

Soil organic matter in major pedogenic soil groups

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Highlights

Organic matter accumulation depends on pedogenic soil differentiation

Pedogenic processes lead to soil-group-specific organic matter accrual in subsoil

Reference Soil Groups have unique process combinations of organic matter accrual

Abstract

Soil organic matter (SOM) accumulation is different in certain soil groups with differences in parent material, degree of weathering and mineral composition. These differences are modulated by climatic factors, but also by pedogenesis, in particular by the formation of reactive mineral surfaces, by soil aggregation, as well as by translocation processes such as elution and illuviation and different types ofurbation. However, there is still a lack of conceptualization of how such processes and thus important Reference Soil Groups influence the composition and properties of OM. Here we summarize the basic processes of OM storage as they differ from soil group to soil group, in order to present a first overview of the processes of OM formation in the different terrestrial soils of the world. We distinguish between soils of different climatic zones, i.e. Cryosols in permafrost regions, soils of limited development (Cambisols), Podzols, Phaeozemes, Chernozems, Kastanozems, and Luvisols in temperate climate zones, as well as Acrisols, Ferralsols, Plinthosols and Nitisols in the subtropics and tropics. We also include soils derived from a specific parent material (Andosols, Vertisols), as well as Anthrosols (paddy soils, Terra Preta, plaggen soils) as examples for human-made SOM accumulations. The compilation of the literature shows that research on OM is clearly focused on specific Reference Soil Groups in temperate climate zones and some man-made soils, while other soils such as Nitisols and Acrisols are clearly underrepresented. The contribution of the different soil groups to global organic carbon (OC) stocks varies, with large amounts of OC found for the first metre in Cryosols, Cambisols, and Podzols, due to the large land area they cover, followed by Acrisols and Ferralsols. In part, these differences can be attributed to differences in the formation of OM, which we ascribe to three main mechanisms. We emphasize that in all major Reference Soil Groups, both the mechanism of sorptive conservation as well as the protection within the aggregates contribute to the storage of OM. However, the reactant partners and aggregate forming agents and therewith the intensity of these stabilisation processes vary among the Reference Soil Groups. As a result, there are differences in the SOM composition in the topsoil. Within the entire soil profile, however, pedogenic processes lead as third mechanism to soil-group-specific accrual of SOM in the

1 subsoil, e.g. by means of illuviation, by cryo-/bio-, and peloturbation, as well as by
2 management. We conclude that the specific pedogenic environment must be considered in the
3 assessment of global SOM storage potentials and thus probably also in future global C models.

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5 Key words: Reference Soil Group; carbon stocks; soil minerals; sorption; aggregation;
6 turbation;

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1 Introduction

With growing world population, an increasing area of soil is currently sealed or converted into production land, e.g., for arable cropping. It is estimated that these activities already led to a degradation of about 33 % (FAO, 2019) to 40% (Smith et al., 2016) of global soils. Particularly many past agricultural practices have reduced soil organic carbon (SOC) stocks and altered their properties, leaving a yet unresolved human debt on future land-use (Sanderman et al. 2017). As a result, global initiatives have been put in place to restore soils and their carbon stocks, such as the 4p1000 initiative launched under the framework of the Paris climate conference in 2015, with the aspirational goal to offset anthropogenic C emissions by sequestering OM in the top 40 cm of soil at an annual rate of 4 per mill. Hence, several papers have been published to describe how this aim might be reached or not (e.g., Rumpel et al, 2020; Baveye et al., 2018; FAO, 2019). However, only recent approaches consider that different soil groups are able to sequester different amounts of C in soil, i.e., that there is an individual contribution of soil groups to OM storage and related ecosystem services (Amelung et al., 2020).

Soils differ according to their soil forming factors, such as parent material, climate, topography, impact by humans and biota, and age (Jenny, 1941). With increased degree of weathering, acidification usually proceeds, resulting in the formation of pedogenic oxides and clay minerals, which offer reactive sites for various surface sorption and aggregation reactions, finally affecting soil OM storage and residence time (e.g., Jenny, 1941, Kleber et al., 2015). The composition and properties of OM thus varies among different soils (Kögel-Knabner and Amelung, 2014), a conceptualization across the major Reference Soil Groups, however, is still lacking. There are attempts, though, to relate global SOC storage to global SOC maps, as, e.g., done in the FAO/ISRIC, Digital Soil Mapping, NRCS or harmonized world soil data bases (FAO Soils Portal, 2020; FAO and ITPS, 2018; Arrouays et al., 2017); however, uncertainties are large and resulted in differences of up to 50 % of total soil C storage estimates among these resources (Hiederer and Köchy, 2014). Moreover, updates from these maps may be

difficult to achieve as long as soil classification systems remain dynamic and make it difficult to re-assign old data entries (e.g., Batjes, 1996) to new soil classification requirements.

The aim of this work is, therefore, to summarize the basic processes that control OM formation and composition as related to pedogenic differentiation, and therewith to provide a first overview on soil OM formation processes within the different soils of the world. We herewith intend to increase awareness, that the formation and stability of OM is soil-specific, and thus the pedogenic environment needs to be considered when investigating SOM accumulation and storage. We refer to the Reference Soil Groups according to the major common soil classification system, the World Reference Base for Soil Resources WRB (IUSS Working Group WRB, 2015), but also give the Soil Order in the United States Department of Agriculture (USDA) Soil Taxonomy (Soil Survey Staff, 2014). The horizon designation is according to FAO (2006).

2 Pedogenic features and associated Reference Soil Groups relevant for organic matter accrual

Accumulation of SOM is different in specific soil groups (Batjes, 1996). The accumulation of SOM is modulated by climatic factors, but also by pedogenic processes, defining, for instance, aggregation and overall soil structure, eluviation and illuviation processes, redoximorphosis orurbation processes, as, e.g., outlined by Duchaufour (1998) and Tisdall and Oades (1982). As pointed out by Rasmussen et al. (2018), additional soil physicochemical properties predict SOM stabilization better than clay content alone. Recent analytical developments provide additional insight into the 2D and 3D structure of soils as well as into the amount and type of clay-sized minerals (Ito and Wagai, 2017), which now enables us to disentangle the different mechanisms responsible for accumulation of SOM as a function of pedogenic environment and degree of soil development, i.e., of the specific soil group. We do not discuss all soil groups, but merely selected major Reference Soil Groups with specific pedogenic properties, but we remind that the underlying WRB classification system has not been designed as being

a pedogenetic one. We describe how these major Reference Soil Groups are linked to SOM formation and properties.

As illustrated by Figure 1, searching for key-word combinations of the terms “soil organic matter” in conjunction with a certain major Reference Soil Group, clearly shows that some soil groups are overrepresented in scientific publications with regard to their importance of total land area, such as Podzols, Chernozems, Andosols and Vertisols. Other soil groups, in turn, are clearly underrepresented, such as Cambisols, Ferralsols, Acrisols, Leptosols, Calcisols, Arenosols, Kastanozems and Lixisols, despite they contribute much more to total land area. Generalizing findings from specific soil groups to the processes of SOM formation and turnover on the global scale may thus be misleading, if not accounting for the quantitative contributions of soil-specific SOM interactions with the global C cycle.

As summarized in Table 1, the soils discussed represent specific mineral, chemical and physical properties together with their inherent pedogenic processes that lead to unique combinations for the (co-)occurrence of OM accumulation mechanisms. The soils considered together with their major pedogenic features (Table 1) are soils of different climatic zones, i.e. Cryosols in permafrost regions, soils with limited development (Cambisols), Podzols, Phaeozemes, Chernozems, Kastanozems, and Luvisols in temperate climate, as well as Acrisols, Ferralsols, Plinthosols and Nitisols in the subtropics and tropics. We then refer to soils that formed from a specific parent material (e.g., Andosols, Arenosols, and Vertisols). We also discuss Anthrosols, i.e., soils that have been formed from terrestrial soils under human-made conditions (paddy soils, Terra Preta, plaggen soils), because they provide information on how soil management can increase SOM accrual.

Histosols and other soils in which OM accrual is controlled by oxygen depletion due to their water regime are not explicitly considered here. Thus we also do not consider to Planosols, Stagnosols, Gleysols, and Fluvisols. Here we refer the reader to a recent review on soil hydromorphy and soil carbon (Amendola et al., 2018). Similarly, we do not consider soils which have a limited input of OM, such as Calcisols, Durisols, and Gypsisols. Finally we also withdraw

1 from discussing soil groups, for which information on the amount of OM accumulation and the
2 underlying mechanisms is scarce, specifically Arenosols, Solonetz, and Solonchaks (Fig. 1).
3 The main SOM accumulation mechanisms operating in different soil groups are identified as
4 sorptive stabilization, aggregate protection and translocation/burial in the subsoil (Table 2;
5 Sollins et al., 1996; Rumpel and Kögel-Knabner, 2011; Caopriocha et al., 2014). Accrual of
6 OM in soils can occur by association of organic compounds of plant or microbial origin with
7 mineral and oxide surfaces. The resulting organo-mineral associations are glued together to
8 silt-sized aggregates, microaggregates and even larger units, the latter also involving the
9 action of soil fauna, fungal hyphae, and roots (see, e.g., Oades and Waters, 1991; Christensen,
10 1996; Six et al., 2004; Totsche et al., 2018, for reviews). A large part of the OM in soils is
11 thermodynamically labile, but persists in soils due to the formation of inaccessible
12 microstructures (Kögel-Knabner and Kleber, 2011; Kleber et al., 2011), which means it is not
13 the thermodynamic properties of OM itself, but rather the association of OM with mineral
14 surfaces and within aggregates that provides long-term OC accumulation. In consequence, an
15 increasing number of authors explain the mechanisms of long-term stabilization of energy rich
16 microbial residues or microbial products to be the result of an interaction with the mineral
17 matter in organo-mineral associations and small aggregates (Christensen, 1996; Chenu and
18 Plante, 2006; Kleber et al., 2015). This explanation replaces the older ideas of stable, newly
19 formed 'humic substances' (see Von Lützow et al., 2006; Schmidt et al., 2011; Lehmann and
20 Kleber, 2015; Kleber and Lehmann, 2019 for a detailed discussion and further references).
21 Beyond the structural and physico-chemical mechanisms of SOM storage occurring within a
22 given soil horizon, additional differences in OM storage capacity occur with depth. Within a soil
23 profile, i.e. the sequence of horizons defining the major Reference Soil Group (Table 1), the
24 degree of aggregation usually declines with soil depth, associated with rooting depth.
25 Depending on soil group, SOC concentrations usually decline non-linearly with depth (e.g.,
26 Amelung et al., 1997; Paul et al., 1997; Batjes, 1996). Very dense soil horizons, however, such
27 as the intentionally formed Ardp horizon in paddy soils, may decouple SOM dynamics in the
28 very surface soil from that of the deeper subsoil (Kögel-Knabner et al., 2010). Once SOM is

buried, however, it may escape the window of high microbial activity and remain in the subsoil (Fontaine et al., 2007); thus, we consider deciphering the degree of subsoil burial as relevant for OM stabilization.

Soil organic matter accumulation is modulated by, e.g., vegetation, management and climate – with different impacts on OM inputs by primary above- and belowground plant production, subsequent recycling of OM by microbes and formation of microbial residues depending on, e.g., soil nutrient status and pH, moisture and temperature conditions. Reviewing respective studies would go beyond the scope of this study. Yet, we would like to highlight that all these modulations contribute to a substantial variability of OM storage in different Reference Soil Groups, which is not only seen on plot scale with variations of, e.g., texture and topography for a particular field and soil group (e.g., Pätzold et al., 2008; Bekele et al., 2013), clearly significant for any soil group at landscape scale with variations in management (Poeplau and Don, 2013, Wiesmeier et al., 2015, 2019; Gesesse et al., 2020), and, therefore, contributing to significant, soil-group-specific coefficients of variations in SOM accrual at global scale (e.g., Batjes, 1996; Sanderman et al., 2017; Duarte-Guardia et al., 2020). A promising approach to deal with complex mapping units and how to derive the variation in soil properties within soil types is described by Stoorvogel et al. (2017).

2.1 Sorptive preservation of SOM at mineral surfaces

2.1.1 Mechanisms

Long-term protection of organic molecules by sorptive interactions is considered to be limited to those organic materials directly attached to the protecting mineral surface (Kleber et al., 2015). Abundant evidence that substantial parts of mineral surfaces are not covered by OM has led to the insight that organic materials must be stacked or clustered on mineral surfaces in small patches with some vertical extension (Kaiser and Guggenberger, 2003, Wagai et al., 2009, Schweizer et al., 2018, 2019). This is consistent with the concept of a pore-filling mechanism going beyond direct interactions between mineral surfaces and OM (McCarthy et al., 2008). The degree of this pore-filling mechanism again depends on pore size and

accessibility to dissolved organic matter (DOM), which may be hampered more in very heavy, clayey soils compared to silty and loamy ones.

The SOM in fine silt and clay fractions has longer turnover times than OM in other soil fractions.

Sorption of soluble OM to soil material (Bw horizon) reduced OM mineralisation to less than 30% compared with the mineralisation in soil solution (Kalbitz et al., 2003). Chenu and Stotzky (2002) suggest that small molecules sorbed to mineral surfaces cannot be utilized by microorganisms. The adsorption of macromolecules is considered to be associated with conformational changes that render macromolecules unavailable to the action of extracellular enzymes (Theng, 1979; Khanna et al., 1998). Evidence for such conformational changes of sorbed organic macromolecules can be deduced from the racemization of amino acids within mineral-bound proteinaceous material (Amelung, 2003; Amelung et al., 2006) or other conformational changes (Quiquampoix et al., 1995).

The extent to which microbial metabolites, extracellular polymers or microbial necromass produced during OM decomposition are stabilized in different soils is controlled by the specific surface area of fine-sized minerals. The latter varies with the size and mineral type of particles, which include layer silicates ($<2\ \mu\text{m}$), oxides (crystals 5-100 nm), short-range ordered Fe-oxides (3-10 nm), and amorphous Al-oxides ($<3\ \text{nm}$) (Kleber et al., 2015). Mineral reactivity, rather than particle size, thus consistently serves as a suitable predictor of the residence time and turnover time of stable SOC, and can be associated with 2-3-fold differences in total SOC storage (Kahle et al., 2004; Kleber et al., 2005; Mertz et al., 2005; Torn et al., 1997; Rasmussen et al., 2005). A given mineral surface type may function differently in different soils, as result of variations in pH, OM chemistry, cation availability, and other environmental controls.

