

Deep soil organic matter—a key but poorly understood component of terrestrial C cycle

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Abstract Despite their low carbon (C) content, most subsoil horizons contribute to more than half of the total soil C stocks, and therefore need to be considered in the global C cycle. Until recently, the properties and dynamics of C in deep soils was largely ignored. The aim of this review is to synthesize literature concerning the sources, composition, mechanisms of stabilisation and destabilization of soil organic matter (SOM) stored in subsoil horizons. Organic C input into subsoils occurs in dissolved form (DOC) following preferential flow pathways, as aboveground or root litter and exudates along root channels and/or through bioturbation. The relative importance of these inputs for subsoil C distribution and dynamics still needs to be evaluated. Generally, C in deep soil horizons is characterized by high mean residence times of up to several thousand years. With few exceptions, the carbon-to-nitrogen (C/N) ratio is decreasing with soil depth, while the stable C and N isotope ratios of SOM are increasing, indicating that organic matter (OM) in deep soil

horizons is highly processed. Several studies suggest that SOM in subsoils is enriched in microbial-derived C compounds and depleted in energy-rich plant material compared to topsoil SOM. However, the chemical composition of SOM in subsoils is soil-type specific and greatly influenced by pedological processes. Interaction with the mineral phase, in particular amorphous iron (Fe) and aluminum (Al) oxides was reported to be the main stabilization mechanism in acid and near neutral soils. In addition, occlusion within soil aggregates has been identified to account for a great proportion of SOM preserved in subsoils. Laboratory studies have shown that the decomposition of subsoil C with high residence times could be stimulated by addition of labile C. Other mechanisms leading to destabilisation of SOM in subsoils include disruption of the physical structure and nutrient supply to soil microorganisms. One of the most important factors leading to protection of SOM in subsoils may be the spatial separation of SOM, microorganisms and extracellular enzyme activity possibly related to the heterogeneity of C input. As a result of the different processes, stabilized SOM in subsoils is horizontally stratified. In order to better understand deep SOM dynamics and to include them into soil C models, quantitative information about C fluxes resulting from C input, stabilization and destabilization processes at the field scale are necessary.

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Introduction

The soil is the largest active terrestrial reservoir in the global carbon cycle. The estimates of the organic C stocks in 0–100 cm depth in the world's soils range from 1,220 Pg (1 Pg=10¹⁵ g) (Sombroek et al. 1993) to about 1,550 Pg (Eswaran et al. 1993; Batjes 1996; Jobbagy and Jackson 2000). Recent studies suggest that the soils C pool may be even greater and could account for 2,000 Pg (Janzen 2005). These higher values may be mainly due to additional recent estimations of the C pool stored in boreal soils under permafrost conditions (Zimov et al. 2006; Tarnocai et al. 2009). Although routine soil surveys collect C stock data down to a depth of 1 m, scientists studying the composition and mechanisms of stabilisation of SOM have mainly focused on the A horizon with the highest SOM concentrations.

Organic matter stored in subsoil horizons below the A horizon has received increasing interest in recent years as high proportions of total C stored within the soil profile may be found in subsoil horizons despite low OM concentrations (Batjes 1996; Jobbagy and Jackson 2000). The proportion of SOM stored in the first meter of the world soils below 30 cm depth ranges between 63 and 46%, except for Podzoluvisols, where 30% of OC is stored below the first 30 cm (Batjes 1996). A recent study suggests that in the northern circumpolar permafrost region, at least 61% of the total soil C is stored below 30 cm depth (Tarnocai et al. 2009). Therefore, subsoil C may be even more important in terms of source or sink for CO₂ than topsoil C. Another property of subsoil C is its high radiocarbon age, which suggests that a high proportion of this C is stable at longer timescales (e.g. Scharpenseel et al. 1989; Paul et al. 1997). Subsoil horizons with low C concentrations may not yet be saturated in organic C. It has therefore been suggested that they may have the potential to sequester organic carbon for example through higher C input into subsoil by roots and DOC (Lorenz and Lal 2005). Recent work, however, suggested that increase of OM storage in subsoils may not be as straight forward, because subsoil C may become available to microbial decomposition following C input (e.g. Fontaine et al. 2007) and/or mechanical disruption (Xiang et al. 2008). It also has been found that subsoil C may respond to land-use and/or management change (Guo and Gifford 2002; Wright

et al. 2007; Follett et al. 2009). In the context of climate change and SOM as potential sink for atmospheric CO₂, it is important to understand what leads to sequestration of large amounts of old C below the A horizon. OM input into subsoil horizons occurs as root litter and root exudates, dissolved OM and/or bioturbation. The relative importance of these four sources may depend on climate, soil and vegetation types. In subsoil horizons, environmental conditions may be different from those in topsoil horizons, and OM storage may be driven by specific processes (von Lützow et al. 2006). For example, Fierer et al. (2003) observed that mineralisation of subsoil C may be much more sensitive to temperature change than those of topsoil C.

In the last 10 years, our understanding of subsoil C has made significant progress, despite the methodological problems encountered due to the low C concentrations. Scientists became aware of the importance of pedological functioning with regards to OM storage in subsoil. In this review, we would like to discuss these findings with regard to the following questions:

- Is there a stabilisation of specific compounds in subsoil horizons ?
- What are the mechanisms that lead to stabilisation of OM in subsoils ?
- To what extent does subsoil OM participate in C and N cycles ?

