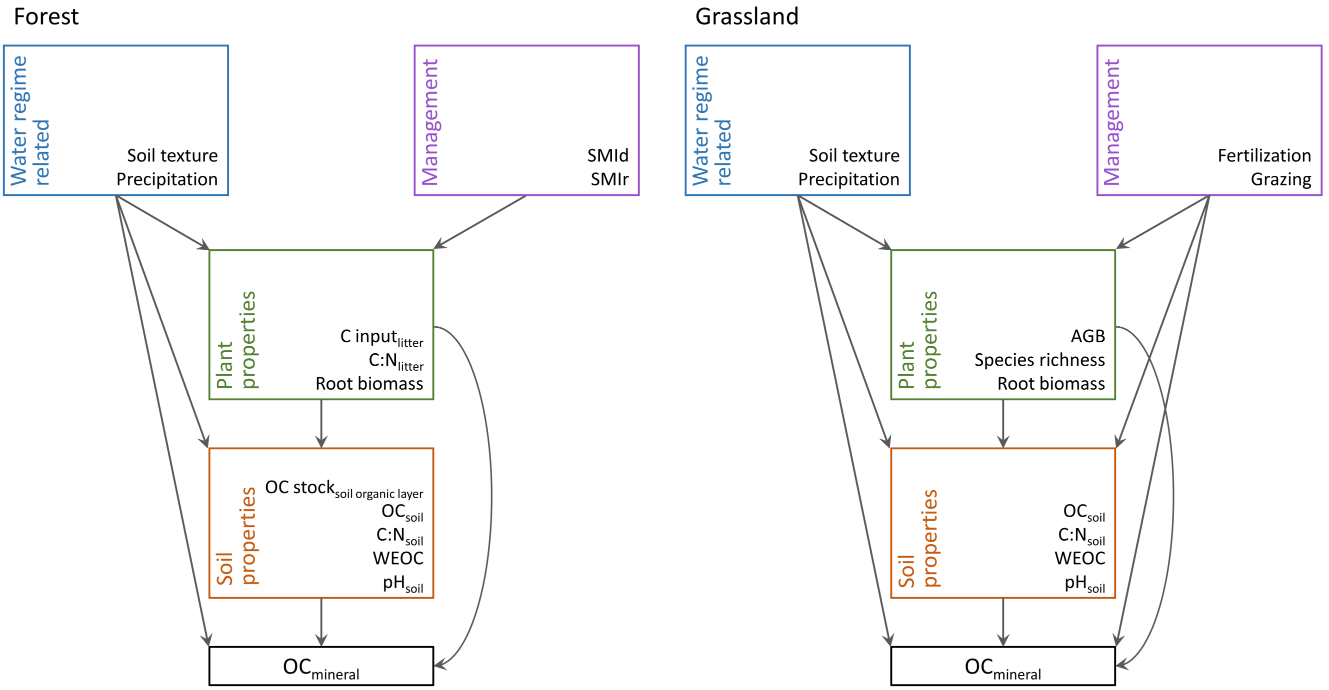

FIGURE 2 Conceptual models for forests and grasslands with all the variables and paths tested in the structural equation models. C:N litter, C:N ratio of litter fall; C:N soil, C:N ratio of the mineral soil; OC input litter, mass of C in litter fall; OC mineral, OC concentration in goethite or illite mineral containers; OC soil, OC concentration in the mineral soil; OC stocks soil organic layer, OC stocks in the soil organic layer; SMId, Density component of the silvicultural management index, which reflects the thinning and harvesting intensity; SMIr, Risk component of the silvicultural management index, which reflects per cent conifer cover; WEOC, water-extractable OC. With the exception of the OC concentration in the overlying soil (in forests and grasslands) and grazing intensity, variables that were not linked to MAOM-C accumulation on pristine minerals were removed from the models. We decided not to remove the OC concentration in the overlying soil to visually highlight the relative importance of soil OM quantity (OC concentration) and quality (C:N ratio) on the MAOM-C accumulation on minerals. MAOM, mineral-associated organic matter; OC, organic carbon.

3 | RESULTS

3.1 | Effect of mineral type on MAOM accumulation

After 5 years of field exposure, the amount of OC that accumulated per gram of pristine mineral was almost two times higher for goethite than illite (4.71 ± 4.85 and 2.45 ± 1.26 mg g^{-1} respectively). These concentrations correspond to 10% and 86% of the sorption capacity of goethite and illite as determined in sorption experiments with DOM from the Oa horizon of a spruce forest (see Supporting Information S2). If OC concentration is expressed per unit SSA of pristine mineral, it was four times higher on goethite than illite (Figure 3). The higher accumulation on goethite was consistent across study regions and vegetation types (Figure 4).

3.2 | Land use and study region effect on MAOM accumulation

On average across study regions, similar amounts of OC accumulated in forests and grasslands for both goethite (0.24 ± 0.02 and 0.22 ± 0.01 mg m^{-2}) and illite (0.06 ± 0.00 and 0.06 ± 0.00 mg m^{-2}). However, when differentiating between coniferous and deciduous forests, MAOM-C accumulation was generally higher under coniferous forests compared to other vegetation types (Figure 4). This effect was most pronounced in the Schorfheide-Chorin region, especially for goethite. Interestingly, MAOM-C accumulation was sometimes higher under grasslands than deciduous forests. In general, more OC accumulated on minerals buried in Schorfheide-Chorin than the other two study regions. This was even the case when only beech forests—the only tree species that was present in all three study regions—was considered (Supporting Information S5).