When considering different Reference Soil Groups, the mineral surfaces available for SOM stabilization have different abundances in different soils. Three-layer (2:1) clay minerals with variable surface charges at their edges are most abundant in soils of temperate regions, such as Phaeozems, Chernozems, Kastanozems, as well as in Luvisols, Vertisols, and Cambisols. In the coarse clay fraction of these soils, silicate mineral surfaces (montmorillonite > vermiculite > illite > kaolinite) are much more important for OC storage than Fe oxides, which dominate in

fine clay fractions (Anderson et al., 1981; Kahle et al., 2003; Kleber et al., 2004). However, kaolinitic and halloysitic 2-layer (1:1) clay minerals, which dominate in many soils of the tropics, rather behave like oxide sorption places, typically found in Ferralsols, Acrisols, and Lixisols. Some of them also occur in Vertisols, but not as dominant clays, since 1:1 clay minerals are not prone to swelling and shrinking and thus gilgai relief formation, as common in this soil group. Thus, Scharpenseel et al. (1989) and Mathieu et al. (2015) found a strong effect of soil group and associated clay content and type on the radiocarbon age of OM (Table 3a, b).

2.1.2 Bonding strength on phyllosilicate clay minerals and pedogenic oxides

The negative charge on the siloxane surface of clay minerals depends on the type and localization of the excess negative charge created by isomorphic substitution. Organic anions are repelled from negatively charged surfaces in soils, but binding occurs when polyvalent cations are present on the exchange complex. Unlike Na^+ and K^+ , polyvalent cations are able to maintain neutrality at the surface by neutralizing both the charge on the negatively charged surface (e.g. in clay minerals) and the acidic functional group of the OM (e.g. COO^-) and thus act as a bridge between two charged sites. In neutral and alkaline soils the major polyvalent cations present in soil are Ca^{2+} and Mg^{2+} , which are decisive for a stable microstructure of clay minerals, such as in Phaeozems, Chernozems, and Kastanozems. In acid soils such as Podzols, Acrisols, and most Ferralsols this occurs via hydroxypolycondensations of Fe^{3+} and Al^{3+} . Stabilization of SOM with the mineral matrix in acid Cambisols and Podzols with large amounts of oxalate-extractable Al and Fe results in a particularly stable and relatively old OC pool, which is potentially stable for thousands of years (Spielsvogel et al., 2008). For a long-chain organic molecule with multiple functional groups, multiple points of attachment to the clay particle (segment-surface contact) on permanent charge sites of phyllosilicates are possible. Microbially secreted polysaccharides frequently carry a negative charge due to the presence of uronic acids that adsorb strongly to negatively charged clay surfaces through polyvalent cation bridging (Chenu, 1995). Quartz particles without layer charge and without interlayer

spaces usually exhibit only weak bonding affinities. Soils dominated by quartz grains such as Arenosols thus often store only low amounts of OM.

In the absence of a layer charge a siloxane surface may be considered uncharged. Nevertheless, the 1:1 clay minerals like kaolinite and halloysite may also be reactive due to available surface of Al-octahedra (Kaiser and Guggenberger, 2003). As a result, it has been put in question whether kaolinites really differ from smectites in their role on SOM stabilization (Feller and Beare, 1997; Wattel-Koekkoek et al., 2001; Bruun et al., 2010). Wattel-Koekkoek and Buurman (2004) observed no significant difference for the mean residence time of the kaolinite-bound OC in Nitisols and the smectite-bound OC in Vertisols in northern Mozambique, and concluded that charge and the amount of mineral surface available was decisive.

It is widely assumed that the energetically strongest associations between OM and mineral surfaces involve the mechanism of ligand exchange between carboxyl groups of OM and hydroxyl groups at the surfaces of mineral phases. Complexation of OM on mineral surfaces via ligand exchange increases with decreasing pH value with maximal sorption between pH 4.3-4.7, corresponding to pK_a values of the most abundant carboxylic acids in soils. Therefore, ligand exchange between reactive inorganic hydroxyls (OH groups of Fe, Al, and Mn oxides; octahedral surfaces of allophanes, imogolites and 1:1 phyllosilicates; and edge sites of phyllosilicates) and organic carboxyl and phenolic-OH groups is restricted to acid soils rich in minerals with protonated hydroxyl groups. Under circumneutral conditions, the respective bonds of these groups to oxidic phases, however, are weaker. Hence, Kleber et al. (2015) suggested that arid and more alkaline soils might be more prone to rapid OM losses than more acidic ones, frequently found under more humid conditions. In any case, these considerations imply a pH-controlled SOM stability that is thus different for soils with different pH and mineral assembly.

In comparison to mineral binding, less information is available about the effect of metal binding (Ca^{2+} , Al^{3+} and Fe^{3+} , heavy metals) on SOM stability or about the mechanisms involved. Several studies have shown effects of Ca^{2+} ions on the mineralisation of SOM and its solubility

(Muneer and Oades, 1989), also the large OM content of calcareous soils is attributed to the effect of Ca^{2+} ions (Oades, 1988). The interaction of OM with Al^{3+} as well as Fe (hydr)oxides is considered to be the main reason for the stability of OM in Podzols (Lundström et al., 2000). The Al/C ratio of DOM seems to be an important parameter for its stability against microbial decomposition. In long-term incubation studies, Schwesig et al. (2003) showed that for natural DOM, Al/C ratios > 0.1 increased the half-life of the stable DOM fraction up to 4-fold. Dissolved organic matter in soils can be precipitated by metal ions and the precipitated OM can be more stable than the DOM remaining in solution. Larger DOM molecules are precipitated preferentially, while smaller molecules stay in solution. Often it is difficult to separate the complexing effect of metal cations (Ca, Mg, Al, Fe) from their ability to form cation bridges.

2.2 Soil organic matter stabilization as influenced by soil aggregation

The soil matrix is separated into compartments of variable size, called aggregates, such that transfer rates of enzymes, substrates, water, and oxygen supply can be limited. Organic matter is stabilized most efficiently in microaggregates and associated organo-mineral associations (Totsche et al., 2018), which are stable over long time periods. The OM stored additionally in macroaggregates has a much shorter turnover time (Von Lützow et al., 2007). In any case, the minerals that bind together to form small aggregate units, usually contain OM already stabilized by sorptive interactions as outlined above. It is on this basis that any time scale of SOM preservation within aggregates can prolong the turnover of SOM in soil as long as the aggregate exists; if it disintegrates, sorptive interactions with minerals and the associated microaggregation still control the mean residence time of this OC. Such a hierarchically organized system of aggregates (Tisdall and Oades, 1982) has been described for a number of Reference Soil Groups including Cambisols, Luvisols, Vertisols, Andosols and Chernozems (Totsche et al., 2018). In contrast aggregate hierarchy is less important in highly weathered soils dominated by Fe oxides, such as Ferralsols and Acrisols (Oades and Waters, 1991; Shang and Tiessen, 1998; Barthès et al., 2008; Peng et al., 2015). In these soils organo-mineral interactions are described to be the dominant binding mechanisms (Dieckow et al.,

2005; Briedis et al., 2020).

Observations of enhanced SOM mineralization following disruption of aggregates confirm that occlusion in aggregates has a retarding effect on SOM decomposition. Protection is greatest where aggregate stability is high and aggregate turnover is low, thus aggregation is the stabilization mechanism that is potentially most susceptible to disturbance. Measured turnover times for OC protected by aggregates indicate an inverse relationship between aggregate size and turnover time (Skjemstad et al., 1993; Balesdent, 1996; John et al., 2005; Liao et al., 2006) with the longest reported turnover times in the lower centennial range (200-320 years) in the smallest aggregates <20 μm . Occlusion at the microstructure level <20 μm has been attributed to abiotic mechanisms such as the precipitation of Fe- and Al-oxides or hydroxides (Duiker et al., 2003), but in general soil biota are thought to be strongly involved in the process of occlusion. Thus, microbial cells, secretions, root exudates and faunal mucus act as gluing agents and are at the same time occluded within microaggregates (Totsche et al., 2018). The final decay of inner-aggregate OM is slow, but if happening may induce aggregate breakdown and re-formation (Six et al., 2000).

In addition to the gluing action of organic materials, cementing agents are relevant for aggregation and thus also affect OC accumulation and turnover in soils (Totsche et al., 2018). Cementing agents comprise all inorganic substances responsible for cementing and embedding the building units that form soil aggregates, specifically as oxides, hydroxides, and oxyhydroxides of Fe, Mn, Al, S), aluminosilicates, and carbonates (Oades and Waters, 1991). Their role for the stabilization of OM has received comparably limited attention.

2.3 Soil organic matter preservation by translocation and burial in the subsoil

The radiocarbon age of SOC usually increases with increasing soil depth, but is specifically affected by the pedogenic translocation of OM to the subsoil (Scharpenseel et al. 1989; Table 3a; 3b). The subsoil at a depth of 30–100 centimetres beneath the surface contains on average 47 per cent of the topmost meter's SOC stocks. But due to the slower turnover rates, the subsoil accounted for just 19 per cent of the SOC that has been incorporated within the past

50 years into the topmost meter (Balesdent et al., 2018). Fontaine et al. (2007) were among the first who recognized that this subsoil OM is not necessarily old because it is stabilized to a high degree; instead, the authors discovered a surprising biological decomposability once labile C sources were added. Later works then confirmed that the long residence time of subsoil OM may largely be attributed to the lack of additional resources for microbial growth (Ahrens et al., 2015), including nutrients such as N and P (Meyer et al., 2018). Burying SOM into the deeper soil may thus enhance its residence time and significantly contribute to long-term OC storage.

Generally, root inputs to subsoil, such as exudates and root litter, are a dominant source of the OM found in the subsoil, with the parent material, predefining soil textural and nutrient composition, determining the capacity of a soil to stabilize OM via organo-mineral association and aggregation, but also governing OM inputs to the subsoil (Angst et al., 2018).

In addition, the different processes that translocate OM to deeper soil such as DOC and particle transport and bioturbation are highly dependent on soil formation processes and thus are different for the specific soil groups. The DOM transport to deeper soil horizons is occurring in many soils but it is a major process in Podzols and acid Cambisols (Kaiser and Kalbitz, 2012; Keyvanshokouhi et al., 2019). Loss of DOC from topsoils typically ranges in the order of 2 to 20 g m⁻² yr⁻¹ (Kindler et al., 2011) but this does not necessarily mean that the transported DOM is re-adsorbed. The degree of weathering declines with depth, and so does the reactivity of soil minerals; hence, mainly hydrophobic compounds may be subtracted from subsoil solution due to entropy-driven sorption interactions (Kaiser et al., 1996). Subsoils typically lose 1-10 g DOC m⁻² yr⁻¹ (Kindler et al., 2011), suggesting that only half of the produced DOC in the surface soil is retained. A large portion of DOM may just escape the soil window, ending in deeper groundwater aquifers and thus contributing to mitigating atmospheric CO₂ emissions by comprising a temporary C storage (Siemens, 2003) before possibly re-entering the oceans or other surface waters. In general, DOM production rates are larger, the larger the soil C/N ratio is, whereas DOM retention in subsoils is inversely related to the ratio of OM to Fe and Al (hydr)oxides (Kindler et al., 2011).

Apart from DOC translocation, specific pedogenic processes may contribute to subsoil OM accumulation, such as bioturbation. Soil biota — especially earthworms, ants, termites, and particular vertebrates — displace large volumes of soil. Bioturbation rates of soil animal groups range between 1 and 5 Mg ha⁻¹ y⁻¹, but may reach up to 10 (crayfish, termites), 20 (vertebrates), and 50 to >100Mg ha⁻¹ y⁻¹ (earthworms) as reviewed by Wilkinson et al. (2009). Earthworms and mammals are important in Phaeozems and Chernozems, and to a lesser degree in the drier Kastanozems. Translocation by bioturbation and clay migration are the relevant processes in Luvisols (Keyvanshokouhi et al., 2019; Torres-Sallan et al., 2018).

In acidic soils, ants may mix the degraded top- and upper subsoil layers with SOM (Kristiansen and Amelung, 2001). In soils of the tropics, such as Ferralsols, bioturbation may in part be carried out by termites (Brussaard et al., 2013). Some of them build nests even deep in the subsoil, while a significant portion may also be free-living soil-dwelling termites (Bignell and Eggleton, 2000; Amelung et al., 2002b; Rückamp et al., 2012).

Soil crack formation with subsequent dry-fall of plant debris into deeper depth, as well as self-ploughing are common processes in Vertisols, whereas cryoturbation is the dominating process that buries litter and topsoil OM into deeper layers in regions influenced by permafrost. Hence, not only the production and stabilization rates but also vertical translocation rates of OM are different for different major Reference Soil Groups. Reliable and consistent data for these processes are missing.

There are several cases in which soils may be buried, thus preserving OM and information on paleoclimate, sudden storm, earthquake or erosion events as well as of ancient land-use. Such burial of soils may be caused by volcanic, aeolian, alluvial, colluvial, glacial, and anthropogenic depositional processes. Organic horizons and surface mineral soils that become buried under layers of sediment can store OC several meters below the earth's surface for millennia or longer (Chaopricha and Marin-Spiotta, 2014).

3 Soil organic matter storage and composition in selected Reference Soil Groups

Table 1 summarizes the main pedogenic processes and properties of major Reference Soil Groups in the order we discuss them here.

3.1 Permafrost soils (Cryosols)

Classification and occurrence of Cryosols

Cryosols according to the World Reference Base for Soil Resources / WRB (IUSS Working Group WRB, 2015) develop in association with near-surface permafrost and have a cryic horizon (Table 1) starting ≤ 100 cm from the soil surface. The soils may also have a cryic horizon starting ≤ 200 cm from the soil surface when there is evidence of cryoturbation in some layer within the top 100 cm soil. In the United States Department of Agriculture (USDA) Soil Taxonomy (Soil Survey Staff, 2014), these permafrost-affected soils are called Gelisols. Cryosols occur in polar and subpolar regions, as well as in higher elevations of other regions (mountain Cryosols). Thus, they are widely distributed in northern Eurasia and northern North America, and are also the dominating soils in the ice-free Antarctic, covering large areas (Table 4), more than 8 % of the ice-free land surface on earth. Cryosols are formed under tundra, boreal forest and cold desert. Mountain Cryosols represent 12 % of the Cryosols worldwide and are most abundant in the western Cordillera of the USA and Canada, the Qinghai-Tibet Plateau, Greenland, the Yablonoi-Sayan-Stanovoi Mountains and the Ural Mountains of Russia (Bockheim, 2015). A comprehensive treatment of Cryosols is found in Kimble (2004).