Sources of organic matter in subsoils

Four main sources of OM input into subsoils have been identified: plant roots and root exudates, dissolved organic matter and bioturbation. In addition there may be translocation of particulate organic matter and transport of clay-bound organic matter in certain soil types. The relative importance of these sources is dependent on climatic parameters, soil inherent processes as well as land-use. For example, high input of dissolved organic matter can be expected under humid climate conditions and when podzolisation is the main soil forming process. DOC transport was largely studied in temperate forest soils (Michalzik et al. 2001) and has been thought to be the main source of subsoil OM under such conditions (Kaiser and Guggenberger 2000). The sharp decrease

of DOC concentrations with depth of mineral soil observed by many authors was explained by strong retention in the mineral soil due to adsorption (Qualls and Haines 1992; Kaiser and Zech 1997). DOC fluxes in the mineral subsoil were reported to range between 10 and 200 kg ha⁻¹ yr⁻¹. These fluxes were not controlled by carbon storage, precipitation, C/N ratio or pH (Michalzik et al. 2001). Recently it was reported, that harvesting management (Strahm et al. 2009) as well as land-use could influence these fluxes and thus subsoil C pools. The process of DOC movement and retention within the mineral soil was found to be responsible for 20% of the total mineral soil C stock to 1 m depth in a forest soil and 9% in a prairie soil (Sanderman and Amundson 2008).

Another important source of subsoil OM are plant roots. These were found to affect the placement of C in soil. In a global review of root distributions, grasses had the shallowest root profiles, trees were intermediate and shrubs had the deepest profiles (Jackson et al. 1996). Specific allocation patterns through vegetation types were also found to govern vertical SOC distribution (Jobbagy and Jackson 2000). The importance of roots for soil C sequestration was underlined by the fact that they have a high potential to be stabilized in soil (Rasse et al. 2006). Despite their importance as a subsoil C source, root C flux to soil are poorly understood mainly due to uncertainties associated with the measurement of total root C input, in particular from root exudation and root cell sloughing. Root litter production can be estimated from root turnover. Root turnover can be measured directly using observation of roots from birth to disappearance with microrhizotrons (Kleja et al. 2008). However, minirhizotrons are only able to estimate the most dynamic roots (<1 mm) and not roots with larger diameter (>1 mm) for which isotope techniques as ¹⁴C and ¹³C may be more suitable (Majdi and Andersson 2005). Depending on the method the longevity of roots was found in the order of 1–18 years (Kleja et al. 2008; Gaudinsky et al. 2001). Using the microrhizontron technique root C input in the mineral soil was estimated 73 to 78 gC m⁻² yr⁻¹ for a northern hardwood forest (Kleja et al. 2008). At this site DOC input ranged between 11 and 26% of the total carbon input. However, considering root litter and DOC decomposition rates, the authors estimated DOC and roots equally important for SOM buildup in soil.

Physical carbon transport down the soil profile as colloidal Fe/Al-humus complexes is an important process increasing SOM of volcanic subsoils (Osher et al. 2003). In Alisols, Luvisols, Acrisols and Lixisols (FAO taxonomy), SOM input into subsoils may occur as organomineral complexes. These complexes were found to be enriched in labile compounds stabilized against decomposition (Schmidt et al. 2000). Particulate organic matter such like black carbon seems to migrate easily into deeper soil horizons (Dai et al. 2005; Rumpel et al. 2009) and could constitute an important input of chemically recalcitrant C into subsoil horizons of fire affected ecosystems. Migration of particles can be enhanced by bioturbation.

Earthworms, termites, ants, arthropods and tree roots are efficient in burying soil while forming voids in the form of burrows, nests, chambers, galleries and root channels (Paton et al. 1995; Lavelle et al. 1997). These “biofabrics” indicate that biotic activity declines non-linearly with depth with notable differences between horizons (Humphreys 1994). Data on biological activity with depth was summarized by Ekschmitt et al. (2008) and reveal that the abundance of organisms in subsoils does not generally follow vertical SOC distribution. Bioturbation affects directly as well as indirectly inputs of SOC in subsoils (Wilkinson et al. 2009). Direct inputs include litter sequestration into nests, termitaria, borrows etc and bioturbator waste disposal in form of dead tissues. Indirect inputs of SOC into subsoils may occur by infilling of biogenic pits with litter, redistribution of SOC and subsurface mixing and burial. Biologically-mediated soil burial rates range between 1–2 m My⁻¹.

Several sources for C input into subsoils have been identified. The relative importance of these inputs has rarely been studied. Data from different climatic regions are necessary to elucidate completely the controls on the different inputs. The importance of biological SOM burial and mixing in subsoil horizons is an important factor that needs to be considered in future studies.

Nature of SOM in subsoils

Mean residence time and SOM turnover

The radiocarbon age of SOM is usually increasing with soil depth, and carbon present in the subsoil horizons is characterized by a low ¹⁴C activity

(Scharpenseel et al. 1989; Paul et al. 1997; Krull and Skjemstad 2003; Eusterhues et al. 2003). Mean radiocarbon ages of subsoils of different soil types are presented in Table 1. In 1-m depth the radiocarbon age of all studied soil types exceeds 1,000 years. The reasons for the increase of the ^{14}C age of SOM with depth are not completely understood (Trumbore 2009). High ^{14}C age of SOM may indicate that stabilized carbon compounds with long residence times are found in subsoil horizons at higher concentrations. However, recycling of old, stabilized SOM in subsoils through microbial biomass may also lead to old ^{14}C age of chemically labile, newly synthesized carbon compounds (Rethemeyer et al. 2005). Thus, old ^{14}C age of subsoil OM may also be observed as a result of continuous microbial recycling of labile material (Gleixner et al. 2002). For SOM in subsoils, it must additionally be considered that the ^{14}C activity may be influenced by the contribution of substrate inherent geogenic carbon, which is usually carbon dead (= older than 50,000 years), not showing ^{14}C activity. This may be the case for soils developed from sedimentary parent substrates, such as loess. The small amounts of carbon associated with loess deposits represent a small proportion of SOC in surface horizons, but could be significant at depth (Paul et al. 2001; Helfrich et al. 2007). Therefore the very old radiocarbon age of some soils may simply be due to dilution of geogenic (rock-derived) dead carbon with younger SOM. However, even for SOM in soils developed from parent substrate free of geogenic C (e.g. granite), radiocarbon ages of several thousand years have been reported (e.g. Eusterhues et al. 2003). Further indication for low turnover of

subsoil carbon was derived from stable carbon isotope analysis on sites, where a C3 vegetation was replaced by a C4 vegetation. At a site, where a forest dominated by C3 vegetation was replaced by corn (C4 species) monoculture in the United States, incorporation of C4 carbon reached 4–15% in 50–100 cm depth after 30 years (Collins et al. 1999). This corresponds to mean residence times of 100 to 700 years. In an agricultural soil in France, 10 years of continuous corn after wheat monoculture resulted in 10, 5 and 2% corn derived SOC at 15, 50 and 100 cm depth, respectively (Rasse et al. 2006).