3.3 | Influence of management practices, plant and soil properties on MAOM accumulation

3.3.1 | Forests

The SEMs showed that SMId, which reflects the thinning and harvesting intensity, had a net negative effect on MAOM-C accumulation for both goethite (standardized coefficient (β) = −.014) and illite (β = −.010). The effect was mediated by litter C input and OC stocks in the soil organic layers (Figure 5). The SMIr, which reflects the stand composition and is strongly linked to conifer share (Supporting Information S1), had a net positive effect on MAOM-C accumulation (β = .25 and .07 for goethite and illite respectively). A strong

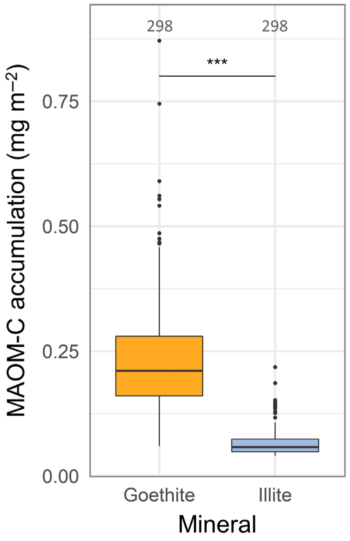

FIGURE 3 Accumulation of MAOM-C on two different pristine minerals (goethite and illite) buried for 5 years at 5 cm depth in the topsoil of forests and grasslands in three regions across Germany. The organic C content is expressed per m^2 of pristine mineral. The horizontal line represents the median. Outliers are represented by black dots outside the whisker of the plot. ***Significant difference at $p \leq .001$ between the two minerals. The number of replicates per box are at the top of the plots. MAOM, mineral-associated organic matter.

positive effect of the SMIr was mediated by the C:N ratio of the litter and the OC stocks in the soil organic layer. A smaller negative effect was again mediated by litter C input and OC stocks in the soil organic layer. For goethite, there was an additional positive direct effect of the SMIr on MAOM-C accumulation. Surprisingly, MAOM-C accumulation was not linked to the OC concentration of the overlying mineral soil (OC_{soil}; Figure 5). The pH and the concentration of WEOC in the overlying soil were also not relevant for MAOM formation (data not shown). Forty-two and 41% of the variation in MAOM-C accumulation on goethite and illite, respectively, was explained by the fixed factors (management, plant and soil properties) in the forest SEMs. The consideration of study region as random factor did not increase the explained variance ($R^2_{\mathrm{c}}=.44$ and .41 for goethite and illite respectively).

3.3.2 | Grasslands

Fertilization positively ($\beta=.14$ and .22 for goethite and illite respectively) and negatively ($\beta=-.16$ and −.12 for goethite and illite, respectively) affected MAOM-C accumulation by increasing aboveground plant biomass and decreasing plant species richness respectively (Figure 6). Therefore, the net effect of fertilization was negative for goethite ($\beta=-.02$) and positive for illite ($\beta=.10$). For goethite, MAOM-C accumulation was further directly and negatively related to soil pH. Grazing was not linked to MAOM-C accumulation. The accumulation of MAOM-C was also not linked to the soil OC concentration if we considered only mineral soils. However, linear regressions revealed a significant relationship between these two variables in the organic soils of the Schorfheide-Chorin region for both minerals (Figure 7). The grassland SEMs did not show a link between MAOM-C accumulation and soil C:N ratio, but the latter negatively covaried with aboveground plant biomass and positively with plant species richness (Figure 6). The concentration of WEOC in the overlying soil was not relevant for MAOM formation (data not shown). Overall, the grassland SEMs explained 22% and 55% of the variance in MAOM-C accumulation on goethite and illite respectively. Compared to the forest SEMs, less of the total variance was explained by the fixed factors (management, plant and soil properties; $R^2_{\mathrm{m}}=.12$ and .11 for goethite and illite respectively).

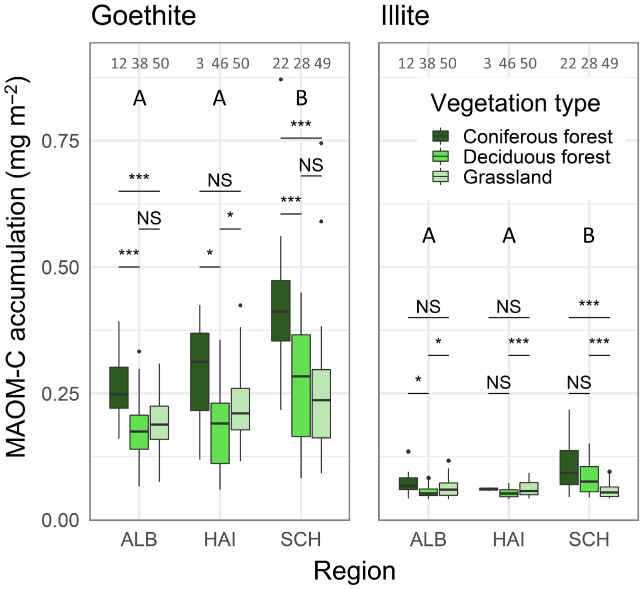

FIGURE 4 Effect of vegetation type on MAOM-C accumulation on pristine minerals (goethite and illite) buried for 5 years at 5 cm depth in the topsoil of forests and grasslands in three regions across Germany. The organic C content is expressed per m^2 of pristine mineral (goethite and illite). Data for each mineral are further separated by study region: Schwäbische Alb (ALB), Hainich-Dün (HAI) and Schorfheide-Chorin (SCH). The horizontal line represents the median. Outliers are represented by black dots outside the whisker of the plot. Significance levels: *$p \leq .05$; ***$p \leq .001$; and NS not significant ($p > .05$). The number of replicates per box are at the top of the plot. Different uppercase letters indicate a significant ($p \leq .05$) difference between study regions. MAOM, mineral-associated organic matter.