Pedogenic processes in Cryosols

Cryosols develop from cryogenic processes that include cryoturbation, ice segregation, or cryodessication in the presence of permafrost. Cryosols are influenced by physical and chemical weathering to a larger degree than previously thought, but the cryopedogenic processes are dominating (Bockheim et al., 2006; Table 1). The Cryosol profile is differentiated in an upper part, the so-called active layer, which freezes and thaws periodically and which consists of an organic layer (O horizon) on top of the mineral soil (A/B horizons). The lower part of the profile is constantly frozen and is the top of the permafrost layer (cryic horizon) which can reach depths of several hundred meters. Cryosol formation is characterized by

1 cryoturbated soil profiles with warped or broken horizons, weak weathering, redoximorphic
2 features in the lower active layers due to saturation above the permafrost, and OM moved into
3 the lower active layer and the upper permafrost by frost churning.

4 *Organic matter accumulation and composition in Cryosols*

5 Michaelson et al. (2004) outlined that the Arctic and boreal zone hold about 12 to 13 % of the
6 total terrestrial OC stocks in soils. Also, a recent study suggests that in the northern
7 circumpolar permafrost region, at least 61% of the total OC is stored below 30 cm depth
8 (Tarnocai et al., 2009). In mountain Cryosols, SOC is concentrated in the upper 30 to 40 cm
9 of the soil profile and decreases regularly with depth, in contrast to SOC in arctic soils, which
10 is concentrated at the base of the active layer and in the transition zone between the active
11 layer and near-surface permafrost, because of intensive cryoturbation accompanied by
12 compaction (Bockheim and Munroe, 2014). Michaelson et al. (2004) report a ratio of 1:1:2 for
13 the distribution of OC stocks between active-layer organic horizons, active-layer mineral
14 horizons and permafrost down to 1 m.

15 Accumulation of OC in the B/O and Cf (permafrost) horizon is strongly associated with Cryosol
16 formation, with major factors being low temperatures and frost action (Ping et al., 2008). The
17 major effect of frost is the formation of ice wedge polygons, resulting in patterned-ground soil
18 surfaces and frost churning/mixing or cryoturbation, i.e. litter produced above-ground or in the
19 active layer (root litter) is drawn down and mixed into deeper layers. In addition to
20 cryoturbation, OC can also be incorporated in deeper layers due to repeated deposition of
21 organic-rich alluvial material, or long-term deposition of OM in peats. Once buried, the
22 permafrost table acts as a barrier to leaching so that weathering products, OM and nutrients
23 accumulate (Gerzabek et al., 2004; Bockheim et al., 2006) and unfavourable conditions due
24 to soil freezing prevent decomposition of the OM. Preservation and protection of SOM is further
25 enhanced as the OM mixed into the lower mineral horizons is exposed to mineral interactions,
26 more reducing redox conditions, and also encasement in the permafrost. Organo-mineral
27 associations exist but do not control overall C storage, particularly when temperatures are
28 below 0°C.

1 A large proportion of the Cryosol OM is composed of detrital plant residues in different stages
2 of decomposition, including cell wall components and remnants. They account for 50-57 % of
3 OC in organic horizons, 35-49 % of OC in B horizons and 49-77 % of OC in the upper
4 permafrost horizons (Michaelson et al., 2004). Intense cryoturbation moves fresh less-altered
5 OM in deeper parts of the soil, resulting in a relatively homogeneous chemical composition of
6 free and occluded particulate and mineral-associated OM (Mueller et al., 2015). Specifically,
7 OM at the top of the boundary of permafrost is a repository for chemically labile, easy-to-
8 decompose OM (Ernakovich et al., 2015 and references therein), consisting mainly of
9 carbohydrate-rich particulate OM (Mueller et al., 2015).

10 Frozen conditions and cryopedogenic processes, such as cryoturbation, have slowed
11 decomposition and enhanced the sequestration of OC in permafrost-affected soils over
12 millennial timescales (Ping et al., 2015). As these materials are easily decomposed under
13 warmer conditions, climate change that affects the temperature and moisture conditions of
14 Cryosols is considered to lead to higher release of OC through increased decomposition rates,
15 as the thickness of the active layer increases (Beer, 2008). As pointed out also by Ping et al.
16 (2015) the susceptibility of the OM for degradation after warming/thawing depends on the
17 genesis and past history of SOM before incorporation into permafrost and the resulting intrinsic
18 relative degradation state. Recent work shows that Cryosols show the formation of organo-
19 mineral associations as well as microaggregation, similar to soils of temperate regions, which
20 may attenuate the response of these soils to temperature increase and thawing (Mueller et al.,
21 2018; Gentsch et al., 2015; 2018). Here both the association with phyllosilicates may become
22 relevant as well as the interaction with iron oxides (Mueller et al., 2018), which makes the OM
23 storage also susceptible to redox changes (Herndon et al., 2017).

24 Considering the present situation with respect to climate change, it seems reasonable to
25 consider that permafrost layers near the surface will melt. This implies strong changes with
26 respect to soil (an)aerobic conditions, drainage and thus also a shift in the pedogenic
27 environment affecting OM accumulation and storage.

3.2 Soils with limited development (Cambisols)

Classification and occurrence of Cambisols

Cambisols (most of them belonging to the Inceptisols in the US Soil Taxonomy, but note that the Inceptisols also include many Gleysoils, Stagnosols and Umbrisols) combine soils with at least an incipient subsoil formation. They have a fully developed A horizon but with less OC accumulation than the Chernozems, Kastanozems, Phaeozems, and Umbrisols. They mainly occur in temperate and boreal regions, but are also found in dry regions. They cover limited areas in tropical and subtropical humid regions (IUSS Working Group WRB, 2015).

Pedogenic processes in Cambisols

Transformation of parent material is evident from structure formation and mostly brownish discoloration, increasing clay percentage, and/or carbonate removal. The soils show medium to fine textures developed from a variety of different parent materials (IUSS Working Group WRB, 2015). Thus Cambisols span a wide variety of soil properties with respect to pH, composition of clay-sized minerals and cation exchange capacity, but no single dominant pedogenic process drives the development of these soils (Smith et al., 2011; Table 1). As a result, also SOM accumulation in these soils may show considerable variation at different scales (Batjes, 1996; Wiesmeier et al., 2019)

Organic matter accumulation and composition in Cambisols

Accumulation of OM occurs mainly in the Ah horizon and is due to formation of organo-mineral associations as well as aggregate formation, in the presence of 2:1 layer clay minerals (Table 2). Nevertheless, this type of SOM accumulation mechanism is not diagnostic for Cambisols as it occurs, e.g., in almost all temperate soils with similar mineral composition and Ah horizon development. In general, we resume that Cambisols do not show specific SOM formation mechanisms due to pedogenic processes other than those occurring in the Ah horizon. However, due to their limited soil development and associated predominance of medium activity clays, the OM in Cambisols shows comparably young radiocarbon data in the subsoil (Table 3b). This reflects the limited formation of reactive surfaces in the Bw horizon and

1 particularly in the deeper subsoil. Therefore, Cambisols often have only a low proportion of
2 their OM accumulation in the subsoil (Wiesmeier et al., 2015). It is thus largely the low subsoil
3 C contribution that differentiates the amount of SOC stored in Cambisols from that in older soil
4 groups. But as Cambisols cover large areas, they store high amounts of OM compared with
5 less abundant other Reference Soil Groups (Table 4).

6 Major differences in the amount and composition of SOM is found between Eutric and Dystric
7 Cambisols. This is mainly due to pH and the presence of bivalent cations. Acid pH values
8 increase the reactivity of oxides for anion adsorption in Dystric Cambisols. Hence, low pH
9 values may inhibit rapid mineralization and transformation of SOM. Indeed, Soucemarianadin
10 et al. (2019) report that particulate OM in Eutric Cambisols is more decomposed than in Dystric
11 Cambisols under forest in France. They also found that the OM in the topsoil of Eutric
12 Cambisols was more oxidized. However, they also found that the SOM was more stable
13 compared to the OM in Dystric Cambisol topsoils, attributed to the presence of bivalent cations,
14 in particular stabilization through Ca-mediated processes. Regarding SOM composition,
15 however, this differentiation likely needs to be expanded to biome: dystric Cambisols, for
16 instance, are frequently associated with gymnosperm forests, providing OM rich in tannins,
17 waxes and lignins, and of different composition than OM derived from angiosperm plants, for
18 instance, that would naturally prefer Eutric Cambisols beside other soil groups. In summary,
19 Cambisols need to be differentiated according to their clay content, mineral types, pH
20 (Soucemarianadin et al., 2018) and vegetation cover, as these may control OC accumulation.

21 22 3.3 Soils of temperate climate

23 3.3.1 Podzols

24 *Classification and occurrence of Podzols*

25 Podzols (Spodosols in the US Soil Taxonomy) usually developed on parent materials
26 producing permeable sandy to loamy sand texture with low contents of Fe and low base
27 saturation and under a vegetation, which produces a slowly degrading, nutrient-poor litter. It
28 forms an organic litter above a thin A and an underlying eluvial (E) horizon that is bleached

and has pH values typically between 2.5 and 4.5. Below the E horizon, illuvial (B) horizons are formed, which typically accumulate OM, Fe, Mn and Al (Table 1). Quartz is the dominating mineral in all horizons. The few clay minerals remaining typically consist of pedogenically transformed minerals like illite or secondary chlorites.

Podzols cover 485 million hectares worldwide (Table 4). The occurrence of Podzols is correlated with that of its parent material and potential natural vegetation. Well-developed profiles are mainly found in cool and semi-humid to humid climates, particularly in the boreal zone, such as in Scandinavia, Russia and Canada. However, Podzols are also found in high mountain regions such as the lower Rocky Mountains or Appalachian Mountains (USA), the Alps or the Himalayan region (Sauer et al., 2007).

Pedogenic processes in Podzols

The low pH value in the A and E horizons facilitates the dissolution of primary silicates and clay minerals, resulting in a release of Al, Fe and Si. This process is promoted by the production of water-soluble acids and other chelating agents in the litter layer. These elements and the mobile OM are then transported into the subsoil, leading to the formation of an illuvial B horizon (Table 1) with humic materials (Bh) or oxides (Bs) or both (Bhs, Bsh). Left behind is an ash-colored E horizon with bleached quartz grains and depleted in OM. The illuvial B horizon is internationally designated as 'spodic' horizon and diagnostic for Podzols in the WRB and Spodosols in the US Soil Taxonomy.

There are different theories about the mobilization and translocation mechanisms involved in the podzolisation process and thus, the related formation of SOM (see, e.g., Sauer et al., 2007, for a review):

- Formation of water-soluble chelates between the DOM and Fe, Al and Si ions
- Reduction of Fe and migration in reduced metal-organic complexes
- Colloidal transport of Fe, Al and Si.

Several other processes then favour the re-immobilization and stabilization of OM and oxides in the spodic horizon, such as precipitation and flocculation at increased pH, filtering in small

pores (e.g., in layered substrates), degradation of the organic complex partner, or as a second step, re-adsorption on subsoil oxide coatings.

Organic matter accumulation and composition in Podzols

The SOM found in Podzols is prone to different and specific stabilization mechanisms in the different soil horizons. The organic surface layers (Oi-Oe-Oa) and specifically the E horizon generally account for only a limited proportion of the total OC stocks in Podzols (Grand and Lavkulich, 2011). In the organic surface layers as well as in well-depleted E horizons, it is likely the refractory nature of the organic compounds, the unfavourable low pH value and Al toxicity (in the E horizon) rather than organo-mineral interactions that contribute to the preservation of SOM. Lignins, tannins, and particularly aliphatic waxes as well as branched alkyl-moieties are decomposed less rapidly than other compounds such as structural carbohydrates (Kögel et al., 1988, Ziegler et al., 1986; Kögel-Knabner and Hatcher, 1989). Thus, in the E horizon a residual accumulation of partly degraded plant and specifically root residues is observed (Beudert et al., 1989).

Despite the predominance of sand, and unlike in the E horizon, OM in the B horizons is associated to a large extent with the fine fraction, underlining the strong mineral control for SOM retention in the subsoil of Podzols, and similarly also in acid Cambisols (Eusterhues et al., 2005a). In contrast to other soil groups, the OM composition in the subsoil spodic horizon is mainly derived from the organic surface layer due to pronounced leaching processes (Table 2), and, although partly microbially processed shows a high similarity in composition (Rothstein et al., 2018) and a comparably young radiocarbon age (Table 3a, b). In the spodic horizons, the OM may coat the mineral surfaces (Amelung et al., 2002a), while the general concept of aggregate hierarchy may not apply in these acid, sandy soils (Table 2). Investigation of pore-waters from different Podzol horizons provide support for the main mechanism of OC accumulation in Podzols being the downward movement of colloids (organic, OC-sorbed mineral and organo-mineral), followed by colloid immobilization due to a combination of increases in pH and metal/C ratio. The occurrence of these three types of colloidal structures in pore waters seemed to depend on the pH and the relative supply of OC and Fe + Al to pore

waters (Bazilevskaya et al., 2018). The lignins and phenols are degraded, but carbohydrates may be stabilized by penetration into or interactions with the Fe-rich microaggregates (Schmidt et al., 2000; Eusterhues et al., 2005a, b; Mikutta et al., 2006; Eusterhues et al., 2011; Table 2).

Podzols belong in a group of soils where, due to the illuviation process, the biogeochemical surfaces in the subsoil may be more reactive than those in the surface soil, even clustering to stable microaggregates, whereas the E horizon is usually not aggregated. Cornelis et al. (2018) found that the associations between Fe oxides and OM involve aggregate formation and not only mere adsorption of organic compounds by inorganic phases or pore filling and point to the importance of soil structure in the spodic horizon for OC stabilization.