Elemental and isotopic composition of subsoil OM

Generally, the SOM content and its C/N ratio are decreasing rapidly below the A horizon. Low C/N ratios have been attributed to highly processed SOM. In most subsoils, C/N ratio is approaching that of microbes (Wallander et al. 2003). In subsoils, which are generally characterized by a very low organic matter content, high nitrogen content may be related to the presence of mineral nitrogen sorbed to clay surfaces. Mineral nitrogen was found to contribute to about 20% to the total nitrogen of deep soil horizons and even when subtracted, C/N ratios of most soils are decreasing with depth (Jenkinson et al. 2008; Krull and Skjemstad 2003). An increase in C/N with depth in some soils may be explained by the presence of charred material (Dümig et al. 2009).

The stable isotope ratios $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are generally increasing with depth and degree of decomposition in soils without vegetation change (Balesdent and Balabane 1996; Balesdent et al. 1993; Nadelhoffer and Frey 1988). Several factors may be responsible for a ^{13}C enrichment of subsoil SOM: (a) increasing atmospheric $^{13}\text{CO}_2$ due to fossil fuel burning (the so-called Suess effect) may account for a 1.5% increase since 1800 (Leavitt and Long 1988); (b) it may be ascribed to a preferential stabilization of ^{13}C enriched compounds, such as polysaccharides and amino acids and the preferential decomposition of ^{13}C depleted compounds, such as lipids and lignin. In some cases, mainly under C4 grassland a decrease of $\delta^{13}\text{C}$ with depth was recorded (Volkhoff and Cerri 1987; Martin et al. 1990; Gill and Burke 1999; Krull et al. 2005; Dümig et al. 2008). This may be explained by the accumulation of ^{13}C depleted charred material, as C4 grasslands are prone

Table 1 Mean radiocarbon ages (years B.P.) for different depths and soil types sampled in Europe, Australia, Israel, Tunisia, Sudan and Argentina (data from Scharpenseel and Becker-Heidmann, 1998)

| Soil type | n | 20 cm Year B.P. | 50 cm | 100 cm |
|------------|----|--------------------|-------|--------|
| Alfisol | 13 | 960 | 2,400 | 4,800 |
| Inceptisol | 16 | 920 | 1,000 | 1,160 |
| Mollisol | 47 | 1,240 | 2,700 | 5,150 |
| Spodosol | 9 | 1,430 | 1,680 | 2,100 |
| Vertisol | 44 | 410 | 1,620 | 3,650 |

to disturbance by fire. Finally, isotopic fractionation during microbial respiration was thought to be another mechanism leading to ^{13}C enrichment. Van Dam et al. (1997) reported ^{13}C enrichment of 3% due to microbial respiration. Recently, it was suggested, that this mechanism does not contribute to ^{13}C enrichment of SOM with increasing depth (Boström et al. 2007). Instead, Boström et al. (2007) hypothesized that the increase of $\delta^{13}\text{C}$ of organic matter as well as the ^{13}C enrichment of respired CO_2 with soil depth is caused by an increasing contribution of microbial derived carbon. This hypothesis may be supported by the observation that the $\delta^{15}\text{N}$ may increase by up to 10% with depth (Högberg 1997). While it has been suggested that the ^{15}N gradient is mainly due to the mineralization-plant-uptake pathway followed by the deposition of ^{15}N depleted litter to the soil surface, it was also shown that microbial derived products contribute to this gradient (Högberg 1997).

Is subsoil carbon microbial derived carbon?

The elemental and isotopic evidence suggests that SOM in subsoils is more microbially processed than topsoil OM and most probably has a higher proportion of microbial derived compounds. When compiling data published by Jenkinson et al. (2008), we noticed a negative correlation between the soils C/N ratio and their ^{14}C activity (Fig. 1). This indicates that N containing compounds may survive in subsoil horizons for a long time, as already reported by Gleixner et al. (1999) for topsoils. Enrichment of microbial derived aminosugars in subsoil horizons was found by Liang and Balser (2008) who stated that ‘microbial residues are refractory and that they contribute to terrestrial carbon sequestration’. Further evidence for the importance of microbial over plant derived carbon in subsoil horizons was obtained from the analysis of non-cellulosic neutral carbohydrates. Microbial-derived sugars associated with the mineral phase were found to be positively correlated to the ^{14}C activity of the bulk sample, suggesting that these easily degradable substances are effectively stabilized by mineral interactions (Rumpel et al. 2010). Microbial sugars in the clay fraction of subsoil horizons were found to be associated with poorly crystalline Fe oxides but this was not the case for plant-derived lignin (Spielvogel et al. 2008). Plant-derived lignin may not be stabilised in subsoil horizons (Rumpel et al. 2004; Mikutta et al.

2006). Together, this points to the importance of microbial-derived organic matter in subsoil horizons. Microbial derived organic matter is enriched in subsoil horizons with regards to plant-derived organic matter and therefore most probably occurs in higher concentrations compared to topsoil horizons. Most studies to date used biomarkers and, therefore, little is known about the quantity of microbial products in subsoils.