4 | DISCUSSION

4.1 | Mineral type effect

The importance of Fe oxides and their superiority to clays regarding the formation of MAOM has been observed in laboratory studies (Han et al., 2021; Kaiser et al., 2007; Neurath et al., 2021). In a laboratory pre-study on the sorption capacity of the minerals, we also found that goethite was capable of sorbing up to

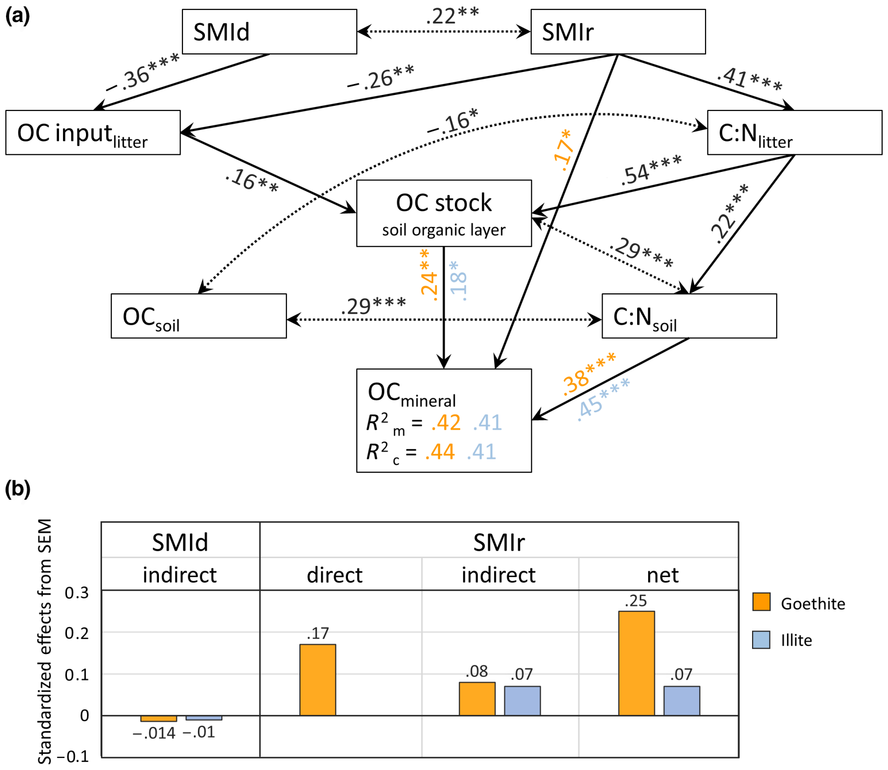

FIGURE 5 Piecewise structural equation model representing the direct and mediated effects of management on MAOM-C accumulation on pristine minerals (goethite and illite) buried for 5 years at 5 cm depth in the topsoil of forests across three regions in Germany (a) and the standardized effects of the management (b). C:N$_{\text{litter}}$, C:N ratio of litter fall; C:N$_{\text{soil}}$, C:N ratio of the soil; OC input litter, mass of C in litter fall; OC mineral, OC content in goethite or illite in mineral containers; OC$_{\text{soil}}$, OC concentration in the soil; OC stocks soil organic layer, OC stocks in the soil organic layer; SMId, density component of the silvicultural management index, which reflects the thinning and harvesting intensity; SMIr, risk component of the silvicultural management index, which reflects per cent conifer cover. Single-headed arrows indicate causal relationships (paths) while doubled-headed arrows indicate covariances. Values on top of the arrows are standardized coefficients (β) with significance levels: NS, not significant ($p > .1$); $^{\text{m}}.05 > p < .1$; $^{*}p \le .05$; $^{**}p \le .01$; $^{***}p \le .001$. Standardized coefficients in black are relevant for both minerals while those in orange and blue are relevant for goethite and illite respectively. Study region was denoted as a random factor in the model. Two coefficients of determination are given for the response variable—marginal (R^2_{m}) and conditional R^2 (R^2_{c}), that is, without and with considering the effect of the random factor respectively. Model parameters: goethite (Fisher's $C = 22.14$; AIC = 70.14; p value = .333; $n = 143$; df = 20) and illite (Fisher's $C = 25.00$; AIC = 73.00; p value = .201; $n = 143$; df = 20). AIC, Akaike information criterion; MAOM, mineral-associated organic matter; C:N, carbon to nitrogen ratio; OC, organic carbon; SEM, structural equation model.