Because Al and Fe translocation to the illuvial horizons are highly dynamic processes, OM binding and stabilization may not be the same for all Podzols but may fluctuate depending on the individual soil (Grand and Lavkulich, 2011), its pedoclimatic environment and associated redox conditions (Vermeire et al., 2019). The specific Podzol-forming processes also imply that high contents of DOM (between 115-500 kg m⁻²; representing 35% of annual litterfall) may be lost from the surface soils, leached to the groundwater or stored in the mineral subsoil (between 19-52% of total C; Kalbitz and Kaiser, 2008). The specific feature of Podzols is that the accumulation of OM in Podzols is thus due to the concerted occurrence of a thick organic surface layer and a spodic B horizon, where most of the OM is stored.

3.3.2 Luvisols

Classification and occurrence of Luvisols

Luvisols develop from a variety of unconsolidated materials, such as glacial till, or eolian, alluvial and colluvial deposits (IUSS Working Group WRB, 2015), rich in base cations such as K. They occur mostly in humid temperate climates on flat or gently sloping land. Luvisols are typically classified as Alfisols in the Soil Taxonomy. The argic B horizon has a cation exchange capacity > 24 cmol_c kg⁻¹ soil (Table 1). The proportion of swelling clays usually increases towards the drier ends of the climatic zones at which Luvisols are found. They are among the

fertile soils of temperate regions that are mainly used for crop production in Europe and the US, and thus they have experienced tillage operations for long time scales (Driessen et al., 2001; Jagercikova et al., 2016). Most of the information regarding OM formation and turnover in temperate soils comes from these soils, i.e., most of the general mechanisms discussed above for SOM storage and turnover have been developed and tested for Luvisols (Fig. 1), but the information is mostly restricted to the (often ploughed) A horizon (Torres-Sallan et al., 2018).

Pedogenic processes in Luvisols

The characteristic soil-forming process is the translocation of clay minerals (usually together with Fe oxides and OM) from the topsoil to the subsoil, leaving an eluvial topsoil E and forming an illuvial Bt horizon (argic horizon) in the subsoil (Table 1). The pH values are slightly acidic, but usually not reaching pH values below 5, which would release sufficient amounts of Al^{3+} into solution to flocculate the clay particles. The typical minerals in the clay fraction of Luvisols are a mixture of non-swelling (illite) and swelling clay-minerals (smectite, vermiculite and mixtures) and low to moderate iron oxide contents (Fernandez-Ugalde et al., 2013), all of these constituents being effective in stabilizing OM (Table 2).

Organic matter accumulation and composition in Luvisols

Co-migration of OM with fine minerals (lessivage) leads to the accumulation of substantial amounts of OM in the argic Bt horizon, but also bioturbation contributes to the transfer of OM into the subsoil, whereas solute transport is negligible (Jagercikova et al., 2016). The OM transfer to the subsoil in Luvisols is in a medium range compared to other soils with OM translocation (Podzols) and turbation (Vertisols), as shown in Table 3b. Generally the OM in the subsoil shows a reduced exchange with the atmosphere, as reported for Alfisols in Table 3a. From a Luvisol C3-C4 long-term experiment John et al. (2005) report turnover times of 54 y (0-30cm), over 144 y (30-45 cm) to 223 y (45-60 cm).

In accordance with the comparably high content of clay minerals, most of the OC content in Luvisols is associated with the fine mineral fraction (Flessa et al., 2008; Jagercikova et al., 2016). Under agricultural use, the surface soil, usually silty in texture, is low in particulate OM,

1 indicating a depletion in OM return to the soil. For Luvisols in Germany, John et al. (2005)
2 found more than 85% of the OC were mineral-associated in Luvisol topsoils under agriculture,
3 but around 50 % under forest, where the proportion of particulate OM is higher. Hence,
4 improved aggregate stability and elevated OC accrual has thus been frequently reported for
5 Luvisols under no-till agriculture and OM additions in both field and lab experiments (Six et al.,
6 2000, 2004; Gulde et al., 2008). With increasing OC saturation at mineral surfaces, additional
7 OM is stored mainly as particulate OM (Six et al., 2002; Gulde et al., 2008, Schweizer et al.,
8 2019), from where it is also more easily lost, e.g., as under fallow (Meyer et al., 2017). It is the
9 bioaccessibility of OM that determines its fate in these soils with strong aggregation, rather
10 than their biological recalcitrance (John et al., 2005; Marschner et al., 2008; Schmidt et al.,
11 2011). This is not specific for Luvisols, but it has been shown most often for this Reference
12 Soil Group.

13 The argic horizon has a strong stable blocky structure. The surfaces of aggregates are usually
14 darker in color, due to OM adsorption at the illuviated clay minerals (and also higher in chroma
15 due to the association of Fe oxides). Hence, sorptive preservation and thus likely also C
16 saturations mechanisms largely contribute also to the storage of subsoil OM. Scanning
17 transmission X-ray microscopy confirmed that cation bridging by Ca^{2+} was the primary
18 mechanism for carboxyl associations with soil aggregate surfaces, which was enhanced upon
19 wetting-drying cycles (Olshansky et al., 2018). Research by Torres-Sallan et al. (2017) shows
20 that most of the stable OC in soils with clay illuviation is located at depths below 30 cm, as
21 42% of subsoil OC in the Luvisols they investigated was located in microaggregates and silt
22 and clay, compared to 16% in the topsoil.

23 Anecic earthworms are considered to be the main actors for bioturbation producing vertical
24 movement of particles and OM in Luvisols (Jagercikova et al., 2014). Bioturbation leads to litter
25 incorporation into deeper layers, but also deposits of deep horizon matter at the surface in the
26 form of casts. The walls of earthworm burrows are coated with clay-organic material with
27 specific bio-physicochemical properties (wettability, hydraulic conductivity, cation exchange
28 capacity) that differ from that of the soil matrix (Leue et al., 2019). Although biopore abundance

1 in such soils hardly exceeds 5% of the surface area, the faeces itself and thus the pore linings
2 are enriched in OM and nutrients (Kautz et al., 2013; Athmann et al., 2017). Due to ploughing,
3 the abundance of these biopores is usually larger in the subsoil than in the surface. According
4 to Leue et al. (2016) biopores were enriched with labile aliphatic moieties and lignin, whereas
5 OM covered cracks showed increasing inputs also from combustion-derived OM.

6 These pore linings lead to a heterogeneous distribution of OC and nutrients on a micro scale
7 (Chabbi et al., 2009). Although bioturbation introduces material from the A-horizon into a
8 subsoil poor in OC and thus contributes to the accumulation of OC in the subsoil, it does not
9 homogenize the soil. Even OC depth gradients remain with earthworm activity. Organic matter
10 in Luvisols is thus heterogeneously distributed between, but also within soil horizons, with hot
11 spots being concentrated within aggregates, on aggregate surfaces and in biopores.

12 3.3.3 *Phaeozems, Chernozems, Kastanozems*

13 *Classification and occurrence of Phaeozems, Chernozems, and Kastanozems*

14 Phaeozems, Chernozems, and Kastanozems (all Mollisols in the US Soil Taxonomy; the
15 Chernozems commonly equated with black earths) are characterized by the diagnostic mollic
16 horizon for Phaeozems and Kastanozems and the chernic horizon (a special case of the mollic
17 horizon with stronger criteria) for Chernozems. Many of them developed on aeolian and
18 carbonaceous sediments, mostly loess. As a result, they are dominated by high activity, 2:1
19 clay minerals, contributing to a high cation exchange capacity. The texture is silty to loamy, the
20 base saturation ranges between 50-100%. Phaeozems have no secondary carbonates (unless
21 at greater depths) but Chernozems and Kastanozems have them, starting within 50 cm below
22 the lower limit of the A horizon. In the Kastanozems, they may even start in the surface soil.
23 The secondary carbonate precipitates at mineral surfaces ('soft powdery lime') or within soil
24 pores ('pseudomycelia', 'white eyes', 'loess kindl'). In both Phaeozems and Chernozems, the
25 very surface soil is mostly free of carbonates, and pH values may be slightly acidic. The three
26 Reference Soil Groups thus separate according to their climatic occurrence, with the
27 Phaeozems being allocated at the wetter and the Kastanozems at the drier edges. Many of
28 them occur in grassland ecosystems, called prairie (N America), pampa (S America), and

steppe (Eurasia). However, some of them are also found under forest vegetation, Chernozems in Russia, e.g., in the forest-steppe.

Pedogenic processes in Phaeozems, Chernozems, and Kastanozems

These soils are characterized by a high degree of biological soil mixing, i.e. bioturbation. As in these soils even larger animals like hamster and gopher are involved, it does not only lead to the formation of OM-rich soil aggregates in the surface soil, but also of so-called krotovinas (animal burrows) in the lower surface soil and subsoil, and altogether of the incorporation of OM into thick black A horizons (Driessen et al., 2001). In its classical case, this dark A horizon is then underlain directly by the parent, calcareous loess (Table 1). The thicknesses of the A horizons vary from 25 - 40 cm in Central Europe and some sites in the US, to > 70 cm in some sites in Russia, and to > 300 cm at certain sites in the Manchurian steppe in China (Rodionov et al., 2010), partly reflecting new A horizon formations within older A horizon materials. These variations in soil depth give support to the hypothesis that other processes than decalcification and bioturbation (Table 1, 2) contributed to soil formation, such as wildfires or slash-and burn agriculture, charcoal amendments, erosion and colluvium formation (see, e.g., Eckmeier et al., 2007; Acksel et al., 2017; Rodionov et al., 2010; for a review, see Gerlach et al. 2012). Also the lack of homogenized radiocarbon ages in the surface soil (Table 3a), as it would have been expected from sole biogenic mixing, support the idea that bioturbation alone may not explain the occurrence of thick dark A horizons (Scharpenseel et al., 1986).

Organic matter accumulation and composition in soils with a mollic/chernic A horizon

The dark color of the mollic horizon and the even black color of the chernic horizon has attracted the geochemical community in the last years, since there is increasing evidence that it correlates with the occurrence of pyrogenic carbon (e.g., Schmidt et al., 2002; Eckmeier et al., 2007; Rodionov et al., 2010). Incomplete biomass burning leaves char and soot behind, its “black carbon” forms may explain the widespread aromatic nature of SOM (Haumaier and Zech, 1995; Schmidt et al., 2002; Ponomarenko and Anderson, 2001). Glaser and Amelung (2003) suggested that there might be a positive feedback-loop: the high fertility of the Chernozems goes along with a high biomass production, which then leaves high amounts of

black carbon behind after vegetation fires, which are common in steppe environments. Eckmeier et al. (2007) outlined that also human-made fires, e.g., as used in early slash-and-burn agriculture, contribute to the origin and formation of OM in these soil groups.

Due to the high fertility of these soils, plant productivity and thus also belowground C input is high. Feng and Simpson (2007) thus traced significant amounts of root-derived suberin in the subsoil horizons of a Chernozem in Alberta. Root-derived C inputs in turn foster microbial activity and microbially-mediated aggregate formation. Apart from aromatic and aliphatic C, Amelung et al. (1997) and Rodionov et al. (1999) thus also found elevated amounts of microbe-derived saccharides, stabilized in mineral fractions with increasingly humid climate, i.e., in the order Kastanozem < Chernozem < Phaeozem.

The composition of OM changes within different C pools. While clay-sized OM is frequently recalcitrant and beside saccharides (Rodionov et al., 1999, Amelung et al., 1999a) is particularly rich in alkyl structures (Baldock and Skjemstad, 2000; Pennock et al., 2011), lignin and plant-derived structures dominate the larger particle sizes (Amelung et al., 1999b; Rodionov et al., 1999; Baldock and Skjemstad, 2000). In the steppe soils, these structures accumulate at the surface of minerals (Amelung et al., 1999a, 2002a), are preserved well by encapsulation within aggregates (Elliott, 1986; Amelung and Zech, 1996; Six et al., 2000), but also by thin CaCO_3 -coatings (Pennock et al., 2011) that increasingly can be found also in the topsoil when moving from Chernozems to Kastanozems.

The formation of organo-mineral associations and aggregates in these soil groups is favoured by a) high abundance of reactive, mainly 2:1 clay minerals, including also reactive Fe oxides, b) high faunal and microbial activity, promoting biological aggregate formation, c) elevated base saturation with abundant bivalent cations, specifically Ca, that act as bridging agents between OM and clay or between clay minerals, d) cementing secondary carbonates in Chernozem and Kastanozem subsoils, and finally e) physical processes like freezing and thawing as well as drying and wetting cycles that are typical for the climate of the Chernozems (and to a lesser extent for Phaeozems and Kastanozems) (Sanborn and Pawluk, 1983; Pawluk, 1988; Pennock et al., 2011).

1 In summary, SOM found in Chernozems (and Kastanozems and Phaeozems) is prone to
2 stabilization by bio-mediated aggregate formation (Table 2). The SOM may thus be rich in
3 saccharides, which are primary binding agents in microaggregates, and which in Chernozems
4 may be preserved in preference to lignins (Cheshire, 1985; Amelung et al., 1997). A significant
5 proportion of the SOM originates from biomass burning. This black carbon is stable in soil and
6 may accumulate relative to other SOM constituents, so that the OM in mollic horizons is
7 comparably aromatic in nature.

8 9 3.4 Soils of the tropics and subtropics

10 3.4.1 Acrisols

11 *Classification and occurrence of Acrisols*

12 Acrisols are low activity clay soils, similar to Lixisols, which the Reference Soil Group classifies
13 as soils with an accumulation of low activity clays in an argic B horizon. The Acrisols have a
14 low base saturation level, which distinguishes them finally from the Lixisols (Table 1). Acrisols
15 correlate with several subgroups of Alfisols and Ultisols (Soil Taxonomy). They form on old
16 landscapes with an undulating topography and a humid tropical climate and often support
17 forested areas. There are about 1 000 Mio ha. Acrisols world wide, similar to the size of Europe,
18 placing this soil at 3rd rank in regard to areal extension (Table 4), though occupying just under
19 8 percent of the continental land surface. Acrisols are mostly found throughout central and
20 northern Latin America, Southeast Asia, and West Africa.

21 *Pedogenic processes in Acrisols*

22 Formation of an argic illuviation horizon involves clay dispersion, clay transport, and clay
23 accumulation in a subsurface horizon, similar as in Luvisols. Yet, due to prevailing low pH
24 values and low activity clays, this clay translocation might not happen recently, i.e., some
25 researchers assign the formation of the argic horizon to a relict of past soil formation processes
26 (Driessen et al., 2001). At least, Acrisols have little weatherable minerals left. The clay fraction
27 consists almost entirely of kaolinite, some gibbsite, and a few Fe oxides. Hence, and unlike in

Luvisols, the presence of an argic horizon does not greatly enhance the overall subsoil OC storage.