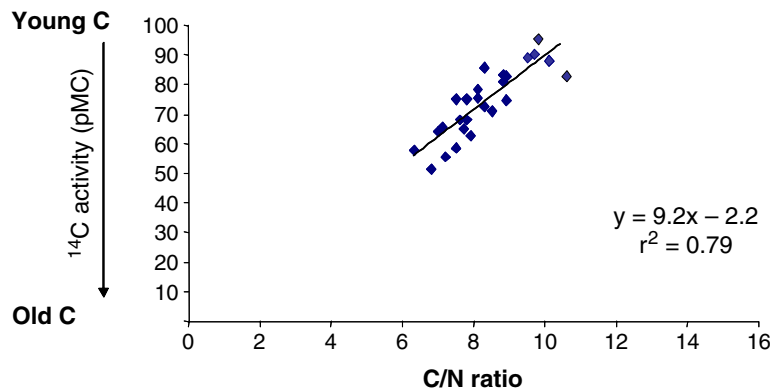
Importance of pedological processes

The question arises, what is the difference between the composition of stabilized SOM in subsoil horizons compared to the topsoil with most likely higher contributions of plant-derived organic matter? Although few chemical structural information is available due to analytical limitations, current evidence suggests, that the chemical composition of SOM in subsoil horizons under temperate climate is soil-type specific and dependent on pedological processes operating within the soil profile (Rumpel et al. 2002; Krull and Skjemstad 2003; Spielvogel et al. 2008; Kögel-Knabner et al. 2008), rather than dependent on the input of chemically stable compounds. This is consistent with results on the chemical composition of mineral-associated SOM in top- and subsoil horizons in a recent study by Mikutta et al. (2009). This study indicates that mineral-associated SOM in topsoil horizons predominantly reflects the uniform source vegetation whereas subsoil mineral-associated SOM shows different contribution of organic compounds related to the composition of the mineral phase. Thus, organic and mineral compounds in subsoil horizons have to be studied simultaneously to understand SOM dynamics (Basile-Doelsch et al. 2005).

Stabilisation processes of SOM in deep soil horizons

Old radiocarbon age of subsoil SOM as well as specific elemental and stable isotope composition could result from diffusion of processed OM at depth, where they are adsorbed on unsaturated mineral surfaces. However, such an explanation does not take into account considerable input of unprocessed litter through bioturbation. The importance of such input is evidenced by the relation between deep soil carbon

Fig. 1 Relationship between the ^{14}C activity and the C/N ratio of subsoil layers from Rothamsted (Data from Jenkinson et al. 2008)



stocks and plant functional types on a global scale (Jobbagy and Jackson 2000).

Chemical recalcitrance

Litter input into deeper soil may mainly occur as root C (Rasse et al. 2005), which could be chemically more recalcitrant than topsoil litter due to higher concentrations of lignin and aliphatic material (Nierop 1998; Lorenz and Lal 2005). Moreover, this material may already be old, as fine roots of forest trees were recently found to live several decades (Gaudinsky et al. 2001; Trumbore et al. 2006). This is longer than expected, but still a lot shorter than the mean residence time of several hundred or thousand of years recorded for the surrounding soil. Of the three

mechanisms of stabilisation reported in the literature (physical protection, physico-chemical interaction and stable chemical structure), chemical recalcitrance due to a highly stable chemical structure of certain organic matter compounds (Derenne and Largeau 2001) is controversially discussed. Krull et al. (2003) highlighted chemical recalcitrance as the only mechanism by which SOC can be protected over long periods of time whereas Marschner et al. (2008) provided evidence that chemical recalcitrance may no longer be regarded as a long-term stabilisation mechanism of SOM. Chemical recalcitrant organic matter may be enriched by acid hydrolysis (Quéneau et al. 2005). This method was frequently used for the isolation of chemical recalcitrant C from subsoil horizons of temperate and tropical soils (Trumbore and Zheng

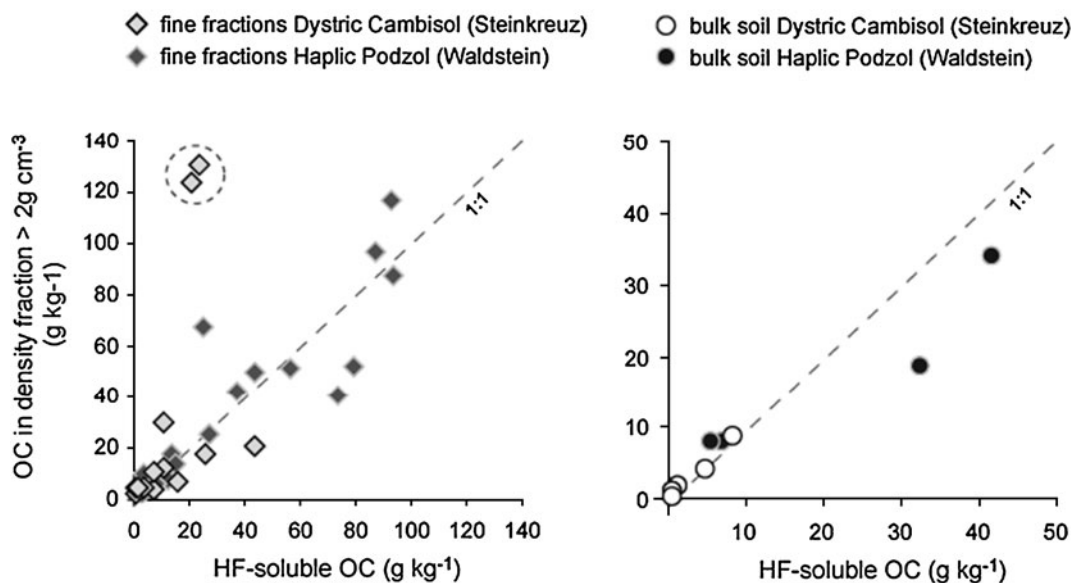
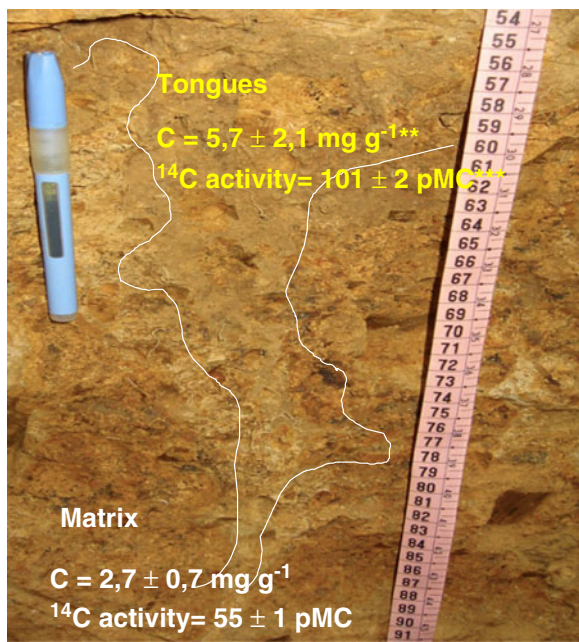