2.5 mg OC per m^2 of mineral surface area, while illite only retained 0.07 mg m^{-2} (Figure S2). We corroborate the results of the laboratory experiments in our 5-year field study, finding much higher MAOM-C accumulation on goethite than on illite. The amount of OC that accumulated during the field exposure corresponds to about 86% of the potential sorption capacity of illite determined in the pre-study, suggesting its potential sorption capacity has almost been reached. In turn, goethite only accumulated OC equivalent to about 10% of its potential capacity. We acknowledge the difference in the ratio of quartz sand to pristine mineral in the two types of mineral containers. While the difference in the content of sand, due to its negligible sorption capacity (Figure S2), did not likely directly affect OC in the mineral containers, it might have impacted the water holding capacity, and thus, the time the minerals were in contact with the soil solution. Since sorption of OM to minerals is a relatively fast process (Dahlgren & Marrett, 1991; Kaiser & Zech, 1998), differences in passage time of the soil solution had presumably no significant effect on the overall difference in the OC accumulated in the two types of mineral containers. This assumption is supported by the OC accumulation on illite already approaching the mineral's maximum sorption capacity despite the potentially faster soil solution passage.

Since minerals tend to accumulate C less efficiently when approaching their maximum sorption capacity (Georgiou et al., 2022), the difference in MAOM-C accumulation between goethite and illite should become even greater with longer field exposure time. This underscores that soils dominated by goethite and other oxides-type phases have a greater capacity to accumulate and store C than those dominated by illite and other clay minerals. To our knowledge, this is the first large-scale direct comparison of the OM sorption capacity of these two mineral groups under field conditions.

The higher capacity of oxides to bind OM is often simply attributed to their high SSA (Sarkar et al., 2018). However, we found that despite having only half the SSA of illite, goethite accumulated on average two times more OC per gram of mineral than illite. This difference was fourfold when MAOM-C accumulation

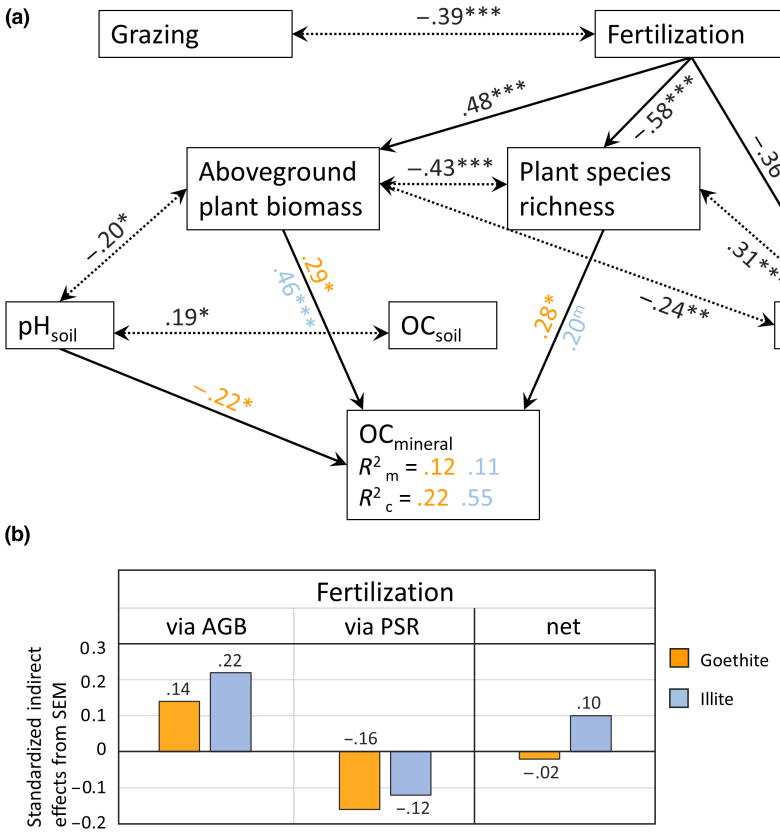

FIGURE 6 Piecewise structural equation model representing the direct and mediated effects of management on MAOM-C accumulation on pristine minerals (goethite and illite) buried for 5 years at 5 cm depth in the topsoil of grasslands across three regions in Germany (a) and the standardized indirect effects of fertilization (b). Organic soils of the SCH region were excluded from the model. AGB, aboveground biomass; C:N$_{soil}$, C:N ratio of the soil; OC mineral, OC content in goethite or illite in mineral containers; OC$_{soil}$, OC concentration in the soil; pH$_{soil}$, pH of the soil; PSR, plant species richness. Single-headed arrows indicate causal relationships (paths) while doubled-headed arrows indicate covariances. Values on top of the arrows are standardized coefficients (β) with significance levels. NS, not significant ($p > .1$); $^m.05 > p < .1$; $^*p \leq .05$; $^{**}p \leq .01$; $^{***}p \leq .001$. Standardized coefficients in black are relevant for both minerals while those in orange and blue are relevant for goethite and illite respectively. Study region was denoted as a random factor in the model. Two coefficients of determination are given for the response variable—marginal (R^2_m) and conditional R^2 (R^2_c), that is, without and with considering the effect of the random factor respectively. Model parameters: goethite (Fisher's $C = 8.906$; AIC = 44.91; p value = .35; $n = 121$; df = 8) and illite (Fisher's $C = 11.68$; AIC = 47.68; p value = .166; $n = 121$; df = 8). AIC, Akaike information criterion; C:N, carbon to nitrogen ratio; MAOM, mineral-associated organic matter; OC, organic carbon.