Organic matter accumulation and composition in Acrisols

Strey et al. (2016) report that Acrisols under native vegetation stored only half the amount of OC as compared to regionally associated Ferralsols in central Brazil. The authors also observed that the effect of land-use types on OC content was consistently smaller than the impact of different pedogenic soil groups. Similarly, Podwojewski et al. (2011) found that OC storage in Acrisols in Vietnam was low compared to other soils in the same region. This finding is supposedly related to the low content of clay-sized minerals and the predominance of the low-activity clays (Telles et al., 2003; Quesada et al., 2020). The amount of dithionite extractable iron oxides and kaolinite in fine particle-size fractions <53 µm correlated with their OC content in Brazilian Acrisols (Bayer et al., 2006). Thus, organo-mineral associations are considered to be the major mechanism for OM accumulation in Brazilian Acrisols, in addition to black carbon which is also often found in these soils (Dieckow et al., 2005; Bayer et al., 2006). Yet, as levels of clay minerals and oxides in the top soil provide only few surfaces to stabilize OM against microbial degradation, Acrisols are usually relatively low in OM, remain poorly aggregated, and are prone to erosion.

3.4.2 Ferralsols

Classification and occurrence of Ferralsols

Ferralsols are the 'classical', deeply weathered, red or yellow soils found primarily in the humid tropics. These soils have diffuse horizon boundaries, a clay assemblage dominated by low activity clays (mainly kaolinite), and a high content of Fe and Al oxide minerals as diagnostic for a so-called ferralic horizon. An argic horizon is lacking. Internationally, Ferralsols are comparable to Oxisols (Soil Taxonomy, USA), Latossolos (Brazil), Sols ferrallitiques (France). Their parent material is strongly weathered material on old, stable geomorphic surfaces of Pleistocene age or older, whereas they are less common on younger, easily weathering rocks. Ferralsols are generally associated with perhumid or humid tropical conditions (Table 1), and

1 minor occurrences elsewhere are considered to be relics from past eras with humid tropical
2 climate. The worldwide extent of Ferralsols is estimated at some 750 million hectares, almost
3 exclusively in the humid tropics on the continental shields of South America (Brazil) and Africa
4 (Democratic Republic of the Congo, southern Central African Republic, Angola, Gabon and
5 eastern Madagascar) corresponding to ~7.5% of the global ice-free land area. Some of them
6 have been subject to shifting cultivation for millennia.

7 *Pedogenic processes in Ferralsols*

8 In Ferralsols deep and intensive weathering (usually to several meters depth) has resulted in
9 ferralitization, i.e. due to high soil temperatures and intense percolation all weatherable primary
10 minerals ultimately dissolved and were removed from the soil mass, whereas less soluble
11 compounds such as iron and aluminium oxides and hydroxides and coarse quartz grains
12 accumulated. As a consequence, quartz is the main primary mineral (if originally present in the
13 parent rock) in most Ferralsols and the clay composition is dominated by kaolinite, goethite,
14 hematite and gibbsite in varying amounts, depending on the type of parent rock and the
15 drainage conditions (Table 1). This mineral composition and the relatively low pH explain the
16 stable microstructure (pseudo-sand) and yellowish (goethite) or reddish (hematite) soil colours
17 typically observed in Ferralsols.

18 *Organic matter accumulation and composition in Ferralsols*

19 Ferralsols store OC to considerable depths. Strey et al. (2017) report that >87 % of the OC in
20 a Brazilian Ferralsol was stored below 30 cm, and around 45 % below 1 m depth. A soil C
21 inventory down to 8 m in a deeply weathered, forested clay soil of Eastern Amazonia (most
22 probably a Ferralsol) showed that the soil below 1 m depth contained more carbon than in 0-1
23 m depth, and as much as 15% of this deep-soil OC turned over on annual or decadal
24 timescales (Nepstad et al., 1994). Ferralsols are deeply rooted (Germon et al., 2020) and thus
25 OC is introduced by root exudation and necromass to several meter depth (Mathieu et al.,
26 2015), but shows a comparably young deep soil radiocarbon age due to the presence of low
27 activity clays (Table 3b).

1 The structure of Ferralsols is stabilized by both, oxides and OM. It is often considered that
2 Ferralsol structure is more stabilized by inorganic cementing agents (iron and aluminum
3 oxides) rather than OM (Oades and Waters, 1991). However, work by Dalmolin et al. (2006)
4 indicated that binding of organic compounds at the surface of mineral phases is a relevant
5 process in Ferralsols, and the accumulation of OM is enhanced by formation of organo-mineral
6 associations. Basile-Doelsch et al. (2009) have shown that OM stabilization in Ferralsols
7 occurs to around 60 % through organo-mineral associations. In contrast, Shang and Tiessen
8 (1997, 1998) and Skjemstad et al. (2008) reported that protection within microaggregates is
9 the major mechanism for protection of OC in Oxisols. Baldock et al. (1992) pointed out that in
10 soils with dominating variable charge the interaction of OM with the mineral matrix may protect
11 it against microbial attack, retarding the mineralization of OM and affecting its chemical
12 composition as well, as observed in Ferralsols being dominated by both O-alkyl and alkyl
13 carbon. Polysaccharide-type OM associated with kaolinite (Wattel-Koekkoek et al., 2001) and
14 that from iron-rich Ferralsols in central Brazil (Neufeldt et al., 2002) seem to be preserved
15 mainly by a surface complexation between variable-charge minerals and OM.

16 In Ferralsols, as in Acrisols, rates of OC loss caused by cultivation are often considered many
17 times faster than those for soils of temperate regions, with a substantial deterioration in soil
18 quality often in less than 10 years (Shang and Tiessen, 1997). Thus proper OM management
19 is necessary for sustainable agriculture on these soils. Much of the potential OM loss is
20 particulate OM, recognizable as plant debris not protected by aggregation (Shang and Tiessen,
21 1998, Vrdoljak and Sposito, 2002). In turn, most of the stabilized OM is found in organo-mineral
22 associations (Roscoe and Buurman, 2003), particularly in microaggregates (Sollins et al.,
23 1996), which show a modified form of aggregate re-formation and hierarchy (Vrdoljak and
24 Sposito, 2002). Skjemstad et al. (2008) found between 17.1 and 31 % of the total organic C in
25 an Australian Oxisol to be derived from C3 rainforest after cultivation under C4 pasture for 90
26 years. Therefore, Ferralsols may store OM for considerable periods of time under sustainable
27 management.

3.4.3 *Plinthosols*

Classification, occurrence and pedogenic processes in Plinthosols

A specific case, often within Ferralsol or Acrisol landscapes, are Plinthosols (Plinthic Great Groups in US Soil Taxonomy). These soils exhibit pronounced accrual of Fe, originating from upwelling groundwater and lateral transport within former unlevelled landscapes (Driessen et al., 2001). The plinthite layer (plinthic horizon) may be soft when moist and firm when dry, after many drying and wetting cycles (e.g. in eroding landscapes) finally developing into petroplinthite (laterite, petroplinthic horizon) that is better used for house construction than for agriculture.

Organic matter accumulation and composition in Plinthosols

As the strong accumulation of iron oxides is mostly in concretions and nodules or even crusts after drying, their capacity to bind OM is low. Thus Plinthosols often show lower OC stocks throughout the soil profile down to 1 m depth compared to Ferralsols or even Acrisols in the same region (Batjes and Dijkshoorn, 1999; Dos Santos et al., 2018).

As a result, losses of SOC with prolonged arable cropping were found to be unrelated to the amount of SOC associated to Fe oxides (Hounkpatin et al., 2018b). In the Dano catchment, Burkina Faso, Hounkpatin et al. (2018a) mapped SOC stocks in different Reference Soil Groups. The area was dominated by Plinthosols, which stored 41 t OC ha⁻¹ in their surface soils but up to 70 t ha⁻¹ in their subsoil. While the average magnitude of SOC storage was similar to that of Lixisols (soils similar to Acrisols but with higher base saturation), the overall range was much larger because Plinthosols are deeply weathered. If they have a plinthic horizon, penetrable to roots, the SOC storage exceeds > 1m. If they contain a petroplinthic horizon, impermeable to roots, the overall SOC sequestration may be restricted to the upper 50 cm and OC is much lower (Hounkpatin et al., 2018a). Frequently, this distribution relates to aspect and other geographical features in the landscape. Nevertheless, the data confirm that soil depth is likely the key parameter that determines the overall storage of SOC in such soils, and all extrapolations from land-surface monitoring to deeper soil carbon storage will fail, if not accounting for root barriers in these soils, and so likely also in other Reference Soil Groups,

particularly those in arid or semiarid climates like Leptosols, Durisols, Calcisols and Gypsisols, which have not been explicitly considered here.

3.4.4 Nitisols

Classification and occurrence of Nitisols

Another important soil group frequently associated with Ferralsols and Acrisols are Nitisols. In the Soil Taxonomy, Nitisols belong to Ustox and Udox and to the kandic great groups and subgroups of Alfisols and Ultisols. This soil group accommodates well-drained reddish (occasionally yellowish) soils of the tropics with diffuse horizon boundaries and a subsoil with at least 30% clay (Table 1). This so-called nitic horizon does not only consist of kaolinite, also 2:1 clay minerals may be present to some degree (Quesada et al., 2011). They show at least 4% Fe in the dithionite-bicarbonate extract. This mineral composition promotes the formation of a strong blocky structure, which, however, easily falls apart into shiny polyhedral, flat-edged or nutty structures. The Nitisols are intensively weathered; however, they are usually much more productive than the above-mentioned Acrisols, Ferralsols, and Plinthosols.

Pedogenic processes in Nitisols

The formation of Nitisols includes three major soil-forming processes (IUSS Working Group WRB, 2015; De Wispelaere et al., 2015): a) Ferralitization, similar to what is observed in Ferralsols but usually much less advanced; b) Nitidization, i.e., the formation of blocky aggregates that break into shiny microstructures, likely as a result of microswelling and -shrinking due to the remaining amounts of expandable clays, as well as due to exceptionally small Fe oxide particles, and c) homogenization by ants and termites, creating diffuse horizon boundaries.

Organic matter accumulation and properties in Nitisols

In many Nitisols, OM storage may exceed that of the Ferralsols (Batjes, 1996). Organic matter-rich Nitisols and Ferralsols are classified with the Humic qualifier. Due to the low pH value, this OM may be tightly bound to both the oxidic phases as well as the phyllosilicates in the nitic horizon of the subsoil, which, however, is still prone to losses upon long-term cultivation

practice (Hernandez-Jimenez et al., 2017). Apart from sorptive preservation, largely the stable aggregates protect the OM in these soils from decay (Chevallier et al., 2011). Ashagrie et al. (2005) reported that converting mixed natural forest into Eucalyptus plantations after 21 years resulted in significant losses of sand-sized, particulate OM, while OC and N concentrations in aggregates were hardly if at all affected. Apart from actual OC stocks, also the OC storage capacity of Nitisols appears, thus, to be larger than that of Plinthosols, Acrisols and Ferralsols, though data for these Reference Soil Groups are limited so that direct soil-specific comparisons remain speculative.

3.5. Soils developed from specific parent material

Other than the soils described so far, some soil groups are restricted to the occurrence of specific parent material, such as more or less pure sands (Arenosols), materials with swelling and shrinking clays (Vertisols), or volcanic glasses (Andosols). In Arenosols, due to the lack of sorption sites, there are few if any effective OM stabilization mechanisms (Table 2). The respective OM contents are thus also low (Batjes, 1996), and largely dependent on vegetation inputs. In addition, OM is largely preserved because of drought (IUSS Working Group WRB, 2015). Arenosols (usually Psamments in US Soil Taxonomy) are thus not discussed here in detail, despite their significant areal extension (Table 4) and agroecological significance in, e.g., the savannah. Specific processes, however, are responsible for SOM storage in Andosols and Vertisols as outlined below.

3.5.1 Vertisols

Classification, occurrence and pedogenic processes in Vertisols

Vertisols are soils rich in clay minerals (> 30%), primarily of smectites, to allow heavy swelling and shrinking dynamics (IUSS Working Group WRB, 2015, Soil Survey Staff, 2014). During dry periods, horizontal shrinking opens cracks (which may be some centimetres wide) and vertical shrinking lowers the soil surface. Swelling in the humid periods closes the cracks but the soil uplifts in unequal. The repeated swelling and shrinking therefore results in a landscape with microhighs and microlows, which is called gilgai relief. The microhighs usually dry out

more rapidly, are prone to accumulate calcium carbonates and show less profile development. The microlows, in turn, are usually moister, darker in colour, richer in OM and pedogenic oxides and show more pronounced carbonate dissolution at greater depth (Nordt et al., 2004). The result is a strong turbation of the whole soil profile (peloturbation), bringing former subsoil to the top while burying former topsoil at greater depth (Table 1). The turbation creates wedge-shaped aggregates and slickensides in the subsoil, which are diagnostic for the vertic horizon. The repeated crack formation turns the very soil surface into a mulch-like coverage with granular or crumb structure (self-mulching). During dry periods, topsoil material, including SOM, is falling into cracks (self-ploughing), thereby facilitating C accrual in the subsoils. Vertisols usually develop on clay-rich sediments but may also be formed by in-situ weathering of mafic rocks like basalt. Nevertheless, the occurrence of Vertisols is restricted to specific climatic conditions. There must be sufficient rainfall to enable swelling and a dry period to enable shrinking, while together supporting weathering of silicates and crystallization of clay minerals. Smectites are the first secondary minerals to form, along with the high abundance of esp. Ca^{2+} , particularly in semi-arid to sub-humid tropics. Water percolation is usually restricted due to the low permeability of the clays in wet state. The pH is relatively high and may be above neutral.

Organic matter accumulation and properties in Vertisols

Peloturbation and self-ploughing repeatedly brings SOM from surface soil into deeper soil layers leading to a deep incorporation of OM from the surface as indicated by radiocarbon analyses (Mathieu et al., 2015). The average radiocarbon ages found for Vertisol profiles (Table 3a,b; Khitrov et al., 2018) are relatively young and do not exceed 4500 years within the top 1 m. In accordance with these data, and different to other soils the composition of SOM hardly changes with Vertisol depth (Leinweber et al., 1999).