Fig. 2 Relationship between HF soluble C and OC in dense fractions > 2 g cm³ (Figures from Eusterhues et al. 2007)



** significantly different from matrix ($p < 0.05$)

***significantly different from matrix ($p < 0.01$)

Fig. 3 A picture from a subsoil showing the presence of tongues and a strong small scale spatial heterogeneity of carbon content and ^{14}C activity (data from Chabbi et al. 2009)

1996; Paul et al. 2001; Leavitt et al. 1996; Poirier et al. 2002; Paul et al. 1997; Rumpel et al. 2008). Acid hydrolysis was thought to remove easily decomposable protein and polysaccharide material leaving behind chemical recalcitrant structures, such as lignin, black carbon and aliphatic molecules. Carbon in subsoils may or may not be lost by acid hydrolysis at higher amounts than topsoil C (Paul et al. 2001; Rumpel et al. 2008; Montané et al. 2007). Acid hydrolysis, however, has been found to produce artefacts, (Allard et al. 1998) through the Maillard or browning reaction (condensation reaction between proteins and polysacchrides, Maillard 1912). Moreover, this method converts crystalline minerals to more amorphous ones (Zimmermann et al. 2007). The C isolated by acid hydrolysis from subsoil horizons is several hundred or thousand years older than bulk SOM (Paul et al. 2001; Rumpel et al. 2008). These results suggest that acid hydrolysis may be able to isolate subsoil C with long-term stability. Black carbon, produced by vegetation fire is chemically recalcitrant, thus may contribute to the stabilized SOM pool in subsoils. Charcoal with a ^{14}C age of several thousand years was isolated by many authors

from subsoil horizons (exp. Ali et al. 2005). Moreover, black carbon seems to be prone to vertical migration (Dai et al. 2005; Rumpel et al. 2009) and may therefore accumulate in deep soil horizons. Black carbon was thought to be preserved in soil due to its stable chemical structure. Several authors evidenced that it is intimately associated with the mineral phase (Brodowski et al. 2005; Czimeczik and Masiello 2007). Stabilization of other, plant-derived OM types in subsoil horizons seems to be more related to adsorption and chemical binding to mineral surfaces or the physical encapsulation of SOM than to recalcitrance of specific chemical compounds (Schöning and Kögel-Knabner 2006).

Association with soil minerals

One of the most prominent properties of SOM in subsoils is its high susceptibility to C-loss upon demineralisation with hydrofluoric acid (HF, Table 2). This is in sharp contrast to carbon loss by HF treatment of topsoil horizons and pure organic matter which is usually lower than 20% (Skjemstad et al. 1994; Schmidt et al. 1997; Rumpel et al. 2006). For many soil types of the temperate and the tropical regions it was observed, that subsoil horizons lose more carbon upon HF treatment than topsoil horizons (Table 2). This is especially evident, when we look at relative carbon losses compared to initial carbon content of the sample. The absolute loss is sometimes similar or higher in topsoil and subsoil horizons. The carbon lost upon demineralisation of soil was hypothesised to be intimately associated with the mineral phase (mineral-bound carbon). This hypothesis was supported by the observation of a strong correlation between HF-soluble C and C recovered in the heavy fraction of subsoil horizons (Eusterhues et al. 2007; Fig. 2). Evidence for the importance of mineral interaction for the stabilisation of subsoil OM was provided by the observation that the radiocarbon activity of SOM in subsoil horizons was related to the contribution of HF soluble C. This was observed in temperate (Eusterhues et al. 2003; Spielvogel et al. 2008) and in tropical soils (Rumpel et al. 2008). However, HF-resistant and presumably mineral-bound carbon in subsoil horizons is not always older than bulk organic C (Eusterhues et al. 2007). The reasons may be that: (a) the mineral associated soil organic matter fraction of deeper horizons may be