was normalized to the SSA of the minerals (Figure 3). Therefore, the reactivity of the surfaces of the two minerals was likely more decisive for MAOM-C accumulation than their SSA. The goethite used has a variably charged surface with a point of zero charge (PZC) at pH of 7.8 (Table 2), below which it is positively charged. Being mainly positively charged in acidic and neutral soils, oxides—such as goethite—attract negatively charged OM while permanently negatively charged clays—such as illite—rather repel the also mainly negatively charged OM (Kleber et al., 2021; Mikutta & Kaiser, 2011). Subsequently, oxides bind OM more strongly than clays via less reversible ligand exchange reactions, while binding to clays is mainly attributed to cation bridging (Kleber et al., 2021; Mikutta et al., 2007). Consequently, OM bound to clays is more desorbable and available for microbial consumption and mineralization than OM bound to oxides (Kleber et al., 2021). In a companion study, we observed a higher phospholipid-derived fatty acids (PLFAs) to OC ratio on illite than on goethite (Brandt et al., 2023). This means illite supported a larger microbial biomass per MAOM-C than goethite, which is in line with our idea that the OM bound to illite might have been more bioavailable than that bound to goethite. Consequently, the interplay between the rate of OM desorption and the growth and activity of mineral-associated microorganisms could be an important determinant of OM accumulating on minerals.

Whatever the exact mechanism(s) causing the higher MAOM-C accumulation on goethite than illite may be, we observed a striking consistency in this trend across study regions and land uses (Figure 4). Therefore, our study provides strong evidence for the primary role of the soil mineral composition for MAOM formation.

4.2 | Land use and study region effects

The accumulation of MAOM-C was consistently higher in coniferous forests than in grasslands (Figure 4). The wider C:N ratio of coniferous

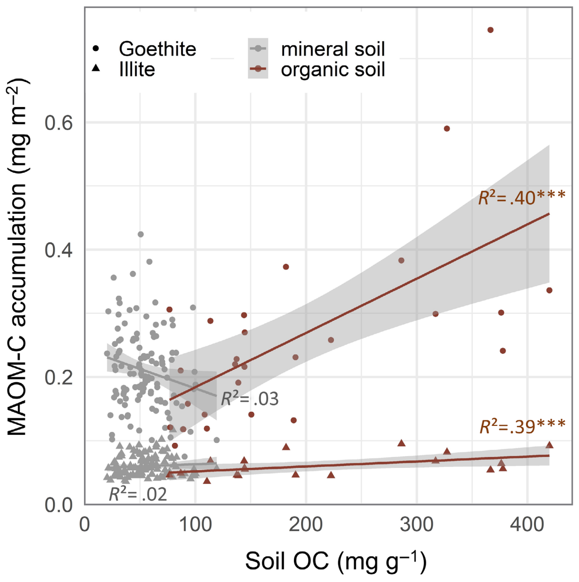

FIGURE 7 Relationship between MAOM-C accumulation on pristine minerals (goethite and illite) over a period of 5 years and soil OC concentration at 5 cm depth in 148 grasslands across Germany. For each mineral, $n = 121$ for mineral soils and 27 for organic soils. Significance level: ***$p \leq .001$. MAOM, mineral-associated organic matter; OC, organic carbon.

litter leads to its decelerated and incomplete mineralization. This causes accumulation of thick organic layers from which large amounts of DOM can originate (Andivia et al., 2016; Trum et al., 2011). The difference in MAOM-C accumulation between these two ecosystems was more pronounced for goethite than illite. This might be due to the higher sorption capacity of goethite, and the more acidic conditions under coniferous forests amplifying the effect of the higher DOM fluxes by increasing the sorption capacity of goethite (Rasmussen et al., 2018). For both minerals, more MAOM-C accumulated under deciduous forests than grasslands in the Schorfheide-Chorin region, but the opposite was true for the Schwäbische Alb and Hainich-Dün (Figure 4). These results might reflect differences in the importance of aboveground and belowground OC inputs for MAOM formation in forests and grasslands, and the modulating effect of soil texture and mineralogical characteristics on the contribution of OC inputs from these sources. Organic inputs in grasslands are probably primarily from belowground sources (Keller, Borer, et al., 2022; Sokol et al., 2019). Inputs from belowground sources are closer to the exposed containers. Therefore, we argue that in the Schwäbische Alb and Hainich-Dün, where the mineral soils are richer in clay and oxides compared to Schorfheide-Chorin (Table 1), sorption of aboveground-derived DOM in the soil overlying the mineral containers would reduce OM inputs to the mineral containers more in forests than grasslands. This effect might be more pronounced in deciduous than coniferous forests because of the lower OC stocks in the organic layers in deciduous forests (Table 1), and thus, potentially lower OC inputs. It is important to note that the study region effect on MAOM formation could be partially influenced by differences in tree species composition. Nevertheless, even after considering only beech-dominated forests, we found that MAOM-C accumulation remained higher in the coarse-textured soils in Schorfheide-Chorin than the other study regions (Supporting Information S5). Therefore, we suggest that the region effect on MAOM-C accumulation might be more ascribed to the difference in soil texture and soil mineral composition. Thicker organic layers in combination with presumably less sorptive soils seemingly favour increased DOM fluxes into the mineral containers, and thus, the MAOM formation.