As other soils rich in smectite, Vertisols have been reported to exhibit higher OM levels compared to soils dominated by kaolinite (Ngole and Ekosse, 2009). The higher level of OM in Vertisols is not only promoted by cracks and peloturbation (Table 1, 2), but likely by intensive associations with high-activity clays (smectite) (Feller et al., 2001), which are preserved under

the oxygen-limited conditions intermittently occurring in these soils and are thus likely better pronounced than related associations with kaolinite. It has been shown in several experiments that OC adsorption capacity is higher for smectite than for other clay minerals (Jones and Singh, 2014, and references therein). In turn, these organo-mineral interactions found for smectite are more stable than for kaolinite or illite (Saidy et al., 2012; Singh et al., 2017). It is therefore often assumed that Vertisols provide a high OC storage capacity (e.g., Chevallier et al., 2004; Hua et al. 2014; Singh et al., 2018). In contrast, a number of direct soil investigations report comparably low OC contents in Vertisols (Ristori et al., 1992; Coulombe et al., 1996), and specifically in their organo-mineral fractions (Jones and Singh, 2014; Yeasmin et al., 2017; Coulombe et al., 1996; Wattel-Koekkoeck et al., 2001). Winkler et al. (2016) and Houtermans et al. (2017) observed lower SOC stocks in Vertisols compared with Alisols and Andosols on Java, despite high contents of clay. Traoré et al. (2020) found a high OC saturation deficit in Vertisols from Burkina Faso and attributed this to a limited input of organic residues under the typical climatic regime of Vertisols, which does not allow to exploit the storage capacity of the clay fraction, but which is also intensified by prescribed fire and soil erosion effects.

Sorptive preservation of OM at the clay-mineral surfaces is likely the dominating mechanism of SOM storage, apart from the mere preservation at limited oxygen supply. Certainly, significant amounts of OM may also be stored within the stable aggregates of the structured soil (Chevallier et al., 2011), as indicated by labelled fresh OM being rapidly incorporated into water-stable aggregates (Bravo-Garza et al., 2010). But, using microtomography and micromorphological approaches, Sorokin et al. (2016) showed that Vertisol aggregates showed a virtual absence of humus-clay plasma in the centre of the aggregates. Leinweber et al. (1999) reported a generally low extractability of SOM, which was dominated by alkyl moieties in ^{13}C NMR spectra, thus confirming earlier observations by Skjemstad and Dalal (1987) and Atanassova et al. (2017), who explained the large water repellency in a Vertisol with the predominance of aliphatic compounds. In addition, Leinweber et al. (1999) detected elevated amounts of peptides, heterocyclic N forms, and carbohydrates relative to other soil orders, mainly ascribed to a microbial origin.

3.5.2 Andosols

Classification, occurrence and pedogenic processes in Andosols

Andosols in WRB (Andisols in US Soil Taxonomy) have distinctive physical, chemical and mineralogical properties that are not found in most other soil groups (Table 1). Vitric Andosols, Silandic Andosols and Aluandic Andosols are distinguished. Vitric Andosols cover small areas, have relatively little accumulation of OM and are not further discussed here. The others have andic properties, which are defined by a low bulk density, high amounts of Al and Fe, extractable in acid oxalate, and a high phosphate retention. All Silandic Andosols and many Aluandic Andosols are formed from volcanic ejecta (ejecta < 2 mm are called 'ashes'), which contain a high percentage of glasses. Rapid chemical weathering of the glasses leads to the formation of a colloidal fraction dominated by short-range order and poorly crystalline constituents and/or by OM associated with Al and Fe. Aluandic Andosols may also develop from glass-free parent materials. Aluandic Andosols have many associations of OM with Al (and Fe), while Silandic Andosols contain allophanes and imogolites that show large surfaces with variable charge. In addition, both have a lot of ferrihydrite. These specific properties allow a high water-holding capacity, thixotropy and the accumulation of large amounts of OM. Soils with andic properties occur in all climatic regimes and cover about 110 million ha (Table 4), which is nearly 1% of the world land surface (Dahlgren et al., 2004), but contain about 5 % of the total OM stored in soils (Eswaran et al., 1993).

Organic matter accumulation and composition in Andosols

Due to the high productivity of Andosols (especially Silandic Andosols), there is typically a large annual OM input via above-ground and below-ground plant litter as well as root exudates. Andosols have the highest OC contents among the mineral soils and thus play an important role in the global C cycle. Radiocarbon age of OM in Andosols is high (Table 3b), and reported mean residence times for OM in Andosols are considerably higher than in other soil taxa, such as Chernozems or Cambisols (Inoue und Higashi, 1988; Nierop et al., 2005; Aran et al., 2001; Tonneijck et al., 2006; Kleber et al., 2005). High rainfall, high primary productivity, and the dominance of highly reactive, short-range-order minerals combine to sequester substantial

1 stocks of soil OC with long mean residence times (Marin-Spiotta et al., 2011). This also implies
2 that Andosols preserve OM originating from previous land cover for a long time as
3 demonstrated by Dümig et al. (2009). In addition, stabilization of OM in Andosols often occurs
4 by burial of the topsoil due to repeated addition of fresh volcanic ejecta. Due to the possible
5 preservation of OM components from earlier vegetation and land-use, knowledge of vegetation
6 cover and its changes in the past is more important than in other soil groups to interpret SOM
7 composition.

8 The degree of weathering and type of minerals formed (short-range order versus well
9 crystalline crystalline), associated with altitude, precipitation and soil depth, seems to be the
10 main factor controlling OM accumulation (Taboada et al., 2019). The capacity for stabilizing
11 OC via organo-mineral interactions is high in Andosols (Table 2), due to the high specific
12 surface area of their short-range order mineral material, specifically allophane, imogolite, or
13 ferrihydrite (Candra et al., 2019). The different mechanisms to explain high OM storage and
14 long OM residence times in soils containing poorly crystalline aluminosilicate phases are (1)
15 strong ligand exchange type bonds combined with large specific surface areas, (2) formation
16 of specific microaggregates (Asano and Wagai, 2014), so that a significant fraction of OM in
17 Andosols is inaccessible to decomposing organisms (Dahlgren et al., 2004, Tonneijck et al.,
18 2010), and (3) direct effects of Al^{3+} on microorganisms or enzymes (Kögel-Knabner and Kleber,
19 2011). Accumulation of OC is therefore related to concentrations of noncrystalline materials,
20 as was shown for soils formed from basaltic lava in Hawaii (Torn et al., 1997) and for allophanic
21 Andosols on La Reunion (Basile-Doelsch et al., 2005). But metal-OM complexes with
22 multivalent cations (Al^{3+} , Fe^{3+}) also play a major role for C sequestration in Andosols,
23 specifically in nonallophanic Andosols (Tonneijck et al., 2010). In a nonallophanic Andosol
24 the minerals form aggregated nano-sized domains, most probably agglomerated nano-sized
25 $\text{Al}_x(\text{H}_2\text{O})_y(\text{OH})_z$ clusters. These extended micropores are combined with a mesopore network,
26 and form the unique physico-chemical properties of such Andosols (Filimonova et al, 2011).
27 Hawaiian Andosols rich in short-range order minerals showed evidence of significant transport
28 of C, Al, and Fe down the soil profile, promoted by the formation of channels and microfractures

(Marin-Spiotta et al., 2011). Here, the accumulation of OM in the subsoils is due to preferential flow of organically rich solutes and/or colloids moving C to depth where C, Fe and Al are preferentially deposited on crack surfaces. Inagaki et al. (2020) showed also for Hawaiian Andosols that associations with Al are more important than Fe for OM stabilization in Andosol subsoils under reducing climate conditions, associated with comparatively low contents of carboxylic acids and high alkyl/O-alkyl ratios.

Pyrolysis studies found no indication for the preservation of plant-derived OM, but high amounts of microbial polysaccharides and chitin point to a stabilization of secondary, microbial components in both allophanic and nonallophanic Andosols (Nierop et al., 2005; Buurman et al., 2007). Consistent with these results, the amount of lignin in Andosols is low, but high aromatic carbon contents are found in Andosols that have undergone vegetation fires (Dümig et al., 2009; Golchin et al., 1997a, b). In acidic non-allophanic Andosols an accumulation of aliphatic lipid-type materials is observed, probably due to toxic levels of Al^{3+} for microorganisms (Tonneijck et al., 2010). Recent work by Asano et al. (2018) and Wagai et al. (2018) shows that binding at higher aggregate hierarchy levels occurs by young OM, whereas the reactive metal phases bound microbially altered, N-rich, ^{14}C -depleted OM and functioned as persistent binding agent. All these mechanisms thus contribute to the persistence and therefore strong accumulation of OM in Andosols.

3.6 Soils with dominant human impact (Anthrosols)

Human have become a soil-forming factor, e.g., by promoting the formation of colluvisols (see Zadorova and Penizek, 2018 for a review), by deep ploughing and soil flipping, such as in vineyard soils, or by breaking the dense sod. Deep ploughing or flipping has been used to meliorate soils poor in nutrients and OM and is also a globally applied method for breaking up hard pans and improving soil structure to optimize crop growing conditions (Alcantara et al., 2016). It results in burial of SOC formed in surface soil horizons into deeper horizons and may increase overall SOC stocks of the whole soil profile and long-term OC preservation (Schiedung et al., 2019). Buried subsoil OC has higher apparent radiocarbon ages indicating

that it is largely isolated from exchange with atmospheric CO₂ (Alcantara et al., 2017). However, as deep ploughing or soil flipping requires heavy machinery and has excessive costs especially for fuel, these soils cover only a minor part of the global land surface. Here, we review Anthrosols that have specific pedogenic features in accumulation of OM (Table 1), cover larger areas and thus are of relevance for OC management within the global C cycle. Paddy soils are very common on Earth since paddy rice is currently a major staple food for more than half of the world population. Other famous examples are soils formed by historical impacts on soil fertility, such as Terra Preta or Terra Mulata soils and plaggen soils. In addition, there is ample evidence on human impacts on soils as found in archaeological excavations (Lauer et al., 2013, 2014) as well as on recent soils not reviewed here, like garden soils with a hortic horizon.

3.6.1 Paddy soils/Hydragric Anthrosols

Classification, occurrence and pedogenic processes in Hydragric Anthrosols

Paddy soils originate from terrestrial soils with different pedogenesis, but are highly modified by specific paddy management operations (Kögel-Knabner et al., 2010). These are artificial submergence and drainage, ploughing and puddling (= ploughing and levelling the surface layer of a submerged soil), organic manuring (animal manure, rice straw and other crop residues, often fermented with sediments taken from the river or channel), liming and fertilization. The flooding and drainage management leads to the development of pedogenic horizons that are specific for paddy soils. Paddy soils are thus classified as Hydragric Anthrosols (IUSS Working Group WRB, 2015) comprising an anthraquic horizon, underlain by a hydragric horizon. The anthraquic horizon consists of two layers, a loose puddled layer and an underlying dense plough pan. The hydragric horizon shows accumulation of Fe and Mn that intruded from the anthraquic horizon during times of flooding, when reducing conditions were active, and oxidized in the hydragric horizon.

Hydragric Anthrosols may originate from soils of different Reference Soil Groups. Still, initial soil properties defined by the parent soil material, most of all soil texture and contents and type

of Fe oxides, affect the evolution of paddy soils and therefore also OM accumulation (Winkler et al., 2016). It is thus important to record paddy soil formation history and, if the paddy soils developed on previously mature soil groups, also the original pedogenic origin.

Organic matter accumulation and composition in Hydragric Anthrosols

The formation of a dense plough pan as a typical feature of paddy soils plays a decisive role for the accumulation of OM in topsoils. The exchange of OM with subsoil horizons will be prohibited resulting in larger OC enrichment of topsoils but at the same time in decreased OC input to subsoils by roots and DOM. Much steeper gradients in OC concentrations in the soil profile in paddy than in non-paddy soils indicate such limited input of OC to subsoil horizons (Wissing et al., 2011, 2014). These specific features of OM distribution and accumulation in paddy soil profiles are confirmed by radiocarbon data (Braeuer et al., 2013; Prastowo et al., 2017).

Paddy soil management has a clear effect on the accumulation of OM. The OM storage in paddy soils exceeded OM storage in corresponding non-paddy soils (Kalbitz et al., 2013; Wissing et al., 2011; Wu, 2011; Shang et al., 2011). After land embankment, OC and N concentrations of the topsoils increased continuously with increased duration of paddy management; however, after 110 years a maximum was reached for N (Roth et al., 2011). Due to high silicon demand of rice plants, the cycling of silicon is a special feature in paddy soils. Phytoliths may play an important role for carbon stabilization (Nguyen et al., 2019), but it remains to be investigated whether OC trapped in phytoliths is available to microbial attack or not. OM accumulation in paddy soils also derives from higher input of plant residues than in respective non-paddy soils (Wissing et al., 2011), partly also in the form of charred residues, under intensive management. Paddy soil management is generally thought to promote the accumulation of aromatic compounds like lignin, because of the recalcitrance of its aromatic structure to biodegradation under anaerobic conditions (i.e., during inundation of paddy fields). However, work by Wissing et al. (2013) and Urbanski et al. (2017) showed that lignin and SOM accumulation are not necessarily linked. Lignin accumulation was not a key driving factor for SOM accumulation in paddy soils and may therefore not be considered relevant for the higher

1 OC sequestration in paddy soils as compared to non-flooded upland soils.

2 Rice straw burning has accompanied paddy management for millennia, introducing black
3 carbon into soil as the residue of incomplete combustion, specifically because paddy-soil
4 flooding might lead to a substantial accumulation of black carbon. Lehndorff et al. (2014, 2016)
5 found that paddy soils show a significant accumulation of C in charred forms in paddy soils,
6 which increased upon prolonged paddy management. However, the contribution of black
7 carbon to total SOC in paddy soils was similar to that in other, aerobic soils. In paddy soils
8 developed from different soil taxa, black carbon storage was controlled by specific pedogenic
9 properties such as soil texture, dense plough layers, and cementation by Fe oxides.