Table 2 Carbon loss after HF-treatment from topsoil and subsoil horizons

| Soil type | Climate | Conc HF % | C-loss | | C-loss | | Source |
|------------------------------|-----------|--------------|--------------|---------|--------------------|---------|-----------------------------------|
| | | | % of total C | | mg g ⁻¹ | | |
| | | | topsoil | subsoil | topsoil | subsoil | |
| | | | | | | | |
| Haplic Podzol | Temperate | 10 | 19 | 45–82 | 7 | 1–41 | Rumpel et al. (2002) |
| Dystric Cambisol | Temperate | 10 | 10 | 15–92 | 8 | 1–5 | Rumpel et al. (2002) |
| n.n. | Temperate | 10 | 18–32 | 31–45 | 3–4 | 1–2 | Lorenz et al. (2006) |
| Typic Haplorthods | Temperate | 2 | 26–31 | 55–67 | 20–56 | 15–44 | Dai and Johnson (1999) |
| Inceptisol and Entisol | Tropical | 10 | 24–42 | 38–63 | 15–20 | 5–13 | Lorenz et al. (2009) |
| Entisol, Alfisol, Inceptisol | Tropical | 10 | 24–32 | 33–70 | 3–7 | 3–5 | Rumpel et al. (2006) |
| Haplic and Stagnic Luvisol | Temperate | 10 | 12–25 | 23–61 | 6–17 | 1–7 | Schöning and Kögel-Knabner (2006) |
| Ferralsols | Tropical | 10 | 44–50 | 52–84 | * | * | Dick et al. (2005) |
| Leptic Cambisol | Temperate | 10 | 19–51 | 32–59 | 8–26 | 2–13 | Mueller and Kögel-Knabner (2009) |
| Entic Podzol | Alpine | 10 | 0 | 26–85 | 0 | 0–20 | Favilli et al. (2008) |

more easily replenished by input of young adsorbing materials compared to particulate organic matter, (b) stabilization due to interactions with the mineral matrix is not as effective as the other mechanisms, which stabilized the particulate organic matter, and/or (c) only the insoluble part of the mineral-associated organic matter fraction is stable or experiences significant stabilization through interaction with the mineral matrix.

Chemical oxidation treatments have been increasingly applied to subsoil OM to isolate old, organic matter stabilised by the interaction with the mineral phase (Eusterhues et al. 2005; Helfrich et al. 2007; Lorenz et al. 2009). The hypothesis that OM stabilised by interaction with the mineral phase may be isolated by chemical oxidation is based on the observation that minerals such as clay and poorly crystalline minerals protect organic matter against oxidative destruction (e.g. Hosking 1932; Singer and Huang 1993). Since chemical oxidation leads to alterations similar to those observed during biodegradation, the residual organic C might also be resistant to biodegradation (Cuyper et al. 2002). A number of different chemicals are used and a presentation of those and their effect on organic matter and mineral phases is beyond the scope of this review. Excellent overviews on these methods were provided by Mikutta et al. (2005) and von Lützow et al. (2007). The amount of non-oxidisable C present in soil samples from different depths along the soil profile

was found to be correlated to the ¹⁴C activity of the sample, suggesting similar to HF soluble C that SOM in subsoil horizons becomes older, when a greater proportion of SOM is associated with the mineral phase (Eusterhues et al. 2005). Material isolated by oxidation treatments from subsoil horizons is generally older than bulk SOM (Helfrich et al. 2007; Kleber et al. 2005) and may therefore represent a significant proportion of the stabilised OM. This may be different for topsoils, where this treatment was unable to isolate old SOM (Bruun et al. 2008). The chemical nature of the material associated intimately with the mineral phase yet needs to be elucidated.

To study the stabilising mineral agents in subsoil horizons, correlations between oxidation resistant OM and mineral parameters were run. The results suggest that in acid subsoil horizons under temperate and dry tropical forests, the amount of oxidation resistant organic matter is strongly related to the content of poorly-crystalline mineral phases (Kleber et al. 2005; Lorenz et al. 2009). Other authors found that Fe and clay minerals are the most important stabilising agents of OM in temperate and tropical subsoils (Eusterhues et al. 2003; Rumpel et al. 2008; Dick et al. 2005). In subsoils of Podzols in a tropical environment, SOM seems to be stabilised in Al-organic matter complexes (Skjemstad 1992; Bardy et al. 2007). Al-organic matter complexes and poorly crystalline Al mineral phases may also be responsible for C stabilisation in subsoil horizons of temperate forest and grassland

soils in Hawaii (Torn et al. 1997), the U.S. (Masiello et al. 2004; Rasmussen et al. 2005) and in Germany (Spielvogel et al. 2008).

Evidence for the high potential of pedogenic oxides to stabilise organic matter in subsoil horizons was obtained under strongly acidic conditions. However, there are indications that the sorptive capacity of the oxides is strongly reduced in near neutral soil environments (Gu 1994). Under near neutral conditions protection of OM via complexation with Ca^{2+} ions was proposed (Muneeer and Oades 1989a, b). Recently, strong organo–mineral associations in the presence of reactive, positively charged mineral phases such as hydrotalcite were reported for young calcareous subsoils (Grunewald et al. 2006). Moreover, as aggregate formation depends on biological activity, this process may be more important in neutral or calcareous soils compared to acid soils.

Aggregate protected SOM

In subsoil horizons, physical protection of occluded particulate organic matter (oPOM) was identified as a second important stabilisation mechanism. The oPOM fraction isolated from subsoil horizons was characterised by the highest ^{14}C age (Rasmussen et al. 2005) compared to all other density fractions. The importance of physical protection for OM stabilisation in subsoil horizons does not only concern the POM fraction, but also clay associated OM in microaggregates. Clay-associated OM in microaggregates was more abundant throughout a soil profile and had a higher ^{14}C age than OM associated with the free clay fraction (Moni et al. 2010). The importance of aggregation for stabilisation of OM in subsoil horizons at different scales is a topic in need for additional research, because the mechanisms leading to aggregate formation in top- and subsoils may be quite different. In subsoils, biological aggregate formation is supposedly less important than physical processes. However, to the best of our knowledge no studies were carried out addressing the incorporation of SOM into the two different types of aggregates in subsoil horizons. The importance of physical processes for the formation of aggregates in subsoils should be soil type specific. Therefore, we suggest that more studies are needed which address the interaction between aggregate formation and OM protection in subsoil horizons.