4.3 | Effects of management and soil conditions

4.3.1 | Forests

Thinning and harvesting led to reduced litter and hence OC input. This translated into a reduction of the OC stock in the organic layer (Figure 5) and likely the DOC flux into the mineral containers, causing less MAOM formation. The OC stocks in the organic layer might have been especially important for MAOM formation in our study as the mineral containers were placed at a shallow depth of 5 cm in the mineral soil. Organic C stored in the soil organic layer is more sensitive to management and global changes than OC stored in the MAOM fraction (Grüneberg et al., 2013; Lugato et al., 2021; Mosier et al., 2019). In previous studies, reduced OC stocks in the soil organic layer did not translate into lower MAOM-C stocks even after several decades of forest management (Grüneberg et al., 2013; Mosier et al., 2019; Schöning et al., 2013). Here, we demonstrate that processes reducing OC stocks in the soil organic layer of forests will also have consequences for the input of OM to the MAOM fraction in the topsoil, and thus likely, MAOM-C stocks in the long term.

The formation of MAOM was positively related to the SMIr, which is positively correlated with conifer share (Figure 5). Interestingly, in the SEMs, the OC concentration of the overlying mineral soil was not relevant for the amount of OC that accumulated on the minerals. The accumulation of MAOM-C was, however, positively related to the C:N ratio of the soil. This was even the case when only deciduous tree species were considered (data not shown). Thus the quality, not the quantity of the OM in the mineral soil determined the mobility of OC and consequently DOC fluxes (Aitkenhead & McDowell, 2000). We quantified the concentration of WEOC in the overlying soil as a measure of the potential input of OC into the mineral containers. However, this is a static measurement that probably does not reflect the actual fluxes of DOM in the field; hence, it was not a suitable predictor of MAOM-C accumulation in our study (data not shown). Nevertheless, the positive relationship between DOM production and soil C:N ratio is well documented (Cools et al., 2014; Gan et al., 2020; Kindler et al., 2011; Thieme et al., 2019).

4.3.2 | Grasslands

Fertilization positively and negatively affected MAOM formation by increasing aboveground plant biomass and decreasing plant species richness respectively (Figure 6). When considering both, the effects mediated by aboveground biomass as well as by plant species richness, fertilization had an overall positive effect on MAOM formation for illite ($\beta = .10$) and negative effect for goethite ($\beta = -.02$). Our study demonstrates that the positive effect of fertilization on MAOM formation can be offset by the fertilization-induced loss of plant diversity.

The aboveground biomass-mediated effect of fertilization might reflect the positive link between nutrient addition, plant productivity and soil C storage (Fornara & Tilman, 2012; Huang et al., 2020). Additionally, fertilization improves the quality of organic inputs (Apostolakis et al., 2022; Poeplau et al., 2018). This could have promoted more efficient utilization of OM by the mineral-associated microorganisms and consequently stimulated microbial biomass production (Cotrufo et al., 2013; Poeplau et al., 2019) and ultimately increased MAOM formation (Angst et al., 2021). This statement is supported by the finding of a positive relationship between PLFAs:MAOM-C ratio and land use intensity (fertilization) in our companion study (Brandt et al., 2023). Brandt et al. (2023) also observed more PLFAs per unit MAOM-C on illite than goethite, which might indicate that microbial-derived OM accounts for a larger share of the OM accumulating on illite. The finding of a stronger positive effect of fertilization (aboveground biomass) on MAOM formation for illite than goethite (Figure 6) suggest that MAOM formation via the microbial efficiency-matrix stabilization pathway (see Cotrufo et al., 2013) might be more relevant in soils where the mineral assemblage favours less direct sorptive accumulation and stabilization of OM (Cotrufo et al., 2015). This warrants further exploration given the growing emphasis on the role of microbial necromass in MAOM formation (Angst et al., 2021; Cotrufo & Lavallee, 2022; Rui et al., 2022).

The differential effect of fertilization on MAOM formation for illite and goethite might also be in part explained by fractional sorption of DOM constituents (Han et al., 2021; Kleber et al., 2015; Schneider et al., 2010). Oxides, such as goethite, are presumed to preferentially sorb aromatic constituents while clay minerals, such as illite, retain less aromatic and smaller compounds of lower molecular weight (Han et al., 2021; Kleber et al., 2015). We suppose fertilization could have reduced the abundance of aromatic compounds (Zhang et al., 2019), which are preferentially sorbed by goethite. This could in part explain the slightly negative net effect of fertilization on MAOM formation for goethite, but further research is needed to validate this claim.

We were surprised to find a positive link between plant species richness and MAOM-C accumulation despite there was a negative association between plant species richness and plant productivity (aboveground biomass) (Figure 6). In previous studies, the link between plant diversity and soil OC storage was mainly ascribed to the positive effect of plant diversity on plant productivity and OC inputs into the soil (Anacker et al., 2021; Chen et al., 2018; Cong et al., 2014; Lange et al., 2015; Prommer et al., 2020). We surmise that while fertilization improves soil nutrition and stimulates aboveground biomass production, it might cause lower belowground investment of C (Keller, Walter, et al., 2022; Poyda et al., 2021). This is because with increased fertilization intensity plants are able to more easily access nutrients without substantial investment in a dense rooting system (Li et al., 2011; Poyda et al., 2021). Lower investment of resources belowground could also result from a shift in plant communities towards more resource acquisitive, fast-growing species that tend to be more abundant in highly fertilized, species-poor grasslands (Apostolakis et al., 2022; Blüthgen et al., 2012). We could not confirm these mechanisms since there was no correlation between the biomass of roots in the overlying soil and MAOM formation (data not shown). We, however, acknowledge that the used estimate of belowground biomass did not capture inputs from rhizodeposition and mycorrhizal fungi, which can serve as important belowground sources of C. While further research is needed to elucidate the precise mechanisms that underlie these results, our study highlights the caveat of applying fertilizers as a strategy to increase soil OC stocks in temperate grasslands.