10 The management of paddy soils further creates an environment of Fe oxide formation different
11 to those in non-paddy soils (Cheng et al., 2009; Kölbl et al., 2014). Paddy soils are dominated
12 by poorly crystalline Fe oxides and significantly lower content of crystalline Fe oxides, in
13 contrast to adjacent non-paddy soils, which are characterized by high proportions of crystalline
14 Fe oxides (Wissing et al., 2013). Wissing et al. (2011) found that a reduced crystallisation of
15 Fe oxides is accompanied by higher proportions of stabilized OM in paddy soils. The higher
16 accumulation of OC in paddy soils seems to be a result of OC association with Fe oxides and
17 – in turn – may hamper the crystallisation of oxalate-extractable Fe oxides. Changes in paddy
18 soil management associated with redox cycle changes will therefore not only affect Fe oxide
19 composition of paddy soils but most probably also OC storage potential (Huang et al., 2019).

20 The cycling of DOC in paddy soils is intimately linked to Fe cycling. Oscillation in redox
21 conditions may enhance retention and stabilization of DOM by minerals such as Fe
22 oxyhydroxides (Winkler et al. 2019). The presence of important amounts of labile residue-
23 derived OC in correspondence with field flooding may result in a positive feedback on the
24 abiotic release of soil-derived DOC by promoting the microbially-driven reductive dissolution
25 of Fe (hydr)oxides present in the soil. The typically high DOC concentrations observed in paddy
26 soils ($>10\text{--}20\text{ mg l}^{-1}$) are strongly linked to the reducing conditions resulting from field flooding.

27 Vertical fluxes of DOC together with the enhanced mobility of Fe^{2+} under reducing conditions,
28 affect OC inputs and accumulation in the subsoil (Said-Pullicino et al., 2016).

1 In summary, the large accumulation of OM observed in some, but not all paddy soils, is
2 considered to be due to high input of plant residues. A specific feature of paddy soils is the
3 coupling of OM turnover with mineral transformations and fluxes, which seem to be intensified
4 by the alternating redox conditions with increasing age of paddy soil development. Stabilization
5 of SOM is ascribed to occlusion into aggregates and phytoliths and specifically to interactions
6 with clay minerals and iron oxides. Organic matter accumulation in paddy subsoils occurs by
7 (limited) downward movement of DOM and its stabilisation by interaction with iron oxides.
8 There is no evidence for a selective accumulation of aromatic C (black carbon, lignin) due to
9 flooding and anaerobic conditions.

10 3.6.2 Terra Preta/Pretic Anthrosols

11 *Classification, occurrence and pedogenic processes in Pretic Anthrosols*

12 Another important Anthrosol that is distributed widely throughout Amazonia and gained
13 increasing attraction in the last years is the so-called “Amazon Black Earth” or Terra Preta do
14 Indio. This soil occurs in patches of <1 ha to 350 ha and has been formed by the indigenous
15 pre-Columbian population about 500-8700 years ago (Smith, 1999; Neves et al., 2003; Liang
16 et al., 2006). Surprisingly, these patches sustained a productivity that even today by far
17 exceeds that of the surrounding Ferralsols. Hence, this soil is preferred by local farmers for the
18 production of nutrient-demanding crops (Woods and McCann, 1999).

19 The typical Terra Preta is characterized by a dark thick A horizon, usually 70 cm deep but
20 occasionally even reaching 2 m (Woods and McCann, 1999; Smith 1980). This top layer is
21 enriched in OM, and, in contrast to the Ferralsols, has elevated contents of plant-available P
22 and Ca, a less acidic pH value and a high cation exchange capacity (Glaser et al., 2001;
23 Lehmann et al., 2003; Liang et al., 2006). Ceramic and lithic debris witness the anthropogenic
24 origin of these soils, though also related dark soils without these artifacts exist. In the WRB,
25 this topsoil forms the diagnostic pretic horizon, and the soils are classified as Pretic Anthrosols
26 (IUSS Working Group WRB, 2015). The rather brown than black soils are called Terra Mulata
27 and they usually encircle the darker Terra Preta sites. They show lower amounts of plant-
28 available P and Ca than Terra Preta but similar contents of OC (Woods and McCann, 1999;

Sombroek, 1966). For Latin America both soils have been conceptualized as Amazonian Dark Earths (Lehmann et al. 2003), but it has been suggested that similar soils probably also exist in other areas of the world, e.g., in Africa (Fairhead and Leach, 2009; Solomon et al., 2016).

Organic matter accumulation and composition in Pretic Anthrosols

As the parent material of the Terra Preta is similar to that of the surrounding soil, it is the addition of the specific type of OM and its resistance against decay that must be responsible for its sustainable productivity over the last centuries. The OM of the Terra Preta has a high proportion of aromatic C compounds (Zech et al., 1979), likely reflecting an input of charred OM (black carbon). Such black carbon particles are stable in soil, but its surfaces slowly oxidize or adsorb OM so that polar functional groups are nowadays found around the black carbon particles (Brodowski et al., 2005; Lehmann et al. 2005; Liang et al., 2006) These functional groups finally explain the large potential cation exchange capacity of the Terra Preta (Cheng et al., 2008). They do not yet explain the elevated contents of nutrient such as P and Ca. These are likely the result of the additional input of different kinds of wastes like ash, bones, excrements and compost (Birk et al. 2011; Glaser et al. 2007; Denevan, 1996, 2001; Schmidt and Heckenberger 2009).

In summary Terra Preta is one of the rare but prominent examples, how the addition and alteration of OM to (oxidic) soils may change their properties so dramatically that they turn into fertile soils for centuries. The high fertility is therewith related to a favourable constellation of several processes, such as the preservation of recalcitrant aromatic C forms in a tropical environment, the transformation of black carbon to particles with high cation exchange capacity, and the long-term increase of the soil pH and the associated mobilization of nutrients, the strong interactions of the added and transformed OM with Fe and Al oxides, and the addition of nutrients such as P and Ca with waste residues to a soil ecosystem that is usually P and Ca deficient.

3.6.3 Plaggen soils/Plaggic Anthrosols

Classification, occurrence and pedogenic processes of Plaggic Anthrosols

1 From roughly 1000 A.D. to the emergence of synthetic fertilizers in the early 20th century,
2 plaggen manuring systems were a dominant form of agriculture in northwestern continental
3 Europe, particularly in Germany, Belgium and The Netherlands. Evidence of plaggen-type
4 agriculture has been found in a wider geographic region, ranging from Greenland, Ireland and
5 Scotland to Norway, Russia, and China (Conry, 1971; He et al., 2002; Hubbe et al., 2007;
6 Donaldson et al., 2009; Buckland et al., 2009; Giani et al., 2014; Schnepel et al., 2014).
7 Plaggen agriculture was used to fertilize nutrient poor sandy soils (e.g., Podzols, Cambisols
8 and Alisols) with the aim of improving the quality of arable lands nearby the farms, resulting in
9 an increased productivity. In continental Europe, mostly heath or grassland sods were used
10 for plaggen manuring. Sods consist of grassy, herbaceous, or dwarf-shrub vegetation, its root
11 mats and soil material sticking to them (IUSS Working Group WRB, 2015). Forest litter and
12 peat material were also used as plaggen material (Pape, 1970; Conry, 1971). Sods were used
13 in cowsheds and sheepfolds as bedding and then applied to the surrounding fields as manure
14 (Blume and Leinweber, 2004; Simpson et al., 1998). The source areas remained degraded.
15 Plaggic Anthrosols (IUSS Working Group WRB, 2015; in German Plaggenesch) are
16 characterized by a humiferous anthropogenic horizon, which in Germany is known as “Esch”
17 and in WRB as plaggic horizon. In the beginning of the plaggen agriculture the amendments
18 were mixed into the soil by ploughing. With increasing time of plaggen agriculture, the plaggic
19 horizon grows in thickness and only the upper part of the plaggic horizon is continuously mixed
20 by ploughing. Continuous addition of sods with time produced a dark OM-rich plaggic horizon
21 of up to 1 m or more (Conry, 1971; Bokhorst et. al., 2005; IUSS Working Group WRB, 2015).
22 The resulting Plaggic Anthrosols are a dominant soil unit in northwestern continental Europe
23 that contains large percentages of OM over considerable depths (Pape, 1970; Blume and
24 Leinweber, 2004). The OC contents of plaggic horizons are variable, but generally higher than
25 in soils with similar texture in the same region without plaggen history (Springob and
26 Kirchmann, 2002; Schulp and Veldkamp, 2008). Therefore, Plaggic Anthrosols represent a
27 relic of historical farming demonstrating the potential for the enrichment of soils with OM. Since
28 the emergence of synthetic fertilizers in the early 20th century and abandonment of traditional

1 plaggen agriculture, most Plaggic Anthrosols have been subjected to conventional agriculture
2 but retain high OC contents.

3 *Organic matter accumulation and composition in Plaggic Anthrosols*

4 Springob et al. (2001) suggested that high background levels of stable OM inherited from the
5 plaggen management were the best explanation for the high OC contents of these soils, with
6 72% – 95% of the total OC being stable and refractory OM (Springob and Kirchmann, 2002).
7 The main constituents of organic residues from heath are fats and waxes with lesser
8 contribution of carbohydrate structures. Plaggic Anthrosols have large proportions of lipids,
9 fatty acids, alkylaromatics and sterols and low contributions of carbohydrates and peptides
10 (Blume and Leinweber, 2004; Sleutel et al., 2008). However, recent findings from biomarker
11 analyses, which provide evidence on the sources of Plaggic Anthrosol amendments (Kirkels
12 et al., 2013), suggested that the use of heath sods as animal bedding was most likely
13 introduced very late in the development of Plaggic Anthrosols (van Mourik et al., 2016). The
14 negligible percentages of *Calluna* in biomarker spectra of plaggenic deposits (n-alkanes), with
15 the exception of the upper part of the plaggenic horizon, suggest an overestimation of the use of
16 heath sods in the traditional interpretation of the genesis of plaggenic horizons (van Mourik et al.,
17 2016) and thus also question the concept of recalcitrant inherited OM.

18 Plaggen agriculture further might have resulted in additional input of charcoal into the soils due
19 to periodical burning of heathlands (Sedlakova und Chytry, 1999; van Mourik et al., 2016) or
20 by admixing of household charred residues with the animal beddings (Simpson et al., 1998;
21 Hubbe et al., 2007). Charcoal residues are found in many descriptions for plaggenic horizons
22 (e.g., Pape, 1970) and may also contribute to the sustained high levels of OC in plaggenic soils.
23 Plaggic Anthrosols have OC contents between 23 – 51 mg g⁻¹ and sandy reference soils
24 between 7 and 15 mg g⁻¹ in northern Germany (Springob and Kirchmann, 2002), despite their
25 clay content (< 2 µm) was similar (1% – 6%). Little information is available concerning the soil
26 mineral composition of Plaggic Anthrosols and its implications for SOM stabilization.
27 Especially, data on phyllosilicates, which might be important for OC accumulation, are not
28 available. Sleutel et al. (2008) concluded that OM adsorption to phyllosilicates seems to be a

relevant protection mechanism for OM in Plaggic Anthrosols. Beside phyllosilicates, some Plaggic Anthrosols have considerable proportions of Fe (hydr)oxides with high amounts (up to 70% – 100%) of short-range ordered Fe oxides (Giani et al., 2014). These high proportions of short-range ordered Fe oxides of the total pedogenic Fe oxides (Blume and Leinweber, 2004; Giani et al., 2014) hint to a high potential for OM stabilization.

In conclusion, Plaggic Anthrosols, formed by diverse inputs of OM, contain exceptionally high amounts of probably chemically resistant organic materials. Knowledge on the distribution of OC in the individual soil fractions and its specific chemical composition and OM mineralization is scarce. It is thus still not clear, why Plaggic Anthrosols have a stable humiferous plaggic horizon with a high level of OC accumulation, even though plaggen agriculture was terminated more than 100 years ago.

4 Synthesis: Organic matter accrual across Reference Soil Groups

Each of the selected Reference Soil Groups is subjected to different and specific pedogenic OM formation mechanisms in varying extent as summarized in Table 2. As a consequence, also the contribution of different major soil groups to the global OC stocks varies, which becomes evident when combining land area coverage given by IUSS Working Group WRB (2015) and mean SOC stocks for pristine soils obtained from Duarte-Guardia et al. (2019) to derive soil group-specific SOC stocks (Table 4). The data confirm that large amounts of OC for the first m are found in Cambisols, Cryosols and Podzols, due to the large land area they cover, followed by Acrisols and Ferralsols. These pedogenic OM formation mechanisms and their effects with respect to climate change are only considered for some soil groups (e.g., for Cryosols) in the current discussions on the role of soils in the global C cycle. Due to the continued adjustment of the WRB soil classification system, relevant information on Reference Soil Groups and their OC stocks, such as provided by Batjes (1996) or Hiederer and Köchy (2011) are not consistent any more with respect to most soil groups. Nonetheless some soil groups with specific pedogenic features such as Andosols, Vertisols or Arenosols have not been re-classified. In addition estimations of the areas covered by the Reference Soil Groups

are still vague. Consequently, our understanding on the OC state of soils and their changes has to rely on very rough estimates of soil changes (Chapter 6 in FAO and ITPS, 2015). There is first evidence that including pedogenic soil classes improves the identification of SOC stability factors (Soucemarianadin et al., 2018) and the prediction of OC stocks in topsoil, and specifically in the subsoil (Keyvanshokouhi et al., 2019; Mayer et al., 2019). Table 4 shows that the pedogenic soil groups considered here with a total of $1148 \cdot 10^{12}$ kg C account for about 80 % of the total SOC stocks for the first m if the estimate given by Scharlemann et al. (2014) with $1415.7 \cdot 10^{12}$ kg C is considered (or around 68 % if the estimate of a total amount of $1700 \cdot 10^{12}$ kg C from FAO and ITPS, 2015 is considered). In these estimations it has to be considered that the data we used here are for pristine soils and do not account for the SOC loss associated with cropping and grazing (Sander mann et al., 2017). As already described by Batjes (1996) large proportions of SOC are stored below 1 m, which requires consideration in relation to pedogenic OM formation mechanisms and specifically the translocation mechanisms as summarized in Table 2.