Destabilisation processes of SOM in deep soil horizons

One of the questions, which need to be answered under the scenario of global change and human interventions, is: “how fast does subsoil C respond to environmental changes” (Trumbore 2009). First evidence about the extent to which subsoil OM participates in C and N cycles can be obtained from sites after land-use change. For example, SOM stock changes of up to 48% may occur in B horizons after land-use change from forest to grassland (Müller and Kögel-Knabner 2009). Similar results were obtained by Don et al. (2009), who showed that 23 to 29 years after conversion of cropland to grassland the subsoil horizons contained fresh carbon. The authors concluded that subsoil C has to be taken into account when land-use change effects on SOC are assessed. The same conclusion was obtained by Osher et al. (2003), who estimated, that they would have greatly overestimated C losses after land-use change if they had not taken into account the subsoil horizons, where some of the C lost from the topsoil had accumulated. As was discussed previously, the degree of response and the mechanisms responsible for carbon stock changes in subsoil horizons are poorly understood.

Characteristics of microbial biomass and activity in subsoil horizons

The abundance of microbial biomass is generally declining with soil depth (Taylor et al. 2002; Andersen and Domsche 1989; Ekklund et al. 2001) as well as its activity (Fang and Moncrieff 2005). The opposite was noted for the Cmic/Corg quotient, suggesting that in deeper horizons a higher proportion of organic C is present as microbial biomass (Agnelli et al. 2004). Despite the low biomass contents, subsoils are metabolically active and contain substantial numbers of microorganisms (Taylor et al. 2002). Studies on pesticide degradation showed, that microbial activity was still significant below the rooting zone down to a depth of 2.5 m (Ajwa et al. 1988; Charnay et al. 2005). Similar observations were made concerning amino acid biodegradation (Kemmitt et al. 2008). Microbial activity in subsurface horizons was found to be similar to that measured in surface soil when normalized to biomass size (Blume et al. 2002). The absence of a decreasing trend is interesting as several authors

observed differences in microbial community structure between surface and subsurface horizons. In general, the genetic and metabolic diversity was reduced in subsoil horizons (Goberna et al. 2005; Agnelli et al. 2004). Carbon sources for soil bacteria with increasing depth increasingly consisted of older SOM derived C (Kramer and Gleixner 2008), suggesting, that those can be used as C sources by the soil organisms present.

Factors influencing the availability of subsoil OM

The availability of SOM to soil microorganisms in subsoil horizons may be affected by depth-specific environmental conditions (Table 3). Oxygen limitations in subsoil horizons could be responsible for long C turnover times. However, no literature evidence has been published so far supporting this assumption. Low oxygen content of 5% had no effect on decomposition of subsoil SOM (Salomé et al. 2010). This result obtained during laboratory incubation was supported by the observation that POM was not accumulating in subsoil horizons (Fontaine et al. 2007). In contrast, the conditions for the decomposition of plant material in subsoils were reported to be better than in topsoil in a Mediterranean environment due to higher moisture (Rovira and Vallejo 2002).

It has been reported that the degradation of old organic matter in subsoil of a Cambisol under prairie is absent due to energy limitation of the microbial biomass as a consequence of reduced input of fresh organic matter (Fontaine et al. 2007). The authors showed that the decomposition of old SOM may be stimulated by the addition of cellulose (priming effect). Temperature and available nutrients may be

additional control mechanisms for C mineralisation in subsoil horizons. Q10 values of subsoil OM were found to exceed those of topsoil SOM (Fierer et al. 2003). In northern boreal regions, permafrost may be the main factor stabilising subsoil C (Trumbore 2009), as soils with similar parent material and vegetation without permafrost were found to contain lower C stocks than their frozen counterparts (Rodionov et al. 2007). Under temperate climate conditions, nitrogen availability seems to have a strong influence on C as well as N mineralization in subsoil horizons of mountain grassland soils (Garcia-Pausas et al. 2008). In contrast, in a well managed agricultural soil receiving regular fertiliser treatment nutrient inputs did not affect subsoil C mineralization (Salomé et al. 2010). In this soil, addition of energy rich material to subsoil OM was not inducing a priming effect. It was rather the location of subsoil C within the soil matrix that appeared to determine its availability (Salomé et al. 2010). Similar observations were made by Xiang et al. (2008) who noticed that the mineralisation of subsoil C could be greatly increased by inducing drying wetting stress. However, the large majority of these studies was carried out under controlled laboratory conditions. The relevance of these works at the field scale yet needs to be demonstrated.

The spatial separation of microbes and degradable substrates may be one of the most important factors influencing C dynamics in subsoils (Von Lützow et al. 2006; Holden and Fierer 2005). It has been recognised that small scale variability of SOM has an important influence on microbial activity and growth in subsoil horizons. In a soil profile, spatial heterogeneity of SOM distribution does not only occur in vertical but also

Table 3 Effects of different factors on microbial activity in subsoil horizons

| Soil type | Depth | Treatment | Microbial activity | Source |
|-----------------------|-----------|-------------------------|--|------------------------|
| Cambisol | 80–100 cm | Physical disturbance | +75% | Salomé et al. (2010) |
| | | Fructose amendment | No effect | Salomé et al. (2010) |
| | | Low oxygen | No effect | Salomé et al. (2010) |
| | | Nutrient amendment | No effect | Salomé et al. (2010) |
| Fluventic Eutrochrept | 30–55 cm | Thrawing-freezing | No effect | Lomander et al. (1998) |
| Cambisol | 60–80 cm | Cellulose amendment | +72% | Fontaine et al. (2007) |
| Pachic Argiustoll | 90–100 cm | Drying-rewetting cycles | +20–426% | Xiang et al. (2008) |
| Pachic Haploxeroll | 50–100 cm | Temperature increase | Q10 values >than those of surface soil | Fierer et al. (2003) |
| | | Nutrient amendment | +50–400% | Fierer et al. (2003) |

horizontal direction. SOM compounds are not randomly distributed, but most likely associated with soil structure. Pedological processes operating within a soil profile may also lead to heterogeneous distribution of stabilised SOM compounds. In fact, the organic C content as well as the ^{14}C activity of SOM were found to be horizontally stratified, within spatially distinct regions of a Cambisol profile (Fig. 3, Chabbi et al. 2009). Three main processes of SOM input into deep soil horizons were identified to be responsible for the heterogeneous distribution of stabilised C compounds: (1) preferential flow of DOC; (2) plant rooting behaviour and (3) SOM transport by bioturbation.