Grazing was not an important factor of MAOM formation (Figure 6). Unlike fertilization, C and nutrient inputs through urine and dung patches are spatially heterogenous (see Maire et al., 2018), and hence, likely not as relevant for MAOM-C accumulation as fertilization across a regional scale.

While it was not statistically relevant in forests, soil pH had a direct negative effect on MAOM-C accumulation for goethite in grasslands (Figure 6). This is likely because the pH of the grassland soils, unlike the forest soils, is in the critical range close to the mineral's PZC where its sorption capacity is significantly reduced (Figure S3). Similar to forests, we did not find a link between the OC concentration in the overlying soil and MAOM formation for the mineral grassland soils (Figure 6). However, for organic grassland soils in the Schorfheide-Chorin region, MAOM formation increased with soil OC content (Figure 7). Possibly, compared to mineral soils, the organic soils facilitated direct fluxes of DOC from immediate surroundings into the mineral containers. The question arises: where did the MAOM-C come from in the mineral grassland soils? We are only able to speculate that because MAOM formation was related to plant properties, direct inputs from roots and mycorrhizal fungi might have been important. Overall, our findings suggest differences in the pathways of MAOM formation in grasslands on mineral soils and those on organic soils. They underscore the need to better constrain the sources of MAOM-C to unravel the enigma of MAOM formation in grasslands.

5 | IMPLICATIONS AND OUTLOOK

Exposing two pristine soil minerals (goethite and illite) for 5 years in topsoils of managed temperate forest and grassland ecosystems, we found that the type of mineral was the principal factor controlling MAOM formation. Our study underpins the relevance of soil mineralogical properties for the accumulation of soil OM. Irrespective of the environmental conditions, goethite accumulated much more OM than illite (Figure 8), even for field conditions previously considered less optimal for oxide–OM interactions (pH >6.5). This is

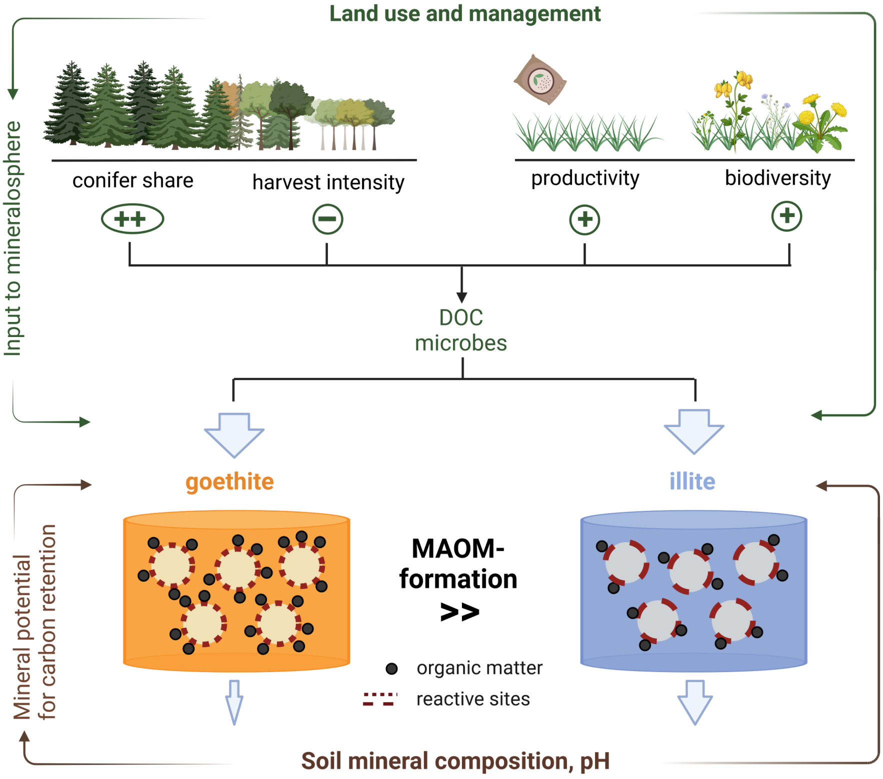

FIGURE 8 Graphical summary of the interplay of land use, management and mineral type in mineral-associated organic matter (MAOM) formation. The upper part of the figure illustrates factors that control the input of OM to the minerals. The double positive sign highlights the much stronger effect of tree species selection (conifer share) than other management practices. The lower part depicts the influence of mineral type for the same level of OM input.

consistent with the long-standing observations for the OM retention by Fe oxides in aquatic systems under circumneutral conditions. (Tipping, 1981). Our study provides direct evidence to support the earlier call by Rasmussen et al. (2018) to consider type and reactivity of minerals rather than only the clay content for predicting soil OM content. It adds to the demonstrated superiority of other predictors, such as the concentration of pedogenic oxides (Herold et al., 2014; Kirsten et al., 2021; Rasmussen et al., 2018; Reichenbach et al., 2023).