The mechanism of OM stabilization differ across major Reference Soil Groups. While sorptive preservation mechanisms occur more or less in all soil orders, though largely in those with larger portions of reactive clay minerals and oxides, physical protection mechanisms dominate in the steppe soils (Chernozems, Phaeozems, Kastanozems) as well as in Andosols, and are relevant also in Nitisols, Ferralsols, Cambisols, and Luvisols. Differentiation of mechanisms largely applies to the topsoils, where pedogenesis altered the composition and properties of soil minerals, and largely controlled OC inputs into the subsoils (Table 1, 2). As analysed by Mathieu et al. (2015) the age of topsoil OC was primarily affected by climate and cultivation. By contrast, the age of deep soil OC was affected more by soil taxa than by climate. For the subsoils, it was the amount rather than the reactivity of clays, which finally determined deviations of the ^{14}C content from that in the atmosphere and thus age of SOC, from Andosols with high amounts and high activity of clays to Podzols with low amounts and low activity of clays (Table 3b).

Our review shows that some soil groups are very well represented in our concepts on SOM

formation and turnover, whereas other soils receive only minor attention and data on amount and composition of OM are limited. This is especially relevant for soil groups that may store limited amounts of OC but cover large areas, i.e. Arenosols and Leptosols (Fig.1, Table 4). If we want to understand SOM formation and turnover, we need to consider all major soil groups and their specific pedogenic features relevant for OM accrual. Here the soil science community has a deliverable. Pedogenic differentiation proofs highly informative, as e.g. shown recently for guiding a global soil climate mitigation strategy (Amelung et al., 2020). Thus, the compilation here is a plea to use our soil knowledge more specifically to provide understanding and soil solutions to the pressing questions that are associated with soils and their OM.

Acknowledgements

We thank Peter Schad (Freising) and Sara Bauke (Bonn) for valuable discussions and information on the WRB soil classification system. IKK is indebted to Karsten Kalbitz (Dresden) for intense discussions on plaggen soils. We thank two anonymous reviewers who provided very constructive reviews and helped to improve the manuscript. We acknowledge financial support by the Deutsche Forschungsgemeinschaft within the framework of the research unit “MAD Soil - Microaggregates: Formation and turnover of the structural building blocks of soils” (DFG RU 2179) through project KO 1035/48-2 and AM 134/25-2. Wulf Amelung additionally acknowledges support from the Deutsche Forschungsgemeinschaft under Germany's Excellence Strategy, EXC-2070–390732324–PhenoRob

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Fig. 1: Data base hits for joint search of the key words “soil organic matter and Podzols” or with any other major Reference Soil Group according to IUSS Working Group WRB (2015), using the literature search program SciFinder Scholar (www.scifinder.cas.org; March 14, 2020; blue bars). The red lines represent the contribution of each soil group to total land area, as given in IUSS Working Group WRB (2015; Annex 1 - Description, distribution, use and management of Reference Soil Groups). The Figure illustrates the frequency of organic matter research for a given soil group. It is not designed to give a full honest overview, because the search did neither include the key-words soil organic carbon, nor any soil group as translated to other classification systems.

Fig. 1

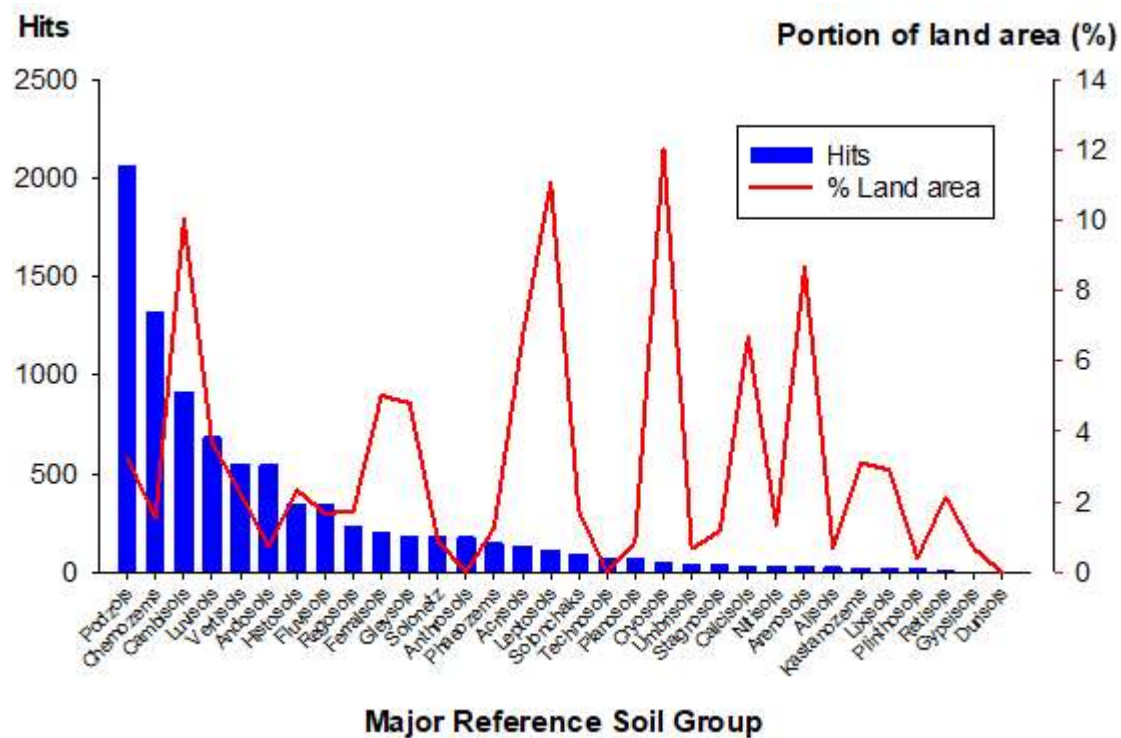


Table 1: Occurrence, diagnostic horizons and typical mineral, chemical and physical characteristics as relevant for soil organic matter accumulation in selected WRB Reference Soil Groups, horizon designations according to FAO Guidelines

Reference Soil Group +Horizons	Major geographic occurrence	Diagnostic horizon	Texture	Mineral components	Chemical properties	Physical properties	Recent formation of pedogenic oxides and clay minerals	Diagnostic pedogenic process
Permafrost soils								
Cryosols Ah-Bw@-Cf	Permafrost regions (e.g., Russia, Alaska, Canada, China)	Cryic horizon	Variable	May contain rock fragments; 2:1 clay minerals	pH 5-7	Heterogeneous, permafrost	Slow	Cryoturbation
Soils with limited development								
Cambisols A-Bw-C	Temperate midlatitudes, young alluvial plains and eroded sites, even in the (sub)tropics	Cambic horizon	Variable	Primary minerals and 2:1 clay minerals	pH 3-6	Young soils, weak to strong subangular blocky structure	Yes	Fe oxide and clay mineral formation
Soils of temperate climate								
Podzols A-E-Bhs-C	Temperate midlatitudes and oceanic boreal regions (Scandinavia, Russia, Canada)	Spodic horizon	Sandy	Quartz, Fe oxides, 2:1:1 clay minerals	pH 3-4, Al toxicity	More developed soils, single grain structure	Not in topsoil (destruction of clay minerals)	Podzolisation
Luvisols A-E-Bt-C	Temperate midlatitudes	Argic horizon with	Silty (topsoil),	2:1 clay minerals	pH 5-6 P available	Subangular blocky in E and	Yes	Clay migration

Vertisols A-Bi-C	Lower landscape positions, clay pans, basalt plateaus (with humid and dry seasons)	Vertic horizon	Clayey	2:1 clay minerals (in places: 1:1 clay minerals); $\geq$ 30% clay	pH 6-8	Cracks; hard when dry, sticky when wet; wedge-shaped aggregates in the subsoil	Yes	Peloturbation
Andosols Ah-C, Ah-B-C	Volcanic regions	vitric or andic properties	Variable	X-ray amorphous minerals (allophane, imogolite, ferrihydrite), 2:1, 2:1:1 and 1:1 clay minerals	pH 4-5	Well-drained, granular structure	Yes, especially X-ray amorphous minerals	Rapid chemical weathering with subsequent mineral formation with the released Fe^{2+} , Si^{4+} and Al^{3+}
Soils with dominant human impact (Anthrosols)								
Paddy soils Alp-Ardp-Bg-Cg	SE Asia, Madagascar	Anthraquic over hydragric horizon	Loamy to clayey	1:1 and 2:1 clay minerals	pH 5-7	Massive when wet, cracks when dry	Yes, with seasonal dynamics	Puddling and formation of Ardp and Bg horizons
Terra Preta Ah-Bo-C	S America	Pretic horizon	Clayey	1:1 clay minerals (kaolinite)	pH 5-6	Well-drained, thick A horizon, strong microstructure (pseudosand, -silt) in the B horizon	Rather not	Ancient additions of P- and black carbon-rich organic materials, aggregate formation
Plaggen soils Ah-Bhs-(Bw-)C	NW Europe	Plaggic horizon	Sandy	Quartz	pH 4-6, high P saturation	Well-drained	Limited	High humus accumulation

* CEC: = cation exchange capacity; BS = base saturation.

Table 2. Conceptualization of the mechanisms of soil organic carbon stabilization in selected Reference Soil Groups

OC-related pedogenic process	Cryosol	Cambisol	Podzol	Luvisol	Chernozem	Acrisol, Lixisol	Ferralsol	Nitisol	Vertisol	Andosol
Sorptive stabilization										
• 2:1 clay minerals	+	++	+	++	++	++	++	++	++	+++
• 1:1 clay minerals	+-	++	-	++	++	+	-	+	+++	?
• Allophanes and imogolites	-	-	-	-	-	+	++	++	+-	+
• Fe oxides and various Al species	+-	+	+	+	+-	++	+++	++	+-	++
Aggregate protection										
• Aggregate hierarchy	+-	++	-+ (very few)	++	+++	+-	++	++	+	+++
• Cementing by carbonates	-	-	-	+	++ (subsoil)	-	-	-	+	-
• Cementing by Fe- oxides	-	-	+	+	+-	+	++	+++	-	-
Subsoil OM translocation/burial										
• Bioturbation	-	-	++	+	++	+	+++	++	+++	+++
• Peloturbation	-	-	-	+	+++	+	++	+	-	?
• Cryoturbation	+++	-	-	-	-	-	-	-	+++	-
• Clay illuvation	-	-	++	++	-	+	not recent	not recent	-	-
• DOM translocation	++	-	++	+	-	+	+	+	-	++?

Table 3a: Average regression, correlation factor and corresponding AMRT (apparent mean residence time, y) levels for different depths of soil profiles from layer-dated soil profiles (from Scharpenseel et al., 1989)

Soil order*	Ascent of regression line Correlation factor	Corresponding AMRT of regression line (BC)					
		10 cm	20 cm	50 cm	100 cm	150 cm	200 cm
Alfisols	0.4651 0.739	480	960	2400	4800	7200	9600
Inceptisols (Plaggepts)	0.0225 0.209	870	920	1000	1160	1350	1490
Mollisols	0.4695 0.888	750	1240	2700	5150	8050	10000
Spodosols	0.0747 0.332	1350	1430	1680	2100	2520	2930
Vertisols	0.4014 0.772	0	410	1620	3650	5670	7700
All soils	0.4415 0.755	460	920	2300	4600	6900	9200

13 Alfisols, 16 Inceptisols (most Plaggepts), 47 Mollisols, 9 Spodosols, 44 Vertisols. Soil profiles were sampled in Europe, Australia, Israel, Sudan and Argentina

* Soil orders according to Soil Taxonomy given by Scharpenseel et al. (1989) refer mainly to the following WRB RSGs: Luvisols, Lixisols (Alfisols), Cambisols (Inceptisols), Plaggic Anthrosols (Plaggepts), Chernozems (Mollisols), Podzols (Spodosols), Vertisols (Vertisols)

Table 3b: Deep soil ^{14}C activity (which is a function of the age of carbon) for different soil types according to soil type and deep soil mineral phase (from Mathieu et al., 2015)

Reference Soil Group	Amount of clay	Type of clay	Deep soil $\Delta^{14}\text{C}$ (‰)
Andosol	High	Very high activity	-539
Nitisol	High	Low activity	-380
Vertisol	High	High activity	-330
Chernozem	Medium	High activity	-281
Ferralsol	Medium to high	Low activity	-190
Luvisol	Medium to high	Medium activity	-175
Cambisol	Low	Medium activity	-28
Podzol	Very low	Low activity	-1

Table 4: Estimation of the contribution of the Reference Soil Groups (RSGs) to the global soil OC stocks in 1m depth. Land area coverage of RSGs from IUSS Working Group WRB (2015; Annex 1 - Description, distribution, use and management of Reference Soil Groups), mean OC stocks for pristine soils from Duarte-Guardia et al. (2019).

Reference Soil Group	Land area M ha	Mean OC stock kg OC m ⁻² and 1m	Global soil-group specific OC stocks kg 10 ¹²
Chernozems	230	8.14	18.72
Phaeozems	190	12.7	24.13
Kastanozems	465	8.43	39.20
Cambisols	1500	23.09	346.36
Luvisols	550	7.73	42.52
Lixisols	435	8.58	37.32
Acrisols	1000	11.58	115.80
Ferralsols	750	11.12	84.30
Podzols	485	23.59	114.41
Cryosols	1800	15.73	283.14
Andosols	110	19.07	20.98
Vertisols	335	7.56	21.11
	Σ7850		Σ1148.10
Arenosols	1300	n.a.	
Alisols	100	n.a.	
Nitisols	200	n.a.	
Anthrosols	0.5#	n.a.	
Calcisols	1000	n.a.	
Durisols	n.a.	n.a.	
Fluvisols	250	n.a.	
Gypsisols	100	n.a.	
Leptosols	1655	n.a.	
Plinthosols	60	n.a.	
Regosols	260	n.a.	
Retisols	320	n.a.	
Umbrisols	100	n.a.	
Technosols	n.a.	n.a.	
	Σ5245.5		
Gleysols	720	n.c.	
Histosols	350 (325-375)	n.c.	
Planosols	130	n.c.	
Solonchaks	260	n.c.	
Solonetz	135	n.c.	
Stagnosols	175 (150-200)	n.c.	
	Σ 1770		

- n.a. no data available, i.e., research needed to conceptualize and understand the SOC stabilization mechanisms and storage potentials
- n.c. not considered in the present review
- # not clear if paddy soils are included

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Supporting information

The manuscript is based on the information given in the references cited in the manuscript. As this is not a meta-analysis, there is no data set that is evaluated and requires to be reported.