Preferential flow paths, which were found to be stable for decades may act as transport pathways for young dissolved SOM into deeper soil horizons (Hagedorn and Bundt 2002). The preferential flow paths were also found to have increased microbial biomass due to enhanced C and nutrient supply (Bundt et al. 2001a). As a consequence, SOM in such paths was found to be younger and less humified than SOM in the soil matrix (Bundt et al. 2001b). The transport of C into deeper soil horizons is strongly dependent on soil texture and homogeneity of plant cover (Chevallier et al. 2000). Preferential SOC transport may occur in vertical cracks of clayey soil and cause an increasing variability of SOC distribution in subsoil horizons (Don et al. 2007).

Soil structure may also lead to a specific root distribution within the soil profile which enhances young carbon input into the mineral soil. Roots move downwards through the soil, release exudates and sloughed-off organic material, ultimately die and decompose. This source for young C in subsoil horizons may persist even for annual plants, as recolonisation of ancient root channel has been reported (Rasse and Smucker 1998). It was found that soil C stock changes were related to fine root length and therefore root activity rather than fine root mass (Guo et al. 2005).

One important but neglected process leading to heterogeneous distribution of SOM is bioturbation. Anecic earthworms for example reach 1–2 m depth but can go down to 5 m. They transport fresh organic detritus from the soil surface into the burrows while mixing with the mineral soil (Lee 1985). Earthworms from different soil horizons which showed a radio-carbon age of several thousand years were found to feed on young carbon (Scharpenseel and Becker-

Heidmann 1989). Therefore, they may transport fresh OM deep into soil. This assumption is reported by a recent study showing that SOM contents as well as stabilised carbon are heterogeneously distributed around the earthworm borrows (Don et al. 2008).

All these observations suggest that spatial distribution of old and young carbon within the soil profile is an important issue and that the study of stabilised SOM in subsoils is probably best approached by visual analysis of the soil profile and adaptation of a specific sampling scheme.

Modelling of SOM dynamics in subsoils

Models of turnover of SOM in subsoils need to address the downward movement of C and its stability in deeper layers. The vertical distribution of C and ^{14}C was modelled by including transport mechanisms in SOM turnover models (O'Brian and Stout 1978; Elzein and Balesdent 1995). In these models, ^{14}C provides the best tracer of SOM dynamics and transport. Model results indicate that diffusion rather than convection is responsible for most C transport to depth. Further progress was made by including process-based information from stable C and N isotopes (^{13}C and ^{15}N). This study indicates that DOC transport represents an important process in annual grassland ecosystems (Baisden et al. 2002). In a recent modelling exercise, Jenkinson and Coleman (2008) intended to develop a version of the dynamic model RothC-26.3 that can be applied to subsoils. Their results showed that this can be achieved by adding two parameters, one that moves organic C down the profile and another which slows decomposition at depth to the original model. However, the processes responsible for the transport of organic matter into subsoil horizons and the mechanisms leading to retarded decomposition of organic matter in subsoil horizons are poorly understood. A major knowledge gap concerns the C fluxes in deep soil horizons. To develop a C model for subsoils, more accurate measurements of deep C inputs and deep C losses are needed. More studies should be carried out to quantify SOM input into subsoils (roots growth, DOC percolation and bioturbation). The factors increasing or slowing down subsoil SOM decomposition need to be related to pedological characteristics of soil. Moreover, dynamic SOM models accounting

for spatial heterogeneity of total and stabilised organic carbon within subsoil horizons need to be developed.

Conclusion

Main C sources of subsoil OM are dissolved organic matter, root biomass and physically or biologically transported particulate organic matter. Organic matter in subsoil horizons is characterized by a high radiocarbon age but the reasons for this are not entirely clear. Decreasing C/N ratio, increasing $\delta^{13}\text{C}$ and analysis of single OM compounds suggest, that microbial-derived OM may contribute with higher proportions to OM in subsoil horizons than plant-derived OM.

It is likely that OM in subsoil horizons contains a high proportion of C compounds stabilized by mineral interactions. Numerous studies on acid subsoil horizons reported the importance of amorphous Fe and Al oxides for OM stabilization. Less information is available for calcareous subsoils. Another important stabilization mechanism in subsoil horizons may be occlusion of OM in soil aggregates.

While we did not find literature evidence for oxygen limitations of SOM degradation in subsoils, it has been suggested, that unfavourable conditions with regards to temperature, nutrients and energy could limit the degradation of OM stored in subsoil horizons. Most studies concerning these controlling factors were conducted at the laboratory scale. The evaluation of their relevance at field scale is very limited.

The most important factor determining the degree of alteration of OM seems to be related to the spatially heterogeneous distribution of fresh C and the soil microbial biomass. Specific pedological processes operating in a given soil type, which influence this distribution (i.e. preferential flow and bioturbation) should be taken into account, when C dynamics in subsoils is to be studied.

To completely understand and model the dynamics of OM in subsoils, quantitative data are necessary on (1) the relative importance and controlling factors of C sources, (2) the contribution of microbial versus plant-derived OM, (3) the C fluxes from deep horizons related to C input and output and C stabilization and destabilization processes at field scale.

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