Within the short time of 5 years, illite already came close to its OM sorption capacity in some cases, despite the amount of accumulated OM being low relative to its SSA. This suggests that not all surfaces of minerals contribute to organo-mineral interactions and underscores the need to go beyond surface area to predict the OM storage capacity of soil minerals (see figure 1 in Kaiser & Guggenberger, 2000). It also suggests that soils dominated by illite (and probably other clay minerals as well) may be relatively limited in their capacity to accumulate and store MAOM-C. In contrast, goethite was nowhere near its sorption capacity and may take decades before reaching saturation. This suggests that soils rich in goethite (and similar oxides and related mineral phases) have a large capacity to store and accumulate MAOM-C. Our findings corroborate the work of Kirsten et al. (2021) who observed a positive relationship between MAOM-C and the ratio of $\mathrm{Fe_d}$: clay. Taken together, these findings suggest that increasing C inputs into soils where oxides are present in appreciable amounts—especially those that are far below their mineralogical capacity to store C (see Georgiou et al., 2022)—may offer great potential to enhance near-term soil C sequestration.

Unlike previous studies conducted in natural soils (Grüneberg et al., 2013; Herold et al., 2014; Keller, Borer, et al., 2022; Mosier et al., 2019; Schöning et al., 2013), we were able to detect significant effects of land use and management intensity on MAOM-C after exposing pristine minerals for only 5 years to ambient soil conditions. This demonstrates that land use and management intensification can be relevant for MAOM formation on relatively short time scales. Our findings are thus important in the context of predicting how MAOM-C responds to anthropogenic interferences. In natural soils, these changes occur in the presence of a long-term background of MAOM accumulation, and thus, might be difficult to discern directly on short time scales.

We observed consistently higher MAOM-C accumulation under coniferous forests compared to deciduous forests and grasslands. Since the minerals were exposed in topsoils, subsoil patterns might differ. Thus, future investigations on the effect of land use on MAOM formation in the subsoil are warranted. The container design reduced the influence of roots and macrofauna, which might play a role for MAOM formation especially in grasslands (Angst et al., 2022; Sokol et al., 2019). Our results suggest that in addition to the forest type, the magnitude of difference in MAOM-C between temperate forests and grasslands might depend on the quantity of aboveground-derived C entering the mineral soil.

Management intensity had stronger effects on the MAOM formation in forests than grasslands (Figure 8). The much lower variance in MAOM-C accumulation explained in the SEMs for grasslands compared to forests suggests research is particularly needed to deepen our understanding of the key controls of MAOM formation in grasslands. There has been growing emphasis on the role of fine roots, hyphae and microbial necromass for the formation of MAOM (Angst et al., 2021; Cotrufo et al., 2013; Cotrufo & Lavallee, 2022; Rui et al., 2022; See et al., 2022; Zhu et al., 2022). Accurately quantifying the contribution of all these potential OM sources, including belowground inputs, to MAOM formation is not without challenge, but might be an important step towards improving our predictive understanding of the response of MAOM-C to management in grasslands.

AUTHOR CONTRIBUTIONS

De Shorn E. Bramble: Conceptualization; data curation; formal analysis; investigation; visualization; writing – original draft. **Susanne Ulrich:** Conceptualization; data curation; formal analysis; investigation; visualization; writing – original draft. **Ingo Schöning:** Conceptualization; methodology; supervision; writing – review and editing. **Robert Mikutta:** Conceptualization; funding acquisition; writing – review and editing. **Luise Brandt:** Visualization; writing – review and editing. **Christian Poll:** Conceptualization; writing – review and editing. **Ellen Kandeler:** Conceptualization; funding acquisition; writing – review and editing. **Christian Mikutta:** Conceptualization; funding acquisition; writing – review and editing. **Alexander Konrad:** Formal analysis; funding acquisition; writing – review and editing. **Jan Siemens:** Funding acquisition; writing – review and editing. **Yang Yang:** Formal analysis; funding acquisition; writing – review and editing. **Andrea Polle:** Funding acquisition; writing – review and editing. **Peter Schall:** Writing – review and editing. **Christian Ammer:** Writing – review and editing. **Klaus Kaiser:** Conceptualization; funding acquisition; supervision; writing – review and editing. **Marion Schrumpf:** Conceptualization; funding acquisition; methodology; supervision; visualization; writing – review and editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

This work is based on data elaborated by the BEmins project of the Biodiversity Exploratories program (DFG Priority Program 1374). The datasets are publicly available in the Biodiversity Exploratories Information System (http://doi.org/10.17616/R32P9Q); BExIS dataset IDs: 14686 (soil texture), 19346 (dithionite- and oxalate-extractable Al and Fe), 20126 (aboveground litter weights), 20127 (aboveground litter CNS), 20826 (elevation and main tree species), 22246 (soil pH), 24346 (OC stock of soil organic layer), 25046 (SMI), 21187 (aboveground biomass and species richness in 2016), 23486 (aboveground biomass and species richness in 2017), 24166 (aboveground biomass and species richness in 2018), 26747 (aboveground biomass and species richness in 2019), 27426 (aboveground biomass and species richness in 2020), 31251 (C and N contents), 31476 (WEOC), 31475 (root biomass in forests in 2021) and 31477 (root biomass in grasslands in 2021).

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